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Experimental and analytic studies to model reaction kinetics and mass transport of carbon dioxide sequestration in depleted carbonate reservoirs

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Executive Summary

There is undeniable evidence that concentration of carbon dioxide in the atmosphere is rising at an increasingly rapid rate primarily as the result of burning fossil fuels. Although the debate continues, most of the scientific community believes that higher levels of atmospheric CO₂ will lead to a significant warming of the Earth's climate and that there is already evidence that this is occurring. There are two ways to ameliorate this problem. One is to significantly reduce production of CO₂, which is primarily a political-economic problem, and the other is to remove CO₂ from emissions and/or the atmosphere and find some way to sequester it. Several possible ways to sequester CO₂ are under investigation or have been suggested. These include removal by chemical reaction, deep seabed disposal, and pumping supercritical CO₂ into various subsurface environments.

Sequestration of carbon dioxide in depleted gas reservoirs appears to be a viable option, with a possible economic spin-off from the recovery of significant gas reserves. At the elevated temperatures and pressures encountered in reservoirs, carbon dioxide behaves as a supercritical fluid. Under these conditions, little was known regarding the diffusion of carbon dioxide in natural gas, and displacement of natural gas by carbon dioxide. A major objective of this research was to obtain the necessary data to model these processes. Also, the added CO₂ will react with reservoir waters that are often chemically complex high ionic strength brines making them more acidic. This can result in the dissolution of calcium carbonate (calcite) that is a common host rock or sandstone cement in reservoirs and lead to potentially serious problems for CO₂ injection and the integrity of the reservoir. It was consequently a second major objective of this project to determine calcite solubility and dissolution kinetics in solutions representative of subsurface brines and produce a general dissolution rate equation. Both objectives were accomplished.

Reservoir simulations indicated a large amount of CO₂ would be sequestered, with the amount depending on reservoir water saturation. Simulation results also indicate a significant amount of natural gas could be produced. For an 80-acre pattern, natural gas production was calculated to be 3.2 BSCF or 63% of remaining gas-in-place for 30% reservoir water saturation. Gas revenues would help defray the cost of CO₂ sequestration. Therefore, CO₂ sequestration in depleted gas reservoirs appears to be a win-win technology.

Considerable effort went into testing and refining the ability to predict calcite solubility in brines using a Pitzer-equation based computer model, with particular difficulties being encountered in solutions with high dissolved calcium concentrations. After that was accomplished, calcite dissolution kinetics were determined a wide range of brine compositions both including and not including potential inhibitors from 25 to 83 °C and a CO₂ partial pressure from 0.1 to 1 atm. The reaction was found to be first order for undersaturations of 0.2 to ~1 and was surface controlled. The rate constant was fit to a multiple regression model, thus making it possible to predict calcite dissolution rates over a wide range of solution compositions, partial pressures of CO₂ and temperature. Results indicate that equilibrium is likely to be reached relatively quickly in front of an advancing supercritical CO₂ fluid.

1. Introduction

Carbon dioxide emission from burning fossil fuels has been identified as the major contributor to the increase in atmospheric CO₂ levels that can potentially lead to global climate change. During the last decade, worldwide concern has focused on possible global warming caused by heat being trapped by CO₂ in the upper atmosphere (the greenhouse effect). In 1993, the European Commission began the Joule II Non-nuclear Energy Research Program, which studied sequestration of industrially produced CO₂. The study concluded that injection of CO₂ into depleted gas reservoirs has the potential to enhance gas recovery, while simultaneously sequestering a greenhouse gas.

A depleted gas reservoir can store significantly more gas than a depleted oil reservoir (with the same initial hydrocarbon pore volume) for two reasons. First, ultimate gas recovery (about 65% of gas initially-in-place) is typically about twice that of oil (average 35% of initially-in-place). Second, gas is some 30 times more compressible than oil or water. CO₂ has a critical temperature of 31°C (88°F) and a critical pressure of 7.38 MPa (1070 psia). Consequently, at pressures and temperatures typically encountered in the field, CO₂ will behave as a supercritical fluid. However, displacement of natural gas by supercritical CO₂ has not been done in the field and not well understood, nor is its potential for exerting potential damage to injection sites and reservoirs via causing calcite dissolution which is a common host rock and cement in gas reservoirs. In this project we have experimentally investigated questions and processes related to these issues.

2. Research Objectives

In the past six years, we have conducted experimental, analytical and simulation studies to better understand the displacement of natural gas during sequestration of supercritical carbon dioxide in depleted carbonate and sandstone gas reservoirs, and calcite solubility and dissolution kinetics in solutions typical of many hydrocarbon reservoirs.

2.1. Gas Displacement by Supercritical CO₂

The research may be divided into two phases, Phase 1 (2000-2003) and Phase 2 (2004-2006). In Phase 1, research focused on understanding and modeling the displacement of natural gas (pure methane) by supercritical carbon dioxide in carbonate (Austin chalk) cores. In Phase 2, research concentrated on the effect of flue gas (CO₂ containing “impurities” such as N₂, O₂, SO₂, and CO) on the displacement of methane in Austin chalk and Berea sandstone cores.

Research objectives:

Phase 1 (2000-2003) – Gas displacement by supercritical CO₂ in Austin chalk cores

Conduct experimental and analytical studies to determine at high pressures of 6.89-34.47 MPa (1000-5000 psia) and high temperatures of 32-93 °C:

- (i) the rate of diffusion of supercritical carbon dioxide in gas-bearing carbonate reservoirs,
- (ii) displacement mechanisms of natural gas by supercritical carbon dioxide in carbonate reservoirs, and
- (iii) change in porosity, permeability, and chemical composition of carbonate rock due to carbon dioxide-carbonate reactions

Phase 2 (2004-2006) – Gas displacement by flue gas in carbonate and sandstone cores

Conduct experimental and analytical studies to determine:

- (i) Investigate the effect of “impurities” such as sulfur dioxide, nitrous oxide, and hydrocarbons on the displacement of natural gas by supercritical carbon dioxide and on the reaction kinetics of calcite dissolution in a depleted carbonate-bearing gas reservoir, and
- (ii) To evaluate the effect of carbon dioxide and these “impurities” on the porosity and compressive strength of carbonate-bearing cores.

2.2. Calcite Solubility and Reactivity in Brines

Conduct experimental and analytical studies to determine and model the dissolution kinetics of the dissolution of carbonate minerals in saline waters. Investigate the effect of “impurities” on the reaction kinetics of calcite.

Using the results obtained develop a dissolution kinetics model for calcite in waters likely to be encountered in a carbonate bearing gas reservoir.

3. Research Results

3.1. Displacement by Supercritical CO₂

3.1.1. Experimental apparatus

The experiments involved injecting supercritical CO₂ into an aluminum Hassler core holder containing a 1-ft long by 1-in. diameter carbonate or sandstone core initially saturated with methane. A schematic diagram of the apparatus is shown in Fig. 1. Rate and composition of the produced gas were measured, enabling determination of mole fraction of produced gas as a function of time. In addition, the core holder was X-ray CT scanned to determine core porosity, and CO₂ and methane saturation.

3.1.2. Experimental and simulation results

3.1.2.1. Phase 1 - Gas displacement by supercritical CO₂ in Austin chalk cores

A total of 22 experimental runs were made, involving the displacement of methane by carbon dioxide in a 1-ft long by 1-in. diameter carbonate core: nine runs at 20°C (68°F), four runs at 40°C (104°F), four runs at 60°C (140°F), and five runs at 80°C (176°F). Depending on the cell temperature, the cell pressure ranged from 500 psig (3.55 MPa) to 3000 psig (20.79 Mpa). Table 1 summarizes operating conditions and main results of runs made. Measured CO₂ concentration in the produced gas are shown in Fig. 2.

Fig. 1 – Schematic diagram of experimental apparatus used in Phase 1 of the research to study displacement of methane in cores by supercritical carbon dioxide.

Table 1 – Summary of operating conditions and results of CO₂ injection in Austin chalk cores.

Run no.	Temperature °C	Pressure MPa	C ₁ production at CO ₂ SL	breakthrough %OGIP	Dispersion coefficient cm ² /min
9	20	7.18	3.135	85.1	0.100
10	20	13.89	5.660	73.0	0.025
14	20	7.00	2.755	77.0	0.100
15	20	7.00	2.620	73.1	0.100
16	20	13.89	5.950	77.0	0.028
17	20	13.89	5.635	72.9	0.032
18	20	20.79	9.125	79.9	0.010
19	20	20.79	9.185	80.4	0.011
20	40	18.72	7.840	84.5	0.021
21	60	18.72	7.145	85.8	0.040
22	40	15.27	6.280	82.9	0.030
23	60	15.27	5.925	87.2	0.060
24	40	11.82	4.935	86.2	0.070
25	60	11.82	4.515	86.8	0.120
26	40	8.38	3.350	84.5	0.120
27	60	8.38	3.130	86.8	0.200
28	20	3.55	1.400	82.4	0.150

Fig. 2 – Experimental and analytical model results of CO₂ concentration in produced gas for runs at 40°C, 60°C and 80°C for supercritical CO₂ injection in Austin chalk cores.

The analytical model used to simulate the experimental results was based on the following convection-dispersion equation.

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D} \dots\dots\dots(1)$$

where: $x_D = \frac{x}{L}$, dimensionless distance, where L is length of core,

$t_D = \frac{tv}{L}$, dimensionless time, and

$P_e = \frac{vL}{K_l}$, Peclet number (ratio of convection to dispersion).

Since the carbon dioxide injection inlet is at $x = 0$, then
initial condition: $C = 0$ at $t_D = 0$, $0 < x_D < \infty$;
boundary conditions: $C = 1$ at $x_D = 0$, $t_D > 0$,
 $C \rightarrow 0$ as $x_D \rightarrow \infty$, $t_D > 0$.

Solution to Eq. 1 may be shown to be as follows.

$$C = \frac{1}{2} \left\{ \operatorname{erfc} \left(\frac{x_D - t_D}{2\sqrt{t_D / P_e}} \right) + e^{P_e x_D} \operatorname{erfc} \left(\frac{x_D + t_D}{2\sqrt{t_D / P_e}} \right) \right\} \dots\dots\dots(2)$$

Using Eq. 2, the best fit line for CO₂ concentration for each run (as shown in Fig. 2) was obtained by varying the coefficient of longitudinal dispersion. Dispersion coefficients inferred were relatively small, ranging from 0.01 to 0.3 cm²/min. As a result of the stable displacement by carbon dioxide, methane recovery at carbon dioxide breakthrough is relatively high, 73 % to 87 % of initial volume of methane in the core.

Figure 3 shows a typical set of CT scan images indicating that at breakthrough, CO₂ concentration in the core is quite uniform, corroborating analytical results of low dispersion.

Fig. 3 – Typical CT scan images of core at breakthrough of liquid CO₂ (red/yellow, bright), with residual methane gas in green (dark). The CT scanner was an invaluable tool for determination of core porosity and saturation and in providing insight into the displacement mechanisms.

The 1 ft long by 1 in. diameter core was simulated using a 96-grid one-dimensional numerical model. History-matching of the experimental results were made as shown for a typical run in Fig. 3, arriving at the gas-liquid relative permeability curves shown in Fig. 4.

Fig. 3 – History-matching of experimental

Fig. 4 – Gas-liquid relative permeability.

A 3D simulation model of one eighth of a 5-spot pattern – using a commercial simulator (CMG) - was constructed to evaluate injection of supercritical CO₂ under typical field conditions (Fig. 5). We evaluated the effect of injection rate and abandoned (initial) reservoir pressure on gas recovery factor, CO₂ breakthrough time, and the amount of CO₂ sequestered for two cases: case 1 (one-eighth of 40-acre unit (1.619E+05 m²)) and case 2 (one-eighth of 80-acre unit (3.237E+05 m²)). Properties of the patterns are summarized in Table 2. For each case, the abandoned (initial) reservoir pressure was fixed at 500 psia (3.447 MPa) to find the effect of injection rate on recovery factor, breakthrough time, and the amount of CO₂ sequestered.

Fig. 5 - Schematic diagram of one-eighth of 5-spot pattern and simulation

Table 2 – Summary of properties of the 5-spot patterns simulated.

Property	Units	Case 1	Case 2
Five spot pattern area	acres	40	80
One eighth five spot area	acres	5	10
Thickness	ft	150	300
Layers	-	10	20
Pore volume	ft ³	7.5141E+06	3.00564E+07
Porosity	fraction	0.23	0.23
X, Y-direction permeability	md	50	50
Z-direction permeability	md	5	5
Initial water saturation	%	0, 25, 30, 35	0, 25, 30, 35
Temperature	°F	152	152
Original reservoir pressure	psia	3,045	3,045

Simulation results indicate the following (Figs. 6 and 7). First, a large amount of CO₂ is sequestered: about 1.2 million tons in 29 years (40-acre pattern), and 4.8 million tons in 56 years (80-acre pattern). Second, a significant amount of natural gas is also produced: about 1.3 BSCF or 74% OGIP (40-acre pattern), and 4.9 BSCF or 68% OGIP (80-acre pattern).

Fig. 6 - Amounts of CO₂ sequestered increases with injection rates.

Fig. 7 – Recovery factor of methane decreases with increase in reservoir abandonment pressure.

3.1.2.2. Phase 2 - Gas displacement by flue gas in carbonate and sandstone cores

A typical flue-gas composition of an electric power plant based on a combustion calculation for a Powder River Basin (PRB) coal, in a 500 MW plant with 20% excess air is shown in Table 3. Flue gas may be treated in order to obtain a stream rich in CO₂ for sequestration purposes. Thus, two types of flue gas were used in our experiments: dehydrated flue gas with 13.574 mole % CO₂ (Gas A), and treated flue gas with 99.433 mole % CO₂ (Gas B) as presented in Table 3. Gas A results from dehydrating flue gas and Gas B results from removing N₂, O₂ and water. Both types of flue gas are used in the displacement experiments. The phase envelopes of the two gases are shown in Fig. 8, indicating the absence of a critical point for Gas A.

Table 3 – Composition of two types of flue gas used in the experiments.

	Composition, mole %		
Component	Flue Gas	Gas A	Gas B
Nitrogen, N ₂	70.726	80.370	---
Water, H ₂ O	12.000	---	---
Carbon dioxide, CO ₂	11.945	13.574	99.433
Oxygen, O ₂	5.258	5.975	---
Sulfur dioxide, SO ₂	0.045	0.051	0.368
Nitrogen oxide, NO ₂	0.016	0.018	0.129
Carbon monoxide, CO	0.010	0.012	0.070
Total	100.000	100.000	100.000

Fig. 8 - Phase envelopes of Gas A and Gas B compared to vapor pressure line for pure CO₂.

Fig. 9 shows the concentration of produced gas versus injected pore volume for runs at 10.44 MPa (1,500 psig) and 70°C. Using the same analytical model for CO₂ injection described earlier, best-fit lines of the data are obtained that represent the best value of the coefficient of longitudinal dispersion. Dispersion coefficients inferred from analytical model are relatively small, 0.13-0.25 cm²/min. Earlier breakthrough time is observed for Gas A when the initial water saturation is 20%. Table 4 summarizes the main results of the runs for the two gases.

Fig. 9 - Experimental and analytical model results of flue gas concentration in produced gas for injection of Gas A and Gas B in Austin chalk cores.

Table 4 – Summary of results of flue gas injection in Austin chalk cores.

Injection gas	S_{wi}	OGIP, std L	C_1 recovery at breakthrough, %OGIP	Breakthrough, Pore Volume	K_L , cm ² /min
Gas A	0.0	3.967	80.66	0.79	0.18
	0.0	4.027	79.46	0.79	0.19
	0.2	3.227	74.36	0.60	0.25
Gas B	0.0	3.982	89.90	0.89	0.15
	0.0	3.060	88.16	0.78	0.13

Fig. 10 – Isosurface images of 3D porosity profiles. These images are very helpful for understanding the porosity distribution in the core.

In experiments using Berea sandstone cores, Gas B was injected at cell temperature of 60°C and pressure of 1500 psig. Results of CO₂ concentration (data and analytical model results) are shown in Fig. 11. Results indicate that the dispersion coefficient for both pure CO₂ and treated flue gas are relatively small, ranging from 0.18-0.23 cm²/min and 0.28-0.30 cm²/min respectively. Methane recovery at breakthrough is relatively high, ranging from 71%-80% of original gas-in-place for pure CO₂ and 90% - 92% of original gas-in- for treated flue gas, the difference resulting from different cell pressures used. Therefore it would appear that, in practice, injection of treated flue gas is a cheaper option compared to pure CO₂ injection.

Fig. 11 - Experimental and analytical model results of CO₂ concentration in produced gas for injection of pure CO₂ (left) and Gas B (right) in Berea sandstone cores.

Table 5 – Summary of results of flue gas (Gas B) injection in Berea sandstone cores.

Injection gas	Pressure (psi)	S_{wi}	Produced gas (std. L)	OGIP (std. L)	CO ₂ recovery at break-through	Breakthrough time (min)	Coeff. long. dispersion (cm ² /min)
CO ₂	1500	0	3.471	4.23	80	92	0.18
CO ₂	1500	0	3.225	4.23	76	84	0.187
CO ₂	1500	0	3.015	4.23	71	80	0.225
Flue Gas B	800	0	1.91	2.11	90	67	0.28
Flue Gas B	800	0	1.95	2.11	92	72	0.3

To simulate the dissolution of Austin chalk by CO₂ injection, a total 2.587 moles of CO₂ was cycled through the core. This is approximately equal to 30 days of injection in the field. Porosity along the axis of the core was measured using the x-ray CT scanner. Unconfined compressive strength (UCS) tests were measured using the *MTS* uniaxial compressive strength apparatus at Civil Engineering Dept. Three samples were used in the tests: without CO₂ injection (one sample) and with CO₂ injection (two samples). Results indicate porosity was increased by as much as 2.5% (Fig. 12). UCS was reduced by about 30% of its original value from $3,949 \pm 966$ psi for the base case to $2,729 \pm 347$ psi for samples subject to dissolution (Table 6).

Fig. 12 - Porosity measurements along core axis using CT scanner (Austin chalk samples).

Table 6 – Unconfined compressive strength test measurements on Austin chalk samples.

Description	Specimen	UCS (psi)	Type of failure
Base Case	1	3,459	Columnar
	2	3,547	Columnar
	3	5,395	Cone and Split
	4	3,394	Shear
		$3,949 \pm 966$	
Sample 1	5	2,951	Columnar
	6	3,110	Cone and Split
	7	2,133	Cone and Split
		$2,731 \pm 524$	
Sample 2	8	3,077	Columnar
	9	2,688	Cone and Split
	10	2,597	Columnar
	11	2,549	Columnar
		$2,787 \pm 255$	

UCS test results for Berea sandstone cores (Table 7) show an apparent increase in rock strength with the increase in the number of hours of CO₂ injection. This is probably due to the heterogeneity of the samples. The peak load for this sample (base case) shows

no consistency as does sample 1 and 2. Sample 3 exhibits the highest peak load, (an average of 3828 PSI) of all other samples. Another possible explanation for this observation is the fact that dissolution of the carbonates holding the quarts grains together causes a quartz to quartz grain contact, which is generally stronger than the rock with pore filling carbonates.

Table 7 – Unconfined compressive strength test measurements on Berea sandstone samples.

Specimen	Peak Load (psi)	Type of failure	Mean (psi)	Std. dev.
Base case				
1	3448	cone and split	2495	795
2	1665	cone and split		
3	2051	cone and split		
4	2816	cone and split		
Sample 3				
1	3132	cone and split	3828	552
2	3637	cone and split		
3	4279	cone		
4	4262	cone		
Sample 2				
1	2470	cone and split	3594	830
2	4343	cone		
3	4073	cone		
4	3488	cone and split		
Sample 1				
1	3149	cone and split	3295	137
2	3250	cone and split		
3	3306	cone and split		
4	3476	cone and split		

3.1.3. Summary of gas displacement research

Main conclusions from our research may be summarized as follows.

1. Displacement of methane by CO₂ – whether CO₂ is a gas, liquid or a supercritical fluid – appears to be a very efficient process. Dispersion coefficients of CO₂ in methane measured are relatively low: 0.01 – 0.3 cm²/min for Austin chalk core samples and 0.18-0.23 in cm²/min for Berea sandstone core samples.
2. Methane recovery at CO₂ breakthrough is high, 62-87% of original gas-in-place (OGIP) for Austin chalk core samples, and 71-80% of OGIP for Berea sandstone core samples. In the field, this could translate into production of hitherto

unrecoverable gas reserves as a result of increase in sweep efficiency and reservoir repressurization. The resulting gas revenue would help defray the cost of CO₂ sequestration.

3. The experiments have been restricted to one-dimensional horizontal displacement of methane by CO₂. The beneficial effect of gravity segregation - a more stable displacement of methane by CO₂ - has been excluded.
4. For the same temperature, coefficient of longitudinal dispersion of CO₂ decreases with increasing pressure. This is due to CO₂ becoming more “liquid-like” at higher pressure. For example, for Austin chalk core samples, at 60°C coefficient of longitudinal dispersion of CO₂ decreases from 0.2 cm²/min at 1200 psig to 0.04 cm²/min at 2700 psig.
5. At constant pressure, coefficient of longitudinal dispersion of CO₂ increase with temperature as a result of CO₂ becoming more “gas-like”. For example, for Austin chalk core samples at 2700 psig, coefficient of longitudinal dispersion of CO₂ increases from 0.02 cm²/min at 40°C to 0.07 cm²/min at 80°C.
6. Reservoir simulation of one-eighth of 5-spot 40-acre patterns indicated a large amount would be sequestered, the amount depending on reservoir water saturation: varying from 1.2 million tons in 29 years for reservoir water saturation of 0% to 0.83 million tons in 20 years for 30% reservoir water saturation. For an 80-acre pattern, the amount of CO₂ sequestered (as comparison) for 30% reservoir water saturation increases to 3.4 million tons in 79 years. The amount of CO₂ sequestered increases with size of the reservoir and degree of reservoir pressure depletion. CO₂ sequestered is not affected by the CO₂ injection rate.
7. Simulation results indicate a significant amount of natural gas is produced. For a 40-acre pattern, natural gas production amounts to 0.84 BSCF or 66% of remaining gas-in-place for 30% reservoir water saturation. For an 80-acre pattern, natural gas production increases to 3.2 BSCF or 63% of remaining gas-in-place for 30% reservoir water saturation.
8. Assuming a natural gas price of \$5.00 per 1000 SCF, the gas produced 0.84 BSCF (40-acre patter) and 3.2 BSCF (80-acre patter) would generate revenues of \$4.2 million and \$16.0 million. These gas revenues would help defray the cost of CO₂ sequestration. CO₂ sequestration in depleted gas reservoirs appears to be a win-win technology.
9. Displacement of methane by Gas A (dehydrated flue gas with CO₂ concentration of 13.6 mole %) at the conditions studied (1,500 psig and 70°C) show larger coefficients of longitudinal dispersion, 0.18-0.25 cm²/min compared to ca. 0.15 cm²/min for pure CO₂ injection.

10. Displacement of methane by Gas B (flue gas with CO₂ concentration of 99.4 mole %) indicate relatively low coefficients of longitudinal dispersion, 0.13-0.15 cm²/min (Austin chalk core samples) and 0.28-0.30 cm²/min (Berea sandstone core samples).
11. Methane recovery at breakthrough appears to be higher with Gas B (88-90% OGIP for Austin core samples and 90-92% OGIP for Berea sandstone core samples) than for Gas A (79-81% OGIP). Gas recovery with Gas A injection is lowest probably due to the large N₂ concentration in the injected gas.
12. It appears that CO₂ injection with less than about 1 mole % “impurities” in the flue gas would result in about the same amount of CO₂ being sequestered as injecting pure CO₂. Gas B would however have the advantage of being a cheaper separation process compared to pure CO₂ as not all the “impurities” are removed in Gas B.
13. Unconfined compressive strength (UCS) tests of Austin chalk core samples indicate a 30% reduction of UCS with CO₂ injection to about 2700 psi from the original value of 3900 psi as a result of carbonate dissolution. UCS tests for Berea sandstone core samples however indicate an apparent increase in UCS with increase in the number of hours of CO₂ injection. This apparent contradiction is probably due to the heterogeneous nature of the samples.

3.2. Calcite Solubility and Dissolution Kinetics in Saline Waters

3.2.1. Calcite Solubility in Saline Waters

Experimental and analytic methods: Synthetic Na-Ca-Mg-Cl brines were prepared gravimetrically on the molal scale (m) from separate concentrated stock solutions of A.C.S. reagent grade NaCl, CaCl₂•2H₂O and MgCl₂•6H₂O. Phosphate measurements of the concentrated stock solutions were made according to the methods of Murphy and Riley (1962) and in all cases found to be below detection (< 1 μM). A broad range of solution concentrations were investigated that ranged from that of seawater (TDS = 35 g L⁻¹) up to 200 g L⁻¹ with calcium concentrations ranging up to approximately 1 m. In general, a multivariate approach was used such that the calcium, magnesium and ionic strength were co-varied as a function of TDS according to Hanor (1994). Exceptions included cases where the specific effects of a given variable were explored. The initial compositions were verified by analytical determination of calcium, total hardness and chloride by the methods described below.

The brines were reacted with a variety of calcite substrates including A.C.S. reagent grade powder (Fisher Scientific) and two size fractions (32 – 63 μm and 63 – 125 μm) of crushed rhombic Iceland spar obtained from Ward’s Scientific Inc. The reagent calcite was pretreated with dilute (0.1 N) HCl according to the methods of Sass et al. (1983). To relieve surface strain and to clean the grains of ultra-fine particles which can enhance solubility, the crushed material was sonicated in methanol for one hour, re-sieved, briefly washed with milliQ[®] (18.1 μΩ) water and freeze dried. The specific

surface area of each of the calcite substrates was estimated from a geometric determination from scanning electron micrographs. The specific surface areas were $0.91 \text{ m}^2 \text{ g}^{-1}$, $0.05 \text{ m}^2 \text{ g}^{-1}$, $0.02 \text{ m}^2 \text{ g}^{-1}$ for the powder, 32 – 63 μm and 63 – 125 μm crushed Iceland Spar calcites, respectively. In addition, a BET determination was performed on the calcite powder and was in excellent agreement ($< 5 \%$) with the geometric determination. BET determinations of the crushed Iceland Spar calcite were found to be suspect and may have been below the detection limit. The mineralogies of both, the reagent grade calcite powder and crushed Iceland Spar calcites calcite, were verified by powder X-ray diffraction as being $> 99\%$ calcite.

A series of open-system free-drift experiments were performed to investigate the dissolution kinetics of calcite in these brines at CO_2 partial pressures of ~ 0.1 , 0.5 and 1.0 bar at 25°C . While the dissolution rates of these experiments are reported elsewhere (Gledhill and Morse, 2004; Gledhill and Morse, submitted), the steady-state measurements that were obtained were in good agreement with those from separate closed-system solubility experiments and were therefore used to compliment the closed-system results. Both systems are discussed below.

The kinetic reactor (Gledhill and Morse, 2004) consisted of a 550 ml water-jacketed vessel that accommodated a gas feed, two electrodes, vent, temperature probe, and sampling port. Commercially purified high-grade CO_2 and ultra-high purity N_2 were precisely mixed and their flow rate controlled using dual MKS[®] Type 1479A mass-flow regulators. The solution was stirred at constant rate with a propeller shaft that passed through the top of the reaction vessel and maintained at constant temperature ($25 \pm 0.01^\circ\text{C}$) using a Neslab[®] RTE-8DD circulating bath. The system remained open during the duration of the experiment and evaporation was minimized by using gas humidifiers and a condenser. Once the system achieved steady-state as observed by monitoring pH, multiple samples were drawn and filtered through a Millipore 0.45 μm syringe filter for analysis as described below.

The solubility reactor consisted of four specially modified glass 125 ml serum bottles. Approximately 100 ml of brine was added to each serum bottle that accommodated a pipette tip and small vent. A CO_2 - N_2 gas mixture was then gently bubbled into the solution through the pipette tip. The serum bottles were then inserted into water-jacketed vessels that were maintained at constant temperature ($25 \pm 0.01^\circ\text{C}$) using a Neslab[®] RTE-8DD circulating bath.

Following equilibration with the gas phase, 2 ml of concentrated primary standard grade Na_2CO_3 was added sufficient to establish approximately 20% saturation with respect to calcite. This was necessary to minimize the amount of calcite dissolution so as to limit changes in the solution Ca^{2+} concentration. Since a precise knowledge of the equilibrium concentrations was not initially known, the amount of sodium carbonate to be added could only be approximated based on EQPITZER predictions. After several attempts, much better estimates could be applied from trial and error. In the final

experiments varying amounts of Na_2CO_3 were added to each of the four serum bottles so as to allow for a small range in final Ca^{2+} concentrations.

The solution was then allowed to reestablish equilibrium with the gas phase prior to the addition of approximately 1 g of calcite. Since the grinding action of magnetic stirrers has been known to produce enhanced solubility, the solutions were instead mixed by mounting the reactors on a Lab-line Instruments® orbit shaker which was oscillated continuously at 250 RPM. The calcite was allowed to react under the constant $\text{CO}_2\text{-N}_2$ gas mixture for 7 h. The gas feed was then removed and the serum bottles sealed with a septum top. This reaction time generally brought the solution to within a few percent of equilibrium so that further consumption of CO_2 was minor. The calcite suspension was then permitted to react with the brine in the closed system for one week. The closed system eliminated evaporation of the brine for these extended duration experiments.

At the experiment completion, a nitrogen gas feed was inserted into the serum bottle septum. A minimal amount of nitrogen was used to displace fluid which was passed through a second syringe needle equipped with an in-line 0.45 μm Acrodisc® filter. The filtered sample was collected into a 20-ml gas tight syringe. This method avoided any atmospheric exchange.

Solution concentrations of Cl^- were determined by AgNO_3 titration ($\pm 1.5\%$) using an Accumet silver ion selective electrode interfaced with a computer via an Orion 720A potentiometer. Calcium was analyzed by EGTA titration with calcium indicator Cal/Ver II®, and Mg^{2+} concentrations were determined by EDTA titration with Erichrome Black (EBT). Endpoint detection was facilitated using a Brinkmann PC 800 colorimeter interfaced with a Brinkmann 682 titroprocessor. Precision was within 2% in most cases. The concentration of Na^+ was calculated from charge balance.

Total carbon dioxide (TCO_2) was immediately determined on the samples according to the method of Dickson and Goyet (1994) with a UIC Inc. Model 5011 CO_2 coulometer. Precision ranged from 3.7% at low concentrations to better than $\pm 0.3\%$ for high concentrations. Total alkalinity (TA) was determined by a Gran-type titration (Gran, 1952) using a Metrohm 655 Dosimat and an Orion 720A pH meter interfaced with a computer. Sample pH was measured using a Corning Inc. semi-micro combination pH electrode calibrated using NBS 4 and 7 buffers. Computer software was used to evaluate the inflection point. An HCl titrant and solutions of primary standard Na_2CO_3 were made in NaCl solutions at ionic strengths specific to each of the brines. The Na_2CO_3 standards were prepared gravimetrically under a nitrogen environment and their concentrations verified by coulometric measurement of their TCO_2 concentrations. Four point calibration curves were made using weighted standards versus the volume at which the apparent inflection point occurred. Precision was better than 0.1 meq kg^{-1} . The titrations were conducted at $25 \pm 0.1^\circ\text{C}$ in a water-jacketed open cell into which CO_2 was continuously bubbled. The bubbling of CO_2 into the cell served to facilitate gas exchange and prevent the solution from becoming oversaturated with respect CaCO_3 mineral phases as a result of degassing prior to the addition of the HCl titrant.

Results: The analytical results are presented in Table 8 and indicate, as expected, a broad range in TA and TCO₂ for different electrolytes reacted with calcite under various CO₂ partial pressures at 25 °C. The different substrates and size fractions used did not, however, impart a measurable effect. The species distributions of the carbonic acid system and ion activities were evaluated using EQPITZER software (He and Morse, 1993) (Table 9). The program provides a *complete* description of the carbonic acid system using at least two fundamental CO₂ system parameters (TA, TCO₂, pCO₂ and pH) and a solutions major ion composition. The measured TA and TCO₂ were coupled to calculate pCO₂ (Table 8).

Table 8. Solubility data for a broad range of Na-Ca-Mg-Cl brines reacted with calcite. Molal values of total calcium (Ca²⁺), magnesium (Mg²⁺) and chloride (Cl⁻) were used to calculate total sodium (Na⁺) and ionic strength (I) from charge balance. The CO₂ partial pressure (pCO₂, bar) was calculate from molal concentrations of total alkalinity (TA) and total carbon dioxide (TCO₂) using EQPITZER. The specific geometric surface area (m² g⁻¹) of the calcite was estimated from scanning electron microscopy.

ID	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	TA	TCO2	I	pCO ₂	Area
				(molal)				(bar)	(m ² g ⁻¹)
<i>Kinetic Reactor Experiments</i>									
PCO2_01a	0.0478	0.0245	0.7237	0.8759	0.0167	0.0432	0.9353	0.93	0.02
PCO2_01b	0.0432	0.0228	0.7128	0.8579	0.019	0.0445	0.927	0.89	0.05
PCO2_01c	0.0437	0.0218	0.7116	0.8591	0.0189	0.044	0.9258	0.88	0.91
PCO2_02a	0.1583	0.0661	1.577	2.212	0.0107	0.0301	2.365	0.86	0.02
PCO2_03a	0.348	0.124	1.555	2.193	0.0067	0.0222	3.8425	0.86	0.02
PCO2_03b	0.3626	0.118	2.217	3.633	0.0068	0.0216	3.8894	0.82	0.05
PCO2_03c	0.3639	0.1184	2.235	3.657	0.0066	0.0211	3.9138	0.82	0.91
PCO2_04a	0.042	0.022	1.561	2.194	0.0135	0.0264	0.9367	0.45	0.02
PCO2_05a	0.1656	0.0696	1.561	2.194	0.008	0.018	2.4913	0.46	0.02
PCO2_05b	0.1569	0.0703	1.67	2.364	0.0078	0.0178	2.353	0.45	0.02
PCO2_05c	0.1594	0.0672	1.567	2.223	0.008	0.018	2.3523	0.44	0.02
PCO2_06a	0.3625	0.1151	2.315	3.766	0.0046	0.0127	3.9979	0.46	0.02
PCO2_07a	0.0409	0.0232	0.7315	0.8935	0.0061	0.0084	0.9437	0.08	0.02
PCO2_08a	0.1573	0.0673	1.594	2.247	0.0035	0.0053	2.3714	0.08	0.02
PCO2_09a	0.3623	0.1136	2.316	3.767	0.0022	0.0036	3.9945	0.08	0.02
Mg_01a	0.1648	0.0217	1.75	2.35	0.0076	0.0175	2.4268	0.45	0.02
Mg_02a	0.1603	0.1173	1.49	2.236	0.0075	0.0176	2.4221	0.45	0.02
Ca_01a	0.0439	0.0707	1.912	2.391	0.0127	0.0222	2.3868	0.44	0.02
Ca_02a	0.3601	0.0658	1.091	2.056	0.006	0.0164	2.4283	0.45	0.02
I_01a	0.156	0.0685	0.2442	0.6992	0.0081	0.022	0.9248	0.47	0.02
I_02a	0.1641	0.0731	2.775	3.867	0.0059	0.0132	3.7988	0.42	0.02
XP_001C	0.017	0.059	0.5117	0.9128	0.0272	0.0544	0.7451	0.91	0.91
XP_001D	0.0148	0.0772	0.4864	0.6256	0.0284	0.0539	0.7542	0.86	0.91
AP_012A	0.0827	0.0747	0.5474	0.8166	0.0142	0.0394	1.0039	0.88	0.91
XP_009B	0.1021	0.0421	0.7476	1.03	0.0135	0.0385	1.1838	0.9	0.91
XP_005B	0.1475	0.0584	0.9992	1.4053	0.0116	0.0353	1.6193	0.92	0.91
XP_013A	0.2654	0.0903	1.17	1.697	0.009	0.0291	2.1498	0.85	0.91

XP_006B	0.4276	0.0889	1.4171	2.4464	0.0073	0.0274	2.9683	0.95	0.91
XP_006D	0.4411	0.0882	1.4111	2.467	0.0076	0.0266	3.0029	0.91	0.91
XP_010A	0.6381	0.1145	1.3705	2.8734	0.0064	0.0239	3.6433	0.89	0.91
XP_007C	0.9071	0.1264	1.2607	3.3263	0.0059	0.0217	4.3634	0.87	0.91
XP_007D	0.9475	0.1574	1.1213	3.3298	0.0056	0.0219	4.4518	0.9	0.91

Solubility Reactor Experiments

KSP_Brine1_1	0.0434	0.021	0.7447	0.8594	0.0138	0.0285	0.9377	0.52	0.05
KSP_Brine1_2	0.0435	0.0213	0.7435	0.8581	0.0158	0.0321	0.9383	0.57	0.05
KSP_Brine1_3	0.0427	0.0229	0.7421	0.8564	0.0161	0.0334	0.9384	0.61	0.05
KSP_Brine1_4	0.0425	0.0219	0.7311	0.8438	0.0163	0.0327	0.9243	0.57	0.05
KSP_Brine2_1	0.1596	0.0679	1.8	2.252	0.009	0.02	2.4854	0.51	0.05
KSP_Brine2_2	0.159	0.0662	1.804	2.25	0.009	0.0195	2.482	0.49	0.05
KSP_Brine2_3	0.1599	0.0661	1.801	2.248	0.0088	0.0186	2.4811	0.45	0.05
KSP_Brine2_4	0.1589	0.0644	1.8	2.241	0.0091	0.0203	2.4716	0.52	0.05
KSP_Brine3_1	0.3648	0.1165	2.67	3.627	0.0056	0.0144	4.1137	0.53	0.05
KSP_Brine3_2	0.3621	0.1173	2.67	3.626	0.0057	0.0145	4.1093	0.53	0.05
KSP_Brine3_3	0.3636	0.1164	2.684	3.646	0.0057	0.0146	4.128	0.54	0.05
KSP_Brine3_4	0.3624	0.1158	2.665	3.62	0.0055	0.0146	4.1014	0.54	0.05
MgFree_1	0.023	0	3.0217	3.0428	0.0247	0.0412	3.0908	0.97	0.91
MgFree_2	0.154	0	2.5834	2.8806	0.0108	0.0285	3.0456	0.97	0.91
MgFree_3	0.9117	0	0.2371	2.0531	0.0071	0.0285	2.9712	0.97	0.91
MgFree_4	0.0234	0	3.0221	3.0433	0.0255	0.0418	3.0921	0.92	0.91
MgFree_5	0.1538	0	2.5834	2.881	0.0104	0.0285	3.0451	0.92	0.91

Table 9. The carbonate ion concentration (CO_3^{2-} , molal) along with the total ion activity coefficients for CO_3^{2-} and Ca^{2+} as derived using EQPITZER.

ID	Ca^{2+}	CO_3^{2-}	
	γ_T	molal	γ_T
<i>Kinetic Reactor Experiments</i>			
PCO2_01a	0.216	8.25E-06	0.035
PCO2_01b	0.213	1.13E-05	0.035
PCO2_01c	0.214	1.13E-05	0.035
PCO2_02a	0.264	1.14E-05	0.009
PCO2_03a	0.396	1.27E-05	0.003
PCO2_03b	0.401	1.44E-05	0.003
PCO2_03c	0.404	1.35E-05	0.003
PCO2_04a	0.216	1.23E-05	0.035
PCO2_05a	0.275	1.27E-05	0.008
PCO2_05b	0.261	1.15E-05	0.009
PCO2_05c	0.263	1.24E-05	0.009
PCO2_06a	0.428	1.25E-05	0.003
PCO2_07a	0.218	1.30E-05	0.035
PCO2_08a	0.265	1.31E-05	0.009
PCO2_09a	0.429	1.53E-05	0.003
Mg_01a	0.283	1.05E-05	0.010
Mg_02a	0.254	1.20E-05	0.008
Ca_01a	0.312	1.86E-05	0.015
Ca_02a	0.202	1.10E-05	0.006
I_01a	0.172	9.54E-06	0.015
I_02a	0.536	1.27E-05	0.005
XP_001C	0.208	2.21E-05	0.038
XP_001D	0.199	2.77E-05	0.035
XP_012A	0.183	1.09E-05	0.021
XP_009B	0.193	9.41E-06	0.019
XP_005B	0.194	9.37E-06	0.014
XP_013A	0.170	9.09E-06	0.009
XP_006B	0.210	9.73E-06	0.005
XP_006D	0.210	1.14E-05	0.005
XP_010A	0.216	1.31E-05	0.003
XP_007C	0.226	1.84E-05	0.002
XP_007D	0.219	1.73E-05	0.002
<i>Solubility Reactor Experiments</i>			
KSP_Brine1_1	0.208	9.84E-06	0.036
KSP_Brine1_2	0.208	1.19E-05	0.036
KSP_Brine1_3	0.208	1.15E-05	0.035
KSP_Brine1_4	0.208	1.24E-05	0.036
KSP_Brine2_1	0.243	1.28E-05	0.010
KSP_Brine2_2	0.243	1.31E-05	0.010
KSP_Brine2_3	0.242	1.37E-05	0.010

KSP_Brine2_4	0.242	1.26E-05	0.010
KSP_Brine2_1	0.353	1.30E-05	0.003
KSP_Brine2_2	0.354	1.33E-05	0.003
KSP_Brine2_3	0.357	1.33E-05	0.003
KSP_Brine2_4	0.353	1.23E-05	0.004
MgFree_1	0.362	1.75E-05	0.027
MgFree_2	0.313	9.24E-06	0.010
MgFree_3	0.131	1.58E-05	0.004
MgFree_4	0.362	1.90E-05	0.027
MgFree_5	0.313	8.46E-06	0.010

The measured TA and TCO₂ concentrations are generally in good agreement with those predicted by EQPITZER for a broad range of geologically relevant Na-Ca-Mg-Cl synthetic brines (35 to 200 g L⁻¹ TDS) equilibrated with calcite at CO₂ partial pressures of ~0.1 (solid triangle), 0.5 (open square) and 1.0 bar (solid square) at 25 °C (Figure 13).

Discussion: The stoichiometric equilibrium constants (pK_{sp}^*) for each of the solutions was calculated from the concentration products as

$$pK_{sp}^* = -\log\left(m_{Ca^{2+}}m_{CO_3^{2-}}\right) \quad (3)$$

and shows a broad range of over nearly two orders of magnitude in the apparent solubility of calcite in these solutions generally increasing (a.k.a. decreasing pK_{sp}^*) with increasing TDS (Figure 14a). Perhaps surprisingly, the actual carbonate carrying capacity of these solutions, although exceeding small in all cases, actually slightly increases with increasing brine concentration despite an increase in calcium activity (Figure 15).

Figure 13. Comparison between the measured and EQPITZER predicted total alkalinity (TA) (a) and total carbon dioxide content (TCO₂) (b) of a broad range of geologically relevant Na-Ca-Mg-Cl synthetic brines (35 to 200 g L⁻¹ TDS) equilibrated with calcite at CO₂ partial pressures of ~0.1 (solid triangle), 0.5 (open square) and 1.0 bar (solid square) at 25 °C.

Figure 14. The negative logarithms of the stoichiometric (pK_{sp}^* , triangles) and thermodynamic (pK_{sp} , squares) equilibrium constants for calcite measured in a broad range of geologically relevant Na-Ca-Mg-Cl synthetic brines (35 to 200 g L⁻¹ TDS). Solid scatter points are experimental data from kinetic experiments measured at steady-state. Open scatter points were measured in closed system solubility experiments and are in good agreement. The solid line represents the thermodynamic equilibrium constant of Plummer and Busenberg (1982).

The negative logarithms of the ion activity products (pK_{sp}) where

$$pK_{sp} = -\log \left(\gamma_{Ca^{2+}} \gamma_{CO_3^{2-}} m_{Ca^{2+}} m_{CO_3^{2-}} \right) \quad (4)$$

yield values in reasonable agreement ($\pm 10\%$) with K_c ($-\log K_c = 8.480 \pm 0.020$, Plummer and Busenberg (1982)) in brines less than 100 g L⁻¹ TDS. However, with increasing concentration there is what appears to be systematic increase in thermodynamic solubility product (i.e. decreasing pK_{sp}).

Figure 15. The Ω values calculated using EQPITZER from the analytical results of this study compared with values calculated from literature data. Open scatter points are experimental data from this study. Open squares were measured in Na-Ca-Mg-Cl brines, while open circles were measured in Mg^{2+} -free brines. Solid triangles are from Millero et al. (1984). Solid circles are from Wolf et al. (1989). The inset figure expands the region investigated in this study as denoted by the dashed box. The solid line represents thermodynamic equilibrium within the uncertainty depicted by the dashed lines (Plummer and Busenberg, 1982).

Although a multivariate approach was applied in which calcium, magnesium and ionic strength were all co-varied with increasing TDS, there is a strong relation between the variability pK_{sp} and calcium activity (Figure 14b). Even experiments performed in Mg^{2+} -free solutions exhibit the same behavior implying that this is not due to the formation of a more soluble Mg^{2+} -rich surface phase. Nor is it specifically related to ionic strength, since in the Mg^{2+} -free solutions the ionic strength was fixed ($I = 3 \text{ m}$) by balancing with NaCl. It should also be noted that in these solutions the Mg:Ca ratio was always < 0.5 . This is much lower than in seawater where a $\sim 8 \%$ Mg-calcite can form at a Mg:Ca ratio of ~ 5 (Mucci and Morse, 1984). The simplest explanation for this apparent deviation from K_c is that there is a small error associated with the EQPITZER calculated carbonate ion activity coefficient ($\gamma_{\text{CO}_3^{2-}}$) in the most calcium-rich brines.

This error would have little consequence in many geochemical contexts, such as in the case of mineral mass transport since the carbonate carrying capacity of these calcium-rich brines is rather small and the difference between the predicated and observed TA and TCO_2 is very minor (Figure 13). However, it may become important

when modeling the reaction kinetics of these minerals when the degree of disequilibrium is used as a key term in the rate equation. An example of this would be the commonly applied general rate equation (e.g., Morse and Berner, 1972) used to describe the rate of calcite dissolution:

$$R = -\frac{dm_{\text{calcite}}}{dt} = \left(\frac{A}{V}\right)k(1 - \Omega)^n \quad (5)$$

where t is time, A is the surface area of the solid, V is the volume of solution (or mass of solvent in cases where molal units are used), k is the rate constant and n is the “order” of the reaction. The saturation state (Ω) is the ratio of the ion activity product of calcium and carbonate (IAP) to K_c , as given by

$$\Omega = \frac{\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}} \gamma_{\text{CO}_3^{2-}} m_{\text{CO}_3^{2-}}}{K_c} \quad (6)$$

If $\Omega = 1$, then the solution is in equilibrium with respect to calcite; if $\Omega < 1$ the solution is undersaturated; and if $\Omega > 1$ the solution is supersaturated. EQPITZER reports saturation states increasingly greater than one with increasing calcium concentration. In this study, brines that contained calcium concentrations nearing 1 molal yielded EQPITZER predicted saturation states more than twice saturated (e.g., $\Omega > 2$, Figure 15).

Millero et al. (1984) measured the solubility of calcite in NaCl solutions up to 6 m. In these experiments the $m_{\text{Ca}^{2+}}$ did not exceed 0.6 mmol kg⁻¹ H₂O. Based on the reported solution compositions and coupling TA and TCO₂ to solve for the carbonic acid system, analogous to the approach used with the analytical data from this study, the derived Ω values using EQPITZER closely approximated 1 (Figure 15, solid triangles). This indicates that EQPITZER is quite capable of predicting equilibrium up to high ionic strengths in the absence of large amounts of calcium. The same approach was applied to the data reported by Wolf et al. (1989) in which calcite dissolution was measured in highly concentrated CaCl₂ solutions (up to 3 m Ca²⁺). In this case a near exponential deviation with increasing $m_{\text{Ca}^{2+}}$ was observed with an apparent supersaturation in excess of 20 times for the most concentrated case (Figure 15, solid circles).

Although these errors may seem dramatic, one has to consider that not only does the carbonate ion occur in very low concentration (<15 μmolal), but its predicted activity coefficient decreases to ~3 x 10⁻³ in the most concentrated brines. Because carbonate ion activities are on the order of 10⁻⁸ in these brines, it is not surprising that such errors in the calculated saturation state arise. In fact, it is rather remarkable how well the current model holds up under these extreme conditions.

Summary of Solubility Studies: Although EQPITZER reasonably predicts equilibrium (± 10%) with respect to calcite in relatively low concentration brines (<100 g L⁻¹ TDS), with increasing brine concentration a systematic increase in the calculated saturation state is

observed, yielding at steady-state more than an apparent 2-fold supersaturation in the most-calcium rich brine. The error is not specifically related to magnesium concentration suggesting that it is not the result of the formation of an enhanced solubility Mg-rich phase. Instead, it strongly correlates with increases in calcium activity. We can not be certain that the apparent increase in steady-state IAP is not related to a complex interaction between the calcite surface and these highly concentrated brines, but perhaps the simplest explanation is that the apparent IAP increase represents minor uncertainty in the carbonate ion activity coefficient. Although this minor error would have little consequence in many geochemical contexts, such as in the case of mineral mass transport, it can impart significant error to kinetic rate models that empirically describe the rate of dissolution as a function of the degree of disequilibrium ($1-\Omega$). Jeschke and Dreybrodt (2002) showed that when rates are modeled by linear fits of $\log R$ versus $\log (1-\Omega)$, small uncertainties in Ω can have a pronounced effect on the interpreted reaction order (n) and rate constant (k). Small errors can create nonlinearity in log-log plots. Such effects are particularly important under near equilibrium conditions. It is therefore advised, that although the program EQPITZER performs well for moderately concentrated brines (<100 g L⁻¹ TDS), caution should be taken well applied to more concentrated calcium-rich systems when a precise knowledge of saturation state is required.

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3.2.2. Calcite Dissolution Kinetics in Saline Waters

NOTE: During the first 3 years of the project kinetic studies presented in Geldhill and Morse (2004) were done at 25 °C and 1 atm pCO₂ in major component brine solutions with a strong emphasis on technique development and discovery of the solubility problem in high calcium brines. During the second 3 years the range in temperature was expanded up to 83 °C, a range of pCO₂ values for 0.1 to 1 atm was used, and additional components were added to brines. Also natural calcite was used in comparison to reagent grade calcite. Here we focus on the general results of the study without dealing with the more preliminary results which can be found in Geldhill and Morse (2004).

Background: A large number of investigators have examined the influences of “foreign” ions, temperature, CO₂ partial pressure and other variables on calcite dissolution rates (see reviews of Plummer et al., 1979; Sjöberg and Rickard, 1983; Morse, 1983; Morse and Arvidson, 2002). Previous investigations sought to understand the behavior of calcite in solutions with ionic strengths that did not generally exceed that of seawater. Calcite reaction kinetics in concentrated solutions, typical of the subsurface, have received relatively little attention. Although a few recent studies included precipitation rate measurements in higher salinity waters (Zhang and Dawe, 1998; Zuddas and Mucci, 1998), fewer have directly addressed the dissolution kinetics of carbonate minerals in complex high ionic strength solutions (e.g., Pokrovsky et al., 2005). Investigation of carbonate mineral dissolution as a function of saturation state requires accurate calculations of the carbonic acid system species distributions. Whereas determination of the activities of these species in high ionic strength solutions continues to be problematic, investigations of the solubility of calcite coupled with the Pitzer parameterizations of the carbonic acid system in synthetic brines (He and Morse, 1993) have made such calculations more reliable.

Although the composition of subsurface formation waters vary considerably, fortunately this variability is not entirely random as Hanor (1994) demonstrated. Instead, much of the variability can be explained by mineral-brine equilibration considerations. This constrains somewhat the concentration of the major dissolved species as a function of TDS. Using this relation, we have determined the dissolution kinetics of calcite in saline waters with compositions approximating those in Northern Hemisphere reservoirs.

The results have important applications to predictive chemical process models in carbonate cemented reservoirs and for carbon sequestration strategies.

Experimental and analytic methods: Synthetic Na-Ca-Mg-Cl brines were prepared gravimetrically on the molal scale (m) from separate concentrated stock solutions of A.C.S. reagent grade NaCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Phosphate measurements of the concentrated stock solutions were made according to the methods of Murphy and Riley (1962) and in all cases found to be below detection ($< 1 \mu\text{M}$). Three ‘model’ brines were investigated containing 50, 125 and 200 g L^{-1} total dissolved solids (TDS). A multivariate approach was used such that calcium, magnesium and ionic strength were co-varied as a function of TDS according to Hanor (1994b). Modifications to each of these ‘model’ brines were then made where the specific effects of a given variable were explored. The initial salt concentrations were verified by analytical determination of calcium, total hardness and chloride concentrations.

Brines were reacted with crushed rhombic Iceland spar calcite obtained from Ward’s Scientific Inc. A 63 to $125 \mu\text{m}$ size fraction was collected by wet sieving. To relieve surface strain and to clean the grains of ultra-fine particles which can enhance solubility, the crushed material was sonicated in methanol for one hour, re-sieved, briefly washed with MilliQ[®] ($18.1 \mu\Omega$) water followed by freeze drying. Specific surface area was estimated to be $0.02 \text{ m}^2 \text{ g}^{-1}$ from a geometric determination using scanning electron micrograph (SEM) imaging. The mineralogy was verified by powder X-ray diffraction as being $> 99\%$ calcite.

Solution concentrations of Cl^- were determined by AgNO_3 titration ($\pm 1.5\%$) using an Accumet silver ion selective electrode interfaced with a computer via an Orion 720A potentiometer. Calcium was analyzed by EGTA titration with calcium indicator Cal/Ver II[®], and Mg^{2+} concentrations were determined by EDTA titration with Erichrome Black (EBT). Endpoint detection was facilitated using a Brinkmann PC 800 colorimeter interfaced with a Brinkmann 682 titroprocessor. Precision was within 2% in most cases. The concentration of Na^+ was calculated from charge balance.

Total carbon dioxide (TCO_2) was determined according to the method of Dickson and Goyet (1994) with a UIC Inc. Model 5011 CO_2 coulometer. Precision ranged from 3.7% at low concentrations (i.e., $< 0.0\text{XX m}$) to better than $\pm 0.3\%$ at high concentrations (i.e., $> 0.0\text{XX m}$). Total alkalinity (TA) was determined by a Gran-type titration (Gran, 1952) using a Metrohm 655 Dosimat and an Orion 720A pH meter interfaced with a computer. Apparent sample pH was measured using a Corning Inc. semi-micro combination pH electrode calibrated using NIST-traceable 4 and 7 buffers. Computer software was used to evaluate the inflection point. An HCl titrant and solutions of primary standard Na_2CO_3 were prepared in NaCl solutions at ionic strengths specific to each of the brines. The Na_2CO_3 standards were prepared gravimetrically under a nitrogen environment and their concentrations verified by TCO_2 coulometric measurement. Four point calibration curves were made using weighted standards versus the volume at which the inflection point occurred. Precision was better than 0.1 meq kg^{-1} . Titrations were conducted at $25 \pm 0.1 \text{ }^\circ\text{C}$ in a water-jacketed open cell into which CO_2 was continuously

bubbled. Bubbling of CO₂ into the cell served to facilitate gas exchange and prevent the solution from becoming oversaturated with respect to CaCO₃ mineral phases as a result of degassing prior to the addition of the HCl titrant.

The solution pH was measured using a Ross[®] H⁺ selective electrode referenced to a Single Refex[®] solid-state reference electrode. The Refex[®] reference electrode uses an ionically conductive hard-non-porous salt loaded polymeric matrix. The matrix acts as an immobilized electrolyte thus avoiding a porous liquid-junction. Calibration of the electrodes to “Pitzer scale” pH was performed according to the methods of Gledhill and Morse (2004). Briefly, the initial and final pH of the brine is calculated by coupling TA and TCO₂ using the Pitzer equation-based program EQPITZER (He and Morse, 1993). The electrode response slope (S_x) can then be established using a two-point calibration from:

$$S_x = \frac{E_f - E_i}{pH_i - pH_f} \quad (7)$$

where E is the emf and pH is the calculated “Pitzer pH”, initial (*i*) and final (*f*).

An open system pH-free-drift method was employed in which the rate of CaCO₃ dissolution was determined by monitoring changes in solution pH as a function of time (Fig. 16). A 550 ml water-jacketed reaction vessel accommodated a gas feed, two electrodes, condenser/vent, temperature probe and sampling port. The solution was stirred at constant rate with a propeller shaft passed through the top of the reactor (Table 10). Temperature was held constant at (± 0.1 °C) using a Neslab[®] constant-temperature bath and *p*CO₂ was maintained by bubbling with a humidified ultra high purity nitrogen-CO₂ gas mixture appropriate for the desired experimental conditions (Table 10). A mass-flow controller interfaced with a computer assured constant flow rate (2 L min⁻¹).

Common to open-system free-drift experiments, if the initial rate of dissolution is too rapid, gas phase disequilibrium can occur in which there is an excess consumption of CO₂ relative to supply in the solution (e.g., Arakaki and Mucci, 1995). This can be prevented by: 1) conducting the dissolutions at high *p*CO₂ where appropriate; 2) reducing the available calcite surface area; and 3) avoiding initiating the experiments at extreme degrees of disequilibrium. These experiments were conducted near 0.1 bar *p*CO₂ or greater and the calcite used exhibited a relatively low specific surface area. The low specific surface area also produced considerably slower initial rates allowing for significant amounts of calcite to be added (~ 4 g L⁻¹), thus minimizing the change in surface area during the experiments. Finally, a concentrated primary standard grade Na₂CO₃ solution was added to establish approximately 20% saturation with respect to calcite. These precautions resulted in little variation between initial and final *p*CO₂ values.

Figure 16. Open system pH-free-drift batch reactor used to measure calcite dissolution rates in concentrated synthetic brines. The elements of the experimental setup are illustrated in the schematic: 1) high grade nitrogen and carbon dioxide gas; 2) dual MKS® Type 1479A mass-flow regulators; 3) computer; 4) gas humidifier; 5) batch reactor; 6) stir motor; 7) Orion® 720A pH meter; 8) Neslab® RTE-8DD circulating bath.

Table 10. Initial solution concentration and experimental conditions. For each experiment concentration (molal), gas composition is X_{CO_2} , temperature (°C), and reactor stirring rate (RPM) are given. The gas mixture was balanced with nitrogen.

~TDS	Experiment	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	I	X _{CO₂} ^a	°C	RPM
50	PCO2_01	0.039	0.0229	0.7390	0.8504	0.0000	0.9235	1.0	25.0	300
125	PCO2_02	0.157	0.0651	1.8210	2.2610	0.0000	2.4889	1.0	25.0	300
200	PCO2_03	0.347	0.1223	2.7310	3.6670	0.0000	4.1395	1.0	25.0	300
50	PCO2_04	0.039	0.0217	0.7351	0.8485	0.0000	0.9175	0.5	25.0	300
125	PCO2_05a	0.162	0.0677	1.8270	2.2830	0.0000	2.5169	0.5	25.0	300
125	PCO2_05b	0.154	0.0703	1.7660	2.2110	0.0000	2.4399	0.5	25.0	500
125	PCO2_05c	0.156	0.0656	1.6980	2.1360	0.0000	2.3611	0.5	25.0	700
200	PCO2_06	0.351	0.1234	2.7270	3.6740	0.0000	4.1501	0.5	25.0	300
50	PCO2_07	0.039	0.0228	0.7398	0.8592	0.0000	0.9247	0.1	25.0	300
125	PCO2_08	0.155	0.0660	1.7690	2.2090	0.0000	2.4312	0.1	25.0	300

200	PCO2_09	0.357	0.1177	2.6560	3.6050	0.0000	4.0806	0.1	25.0	300
125	TEMP_03a	0.159	0.0656	1.7640	2.2100	0.0000	2.4363	0.5	52.5	300
125	TEMP_04a	0.153	0.0678	1.7740	2.2140	0.0000	2.4366	0.5	80.0	300
125	Ca_01a	0.041	0.0705	2.2220	2.4340	0.0000	2.5549	0.5	25.0	300
125	Ca_02a	0.358	0.0626	1.2200	2.0570	0.0000	2.4815	0.5	25.0	300
125	I_01a	0.152	0.0701	0.2504	0.6903	0.0000	0.9172	0.5	25.0	300
125	I_02a	0.161	0.0743	3.3700	3.8370	0.0000	4.0763	0.5	25.0	300
125	Mg_01a	0.164	0.0172	1.9740	2.3320	0.0000	2.5165	0.5	25.0	300
125	Mg_02a	0.158	0.1235	1.6870	2.2460	0.0000	2.5307	0.5	25.0	300
50	SO4_01a	0.040	0.0237	0.7296	0.8215	0.0115	0.9303	1.0	25.0	300
125	SO4_02a	0.154	0.0772	1.7770	2.2090	0.0117	2.4816	1.0	25.0	300
200	SO4_03a	0.345	0.1292	2.6300	3.5490	0.0127	4.0656	1.0	25.0	300

$$(a) X_{co_2} = 1 - \frac{CO_2, L \min^{-1}}{CO_2 + N_2, L \min^{-1}}$$

Prior to calcite addition, a 20 ml sample was drawn for initial solution analysis. The calcite was then allowed to react with the solution while changes in solution pH were monitored at 5 s intervals. Experiments were terminated typically after 5 hours, at which point changes in solution chemistry were within the measurement precision. Triplicate 20 ml samples were drawn and filtered through a Millipore 0.45 μm syringe filter for final solution analysis. Calcite remaining in solution was collected by vacuum filtration and briefly rinsed with MilliQ[®] (18.1 $\mu\Omega$) water. The filtered material was freeze dried and stored in a vacuum desicator for later SEM imaging to confirm that there was no excessive alteration to the specific surface area.

Results: Table 10 reports measured salt concentrations prior to reaction with calcite along with the experimental conditions including gas mix ($X_{co_2} = 1 - \frac{CO_2, L \min^{-1}}{CO_2 + N_2, L \min^{-1}}$,

where $CO_2 + N_2 = 2 \text{ L min}^{-1}$), temperature ($^{\circ}\text{C}$) and stir rate (revolutions per minute). Table 11 lists the CO_2 -related parameters at the start of each experiment and the mean ($n = 3$) steady-state values following reaction with calcite. The electrode response yielded good agreement ($90 \pm 5\%$) with the ideal Nernst value even at high temperature. Although EQPITZER accurately modeled changes in TCO_2 relative to TA, with increasing calcium concentration the program systematically overestimated calcite solubility (see Gledhill and Morse, 2006, for a complete discussion). The pCO_2 , calculated from TA and TCO_2 , showed good agreement between initial and final values.

Table 11. Initial (i) and steady-state (ss) carbonic acid system parameters along with the final calcium concentrations (molal). Electrode response is reported as percent Nernstian. The $p\text{CO}_2$ was derived using EQPITZER from coupling TA and TCO_2 and the value reported is the mean of the initial and final conditions.

Experiment ID	Ca_{ss}^{2+}	pH_i	pH_{ss}	electrode response	TA_i ($\text{meq kg}^{-1} \text{H}_2\text{O}$)	TA_{ss} ($\text{meq kg}^{-1} \text{H}_2\text{O}$)	TCO_{2i} (molal)	TCO_{2ss} (molal)	$p\text{CO}_2$ (bar)
PCO2_01	0.042	5.65	5.820	84%	11.6	167 $\pm$ 0.1	0.0387	0.0432	0.98
		5	$\pm$ 0.019					$\pm$ 0.0012	$\pm$ 0.01
PCO2_02	0.158	5.31	5.624	90%	5.6	107 $\pm$ 0.0	0.0255	0.0301	0.89
		2	$\pm$ 0.015					$\pm$ 0.0004	$\pm$ 0.04
PCO2_03	0.348	5.06	5.427	86%	3.3	67 $\pm$ 0.2	0.0194	0.0222	0.92
		4	$\pm$ 0.016					$\pm$ 0.0001	$\pm$ 0.08
PCO2_04	0.042	5.82	6.039	90%	8.2	264 $\pm$ 0.1	0.0212	0.0264	0.45
		3	$\pm$ 0.028					$\pm$ 0.0005	$\pm$ 0.00
PCO2_05a	0.166	5.44	5.769	94%	4.0	80 $\pm$ 0.0	0.0143	0.0180	0.47
		8	$\pm$ 0.006					$\pm$ 0.0000	$\pm$ 0.01
PCO2_05b	0.157	5.44	5.769	97%	3.9	78 $\pm$ 0.1	0.0140	0.0178	0.46
		8	$\pm$ 0.004					$\pm$ 0.0001	$\pm$ 0.01
PCO2_05c	0.159	5.44	5.785	91%	3.9	80 $\pm$ 0.1	0.0145	0.0180	0.46
		2	$\pm$ 0.010					$\pm$ 0.0002	$\pm$ 0.02
PCO2_06	0.363	5.20	5.542	97%	3.4	46 $\pm$ 0.1	0.0115	0.0127	0.47
		5	$\pm$ 0.005					$\pm$ 0.0001	$\pm$ 0.02
PCO2_07	0.041	6.22	6.45	85%	3.9	61 $\pm$ 0.1	0.0063	0.0084	0.08
		2	$\pm$ 0.002					$\pm$ 0.0001	$\pm$ 0.00
PCO2_08	0.157	5.78	6.171	69%	1.7	35 $\pm$ 0.0	0.0038	0.0053	0.09
		1	$\pm$ 0.010					$\pm$ 0.0001	$\pm$ 0.01
PCO2_09	0.362	5.58	5.959	83%	1.0	22 $\pm$ 0.1	0.0026	0.0036	0.09
		3	$\pm$ 0.005					$\pm$ 0.0001	$\pm$ 0.01
TEMP_03a	0.151	5.43	5.754	93%	2.0	42 $\pm$ 0.0	0.0072	0.0094	0.37
		1	$\pm$ 0.006					$\pm$ 0.0001	$\pm$ 0.01
TEMP_04a	0.159	5.39	5.731	99%	1.2	24 $\pm$ 0.1	0.0048	0.0059	0.33
		9	$\pm$ 0.003					$\pm$ 0.0001	$\pm$ 0.01
Ca_01a	0.044	5.73	5.978	87%	7.8	127 $\pm$ 0.0	0.0177	0.0222	0.46
		4	$\pm$ 0.003					$\pm$ 0.0000	$\pm$ 0.03
Ca_02a	0.360	5.43	5.671	93%	3.6	60 $\pm$ 0.0	0.0142	0.0164	0.46
		8	$\pm$ 0.002					$\pm$ 0.0001	$\pm$ 0.01
I_01a	0.156	5.56	5.813	86%	4.7	81 $\pm$ 0.0	0.0188	0.0220	0.47
		7	$\pm$ 0.001					$\pm$ 0.0001	$\pm$ 0.01
I_02a	0.164	5.34	5.664	88%	3.1	59 $\pm$ 0.1	0.0105	0.0132	0.44
		0	$\pm$ 0.008					$\pm$ 0.0001	$\pm$ 0.03
Mg_01a	0.165	5.37	5.762	98%	3.3	76 $\pm$ 0.0	0.0134	0.0175	0.46
		7	$\pm$ 0.006					$\pm$ 0.0002	$\pm$ 0.02
Mg_02a	0.160	5.38	5.749	92%	3.4	75 $\pm$ 0.0	0.0137	0.0176	0.46
		6	$\pm$ 0.004					$\pm$ 0.0001	$\pm$ 0.02
SO4_01a	0.043	5.66	5.869	90%	11.2	179 $\pm$ 0.1	0.0365	0.0432	0.88
		2	$\pm$ 0.004					$\pm$ 0.0001	$\pm$ 0.00
SO4_02a	0.156	5.35	5.620	90%	5.9	105 $\pm$ 0.1	0.0252	0.0296	0.87

		3	±0.002					±0.0002	±0.03
SO4_03a	0.356	5.24	5.441	90%	4.4	66 ±0.1	0.0191	0.0212	0.84
		0	±0.007					±0.0001	±0.04
PCO2_01b	0.043	5.64	5.894	91%	10.8	190 ±0.1	0.0365	0.0445	0.89
		2	±0.005					±0.0002	±0.01
PCO2_01c	0.044	5.66	5.897	90%	11.4	189 ±0.1	0.0374	0.0440	0.89
		3	±0.004					±0.0003	±0.02
PCO2_03b	0.363	5.07	5.457	85%	3.1	68 ±0.1	0.0183	0.0216	0.86
		4	±0.005					±0.0002	±0.06
PCO2_03c	0.364	5.06	5.442	87%	3.1	66 ±0.0	0.0184	0.0211	0.87
		6	±0.011					±0.0004	±0.07

Discussion: The dissolution of 1 mole of calcite contributes 2 moles of TA, as given by the overall reaction,

Thus, the dissolution rate can be defined from the time dependent rate of change in TA:

$$\frac{d\text{CaCO}_3}{dt} = \frac{1}{2} \left(V \frac{d\text{TA}}{dt} \right) \quad (9)$$

where V is the mass of solvent since molal units are used. This requires that the pH-time data be converted to TA-time. The TA at time = t can be calculated using EQPITZER by coupling $p\text{CO}_2$ (~ constant) and pH at time = t.

A high order (7th-order) polynomial equation was necessary to fit the resulting TA-time data (Fig. 17) and accommodate the sharp hysteresis that occurs as the system nears equilibrium. A first derivative of the fitted equation was then used to calculate $\frac{d\text{TA}}{dt}$ and applied to equation 9. As a result of the poor asymptotic properties of high order polynomial equations, the $\frac{d\text{TA}}{dt}$ data had to be truncated near the terminus. The

dissolution rates were then normalized to the available surface area. Given the high volume to surface area ratio (V:A = 1.1 cm) and small changes in alkalinity, no observable change in specific surface area was measured as evidenced from SEM imaging. Therefore, the available surface area was assumed to remain constant over the course of the dissolution.

Figure 17. The TA-time dependence of 2 g of calcite dissolved in a 0.5 L of 125 g L⁻¹ ‘model’ brine at 25 °C and X_{CO2} = 1.0. TA was calculated from *p*CO₂ (~constant) and pH measured every 5 seconds using EQPITZER.

Rate data were modeled using an empirical rate equation (see Morse and Arvidson, 2002, for discussion of application of different types of rate equations to calcite dissolution). The general rate equation is (e.g., Morse and Berner, 1972):

$$R = -\frac{dm_{\text{calcite}}}{dt} = k(1 - \Omega)^n \quad (10)$$

where *R* is the rate (mole m⁻² hr⁻¹), *m* is moles of calcite, *t* is time, *k* is the empirical rate constant, and *n* is the reaction order. The equation describes the rate as a function of saturation state (Ω) with respect to calcite as defined simply as the ratio of the ion activity product (IAP) to the thermodynamic solubility constant (*K_c*), as given by

$$\Omega = \frac{IAP}{K_c} \quad (11)$$

and

$$IAP = \gamma_{Ca^{2+}} m_{Ca^{2+}} \gamma_{CO_3^{2-}} m_{CO_3^{2-}} . \quad (12)$$

where the carbonate ion concentration ($m_{CO_3^{2-}}$) and activity coefficients (γ) were calculated using EQPITZER. If $\Omega = 1$, then the solution is in equilibrium with respect to calcite; if $\Omega < 1$ the solution is undersaturated; and if $\Omega > 1$ the solution is supersaturated.

Gledhill and Morse (2004, 2006) recently reported that, in brines $> 50 \text{ g L}^{-1}$ TDS, the EQPITZER calculated IAP at steady-state systematically exceeds K_c at high calcium concentrations (i.e., $> 0.03 \text{ m}$). Consequently, calculated calcite saturation states may erroneously suggest in excess of a 2-fold supersaturation in the most concentrated brines. This was interpreted (Gledhill and Morse, 2006) as being the result of a small uncertainty in the modeled carbonate ion activity coefficient. In these solutions, the carbonate ion occurs in very low concentration ($< 15 \text{ } \mu\text{molal}$) and the predicted activity coefficient decreases to $\sim 3 \times 10^{-3}$ in the most concentrated brines. Jeschke and Dreybrodt (2002) showed that when rates are modeled as function of the degree of disequilibrium ($1-\Omega$), small uncertainties in Ω can have a pronounced effect on the interpreted reaction order (n) and rate constant (k). Therefore, given the small uncertainty associated with the EQPITZER carbonate ion activity, to model the rate data the Ω value in equation 10 was derived from an apparent steady state solubility specific to each rate experiment.

Figure 18 shows the change in carbonate ion activity as a function of dissolution rate for each of the ‘model’ brines. In all cases a near linear correlation was observed. The apparent steady state carbonate ion activity ($a_{CO_3^{2-}}^*$) was estimated from the intercept of a linear least square regression (i.e., when the rate is zero; Table 12). Given that in these calcium-rich solutions the calcium activity remains nearly constant, the apparent saturation state (Ω^*) could be closely approximated by

$$\Omega^* = \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{eq}^*} \approx \frac{a_{CO_3^{2-}}}{a_{CO_3^{2-}}^*} \quad (13)$$

where K_{eq}^* is the apparent IAP at equilibrium (IAP^*) calculated as the product of $a_{CO_3^{2-}}^*$ and the average steady state calcium ion activity, which only varied a few percent from the mean value during experiments due to the generally relatively high calcium concentrations used. When modeled with respect to this apparent saturation state, first-order kinetics ($n = 1$) were sufficient to provide an excellent fit to the rate data. Reported in Table 12 are the k values ($\text{mmol m}^{-2} \text{ hr}^{-1}$) along with the correlation coefficients.

Figure 18. The apparent carbonate ion activity, as calculated from the experimental data using EQPITZER, as a function of dissolution rate. Solid lines are linear least square regression fits of the experimental data. Dissolution in three ‘model’ brines with TDS concentrations of 50 (open square), 125 (half full square) and 200 (full square) g L⁻¹ at 25 °C and X_{CO2} = 1.0.

Dissolution rates measured in each of the ‘model’ brines at three CO₂ partial pressures (X_{CO2} = 1.0, 0.5 and 0.1) are shown in Figure 19 and their corresponding rate constants are plotted in Figure 20 as a function of TDS. The EQPITZER calculated partial pressures as derived from TA and TCO₂ were 0.88 ±0.04, 0.45 ±0.01 and 0.08 ±0.00 bar respectively, reflecting the contribution of water vapor pressure.

Table 12. The apparent carbonate ion activity and ion activity product (IAP^*) at equilibrium as extrapolated from rate data ($a_{CO_3^{2-}}^*$). The rate constant in $\text{mmol m}^{-2} \text{hr}^{-1}$ for the general rate equation in which $n = 1$.

Experiment ID	$a_{CO_3^{2-}}^* \times 10^8$	$IAP^* \times 10^9$	k	r^2
PCO2_01	28.8	2.61	72.8	1.00
PCO2_02	10.0	4.17	48.6	0.99
PCO2_03	3.7	5.09	33.9	0.99
PCO2_04	39.8	3.62	44.8	1.00
PCO2_05a	9.8	4.46	27.4	0.99
PCO2_05b	10.0	4.10	31.8	0.99
PCO2_05c	10.1	4.23	30.2	0.99
PCO2_06	3.4	5.28	22.8	0.99
PCO2_07	40.9	3.64	16.0	0.99
PCO2_08	11.4	4.75	12.0	0.99
PCO2_09	4.1	6.37	12.0	0.99
TEMP_03a	6.6	2.28	58.1	0.99
TEMP_04a	2.5	0.74	106.9	0.98
Ca_01a	25.8	3.53	25.3	0.98
Ca_02a	6.6	4.80	32.5	0.99
I_01a	13.8	3.71	43.7	0.99
I_02a	5.6	4.93	19.3	0.99
Mg_01a	9.7	4.52	30.0	0.99
Mg_02a	9.2	3.75	27.7	0.99
SO4_01a	34.4	3.09	49.6	0.99
SO4_02a	9.6	3.88	37.2	0.99
SO4_03a	3.5	4.98	22.8	0.98
PCO2_01b	38.0	4.03	85.7	0.99
PCO2_01c	37.6	3.51	32.8	0.99
PCO2_03b	3.8	0.12	44.2	0.99
PCO2_03c	3.9	5.74	12.3	0.93

Figure 19. The $p\text{CO}_2$ effect on rates of calcite dissolution in three ‘model’ brines with TDS concentrations of 50 (open square), 125 (half full square) and 200 (full square) g L^{-1} at 25 °C where $X_{\text{CO}_2} = 1.0$ (a) , 0.5 (b) and 0.1 (c).

Figure 20. The rate constant (k) as a function of TDS (g L^{-1}). In general, as brine TDS concentrations increase, the rates decrease, but this compositional effect is dependent on $p\text{CO}_2$. $X_{\text{CO}_2} = 1$ (solid circle), 0.5 (solid square) and 0.1 (solid diamond). Error bars represent analytical uncertainty.

Other investigators (e.g., Sjöberg, 1978; Busenberg and Plummer, 1986) have demonstrated a rate dependence on CO₂ for partial pressures above 0.1 bar and for pH values greater than about 4.5 when the rate is dominated by surface control reactions. Pokrovsky et al. (2005) found that, in the transport controlled region far from equilibrium, solutions of up to 1 M NaCl also showed *p*CO₂ dependence. However, the dependence did not only persist beyond ~20 atm *p*CO₂. A strong *p*CO₂ dependence was observed in this study, where a 5-fold decrease in the rate constant was measured, when the partial pressure was reduced from near 1 to approximately 0.1 bar (Fig. 20). Van Cappellen et al. (1993) attributed this CO₂ dependence to the formation of carbonate complexes with surface lattice calcium ions. According to their surface complexation model, the CO₂-promoted dissolution rate is directly proportional to the concentration of >CaHCO₃⁰ sites (where > represents the mineral lattice) and is an example of ligand promoted dissolution in which the formation of the bicarbonate surface complex increases the rate of detachment of Ca²⁺ from surface positions.

The inhibitory effects of the salts also appear to exhibit CO₂ dependence. Rates become progressively more depressed with increasing brine concentration but the effect is more pronounced at the higher partial pressures and all but absent at 0.1 bar.

The independent effects of Ca²⁺, Mg²⁺ and ionic strength were investigated by measuring the dissolution rate in solutions that were modifications of the 125 g L⁻¹ ‘model’ brine. In each case, one factor was varied while all other variables were held constant. For example, in the case of the Ca²⁺ effect experiments, two brines were prepared with Mg²⁺ concentration and ionic strength equivalent to the 125 g L⁻¹ ‘model’ brine, but with Ca²⁺ concentrations equivalent to the 50 g L⁻¹ ‘model’ brine (Experiment Ca_01a) and the 200 g L⁻¹ ‘model’ brine (Experiment Ca_02a) respectively (Table 10). The experiments were performed under a X_{CO2} = 0.5 atmosphere at 25 °C and the rates compared against experiment PCO2_05a. By using this approach, the specific contribution to the net inhibition observed with increasing TDS (Fig. 19 and 20) could be evaluated.

An interesting finding was that the greatest inhibition to the rate was attributed to increasing ionic strength (Fig. 21a). Relatively few studies have examined the specific effect of ionic strength on calcite dissolution rates. Buhmann and Dreybrodt (1987) found that ionic strength was only of minor importance, but the study investigated very dilute solutions (< 2 mM) compared with those studied here. Similarly, Pokrovsky et al. (2005) found that the rates, in the transport controlled region far from equilibrium, did not depend on ionic strength for NaCl solutions of up to 1 M. In contrast, Zhang and Dawe (1998) found that, in high salinity waters (up to 2 mol kg⁻¹), the calcite precipitation rate increased as a function of the square root of ionic strength. Similarly, Bischoff (1968) found that nucleation rates of calcite also increased proportionally to the square root of ionic strength. Zuddas and Mucci (1998), in an extensive study of the influence of ionic strength on calcite precipitation from seawater, found the partial reaction order with respect to the carbonate ion concentration increased with ionic strength as did the forward reaction rate constant. It was suggested in these studies that with increased electrolyte concentrations, a stronger inter-particle attraction helps to

catalyze calcite growth in a manner analogous to colloid flocculation. Such processes may conversely inhibit dissolution.

Figure 21. The specific effects of ionic strength, Mg^{2+} and Ca^{2+} concentrations. The rate constant (k) ($\text{moles m}^{-2} \text{hr}^{-1}$) as a function of the molal concentration of Ca^{2+} (a), Mg^{2+} (b) and ionic strength (c).

An alternative, though more speculative, explanation first put forth by Sjöberg (1978) that could account for both the increase precipitation rates observed in the prior studies, and the decreased dissolution rates measured in this study, is related to the effect of water activity on the hydration of metal ions. Lippmann (1973) and Arvidson and Mackenzie (1999) proposed the dehydration of cations poses a fundamental energetic barrier to precipitation. Conversely, the hydration of the calcium ion may pose an energetic barrier to dissolution. In order for calcite to dissolve, the attractive interaction of water molecules must overcome the ionic attraction within the mineral lattice. If, as a result of high ionic strength, the water activity is significantly diminished, one would expect the hydration efficiency of the calcium ion to be retarded. The rate constants shown in Figure 21a change in a close to linear manner, in excess of a factor of two, over the range water activity in these experiments.

There have been a considerable number of investigations on the effects of magnesium ions on calcite dissolution (Weyl, 1967; Berner, 1967; Sjöberg, 1978; Buhmann and Dreybrodt, 1987; Compton and Brown, 1994; Gutjahr et al., 1996b; Alkattan et al., 2002). Whereas the magnesium ion has clearly been shown to strongly inhibit the rate of dissolution in neutral to basic solutions (e.g., Compton and Brown, 1994; pH 8–9), in acidic solutions the inhibition is absent (Alkattan et al., 2002; pH 1–3).

At intermediate pH, such as in this study, the findings are often contradictory. Both Buhmann and Dreybrodt (1987) and Sjöberg (1978) report a strong inhibitory effect whereas Gutjahr et al. (1996b) found no effect.

In this study only a modest inhibition was observed when magnesium was varied between 0.02 and 0.12 molal (Fig. 21b). Sjöberg (1978) described the inhibition due to magnesium in solutions containing $< 50 \text{ mM Mg}^{2+}$ in terms of a Langmuir-type adsorption isotherm. The Langmuir-Volmer model would predict that, beyond some inhibitor solution concentration, the dissolution rate would become independent of the inhibitor concentration. It is possible that the absence of a strong effect in this study reflects that the magnesium concentrations of these brines have exceeded this inhibition plateau. Although Compton and Brown (1994) did measure an inhibition effect in solutions containing up to 80 mM Mg^{2+} , the pH of their experimental solutions was greater than 8, which may be above the pH of zero surface charge ($\text{pH}_{\text{zpc}} \approx 8.2$) (e.g., Hohl et al., 1980). Below the pH_{zpc} the effects of cationic inhibitors may be greatly diminished (Van Cappellen et al., 1993; Pokrovsky and Schott, 2002).

Several studies have also investigated the effect of the calcium ion on calcite dissolution (Sjöberg, 1978; Sjöberg and Rickard, 1985; Buhmann and Dreybrodt, 1987; Gutjahr et al., 1996a, 1996b), often with contradictory results. Sjöberg (1978) found that increasing the Ca^{2+} concentration from 0 to 10 mM resulted in about a 17% decrease to the rate constant that he described in terms of a Langmuir-type adsorption isotherm similar to that of magnesium. In contrast, Gutjahr et al. (1996b) found that the rate constant actually increased by roughly 40% when Ca^{2+} concentrations were increased from 0.160 to 4.090 mM . The cause of the disparity between the different studies is unclear since amongst these studies the pH, $p\text{CO}_2$ and degree of disequilibrium are relatively similar.

In this study an increase in the measured rate constant was observed when calcium was increased from 0.04 to 0.36 molal (Fig. 21c). The experimental conditions of the previous studies, however, do differ considerably from this study, which was performed in moderately acidic (pH (i.e., < 6.5), high $p\text{CO}_2$, magnesium-bearing solutions.

An important consideration is the effect that calcium has on the carbonate carrying capacity of the solution (e.g., Morse and Mackenzie, 1993). For a given degree of undersaturation, the relative amount of carbonate ion in solution is reduced when the initial calcium concentration is increased. The inhibiting effect of CO_3^{2-} has been demonstrated for dissolution far from equilibrium in the case of ZnCO_3 and MnCO_3 (Pokrovsky and Schott, 2002), dolomite and magnesite (Pokrovsky et al., 1999; Pokrovsky and Schott, 1999), and calcite (Lea et al., 2001; Arvidson, personal communication). Whether such inhibition effects occur near equilibrium or at this low CO_3^{2-} concentration has not yet been established, but they might contribute to the positive correlation between calcium and the rate constant measured here.

Temperature is one of the most important variables when considering reaction rate constants. Drastic variations in rates can occur owing to the exponential dependence

of reaction rate on temperature, which is often assumed to follow the classic Arrhenius equation:

$$k = Ae^{-\left(\frac{E_a}{RT}\right)} \quad (14)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1}$) and T is the temperature in degrees Kelvin. The apparent activation energy for the dissolution reaction can be calculated from the slope of a plot of $\log k$ versus the reciprocal absolute temperature since

$$\ln k = \left(\frac{-E_a}{RT}\right) + \ln A. \quad (15)$$

A plot of $\ln k$ against $1/T$ for dissolution experiments performed using the 125 g L^{-1} ‘model’ brine conducted under a $X_{\text{CO}_2} = 0.5$ atmosphere at 25.0 , 52.5 and $82.5 \text{ }^\circ\text{C}$ is shown in Figure 22. The apparent activation energy is calculated to be $21 \pm 1 \text{ kJ mol}^{-1}$ for this reaction. There are a wide range of activation energies reported for calcite dissolution (about $8\text{--}60 \text{ kJ mol}^{-1}$; see Morse and Arvidson, 2002 for review). In dilute solutions far from equilibrium where diffusion-controlled processes dominate, most reported values are close to 10 kJ mol^{-1} (e.g., Plummer et al., 1978; Sjöberg, 1978; Salem, 1994). However, larger values are believed to be typical of surface-controlled processes (Lasaga, 1998). The value determined in this study is in excellent agreement with the $E_a = 19 \pm 4 \text{ kJ mol}^{-1}$ reported by Alkattan et al. (1998).

As further evidence of surface controlled kinetics, when experiment PCO2_05 (i.e., 125 g L^{-1} TDS, $X_{\text{CO}_2} = 0.5$, $25.0 \text{ }^\circ\text{C}$) was replicated at 500 and 700 rpm , the rates varied by less than 8% , probably within experimental error when compositional effects among the replicates are considered. This stirring rate independence is consistent with surface-controlled dissolution.

The kinetics of calcite dissolution have typically been described in terms of empirical or semi-empirical rate equations (e.g., Morse, 1978; Sjöberg, 1978; Busenberg and Plummer, 1986), classical chemical kinetics (e.g., Plummer et al., 1978) or surface speciation (Van Cappellen et al., 1993; Arakaki and Mucci, 1995; Pokrovsky and Schott, 2002) models. With the exception of some empirical models applied to seawater, these models are only applicable to relatively dilute solutions since accurately quantifying many of the required species (e.g., surface complexes) in concentrated solutions (i.e., $>1 \text{ m}$) is beyond current geochemical models.

Figure 22. Arrhenius plot for rates measured in the 125 g L⁻¹ ‘model’ brine under a X_{CO2} = 0.5 atmosphere at 25.0, 52.5 and 82.5 °C. The apparent activation energy is 20.9 kJ mol⁻¹ indicating a surface-controlled reaction.

A disadvantage of the general rate equation ($R = k(1-\Omega)^n$) is that it requires fitting parameters (k and n) specific to the solution composition of interest, where the major solute and inhibitor concentrations and environmental conditions (e.g., P , T and $p\text{CO}_2$) are known. The first-order kinetics observed in this study across a broad range of typical brine concentrations requires that only one term, k , be determined. This greatly simplifies the approach since conventional statistical methods can be applied to account for the variability in k as a function of the key factors investigated.

A multiple regression analysis was used to evaluate to what extent the observed rate constant is dependent on each of the variables Ca^{2+} , Mg^{2+} , ionic strength, temperature and $p\text{CO}_2$. As with other regression models, multiple regressions (MR) may not be capable of yielding specific reaction mechanisms, but can estimate the relative strength of individual effects and, thus, be used to provide a predictive statistically-based empirical rate equation. The goal of this approach is to fully describe the observed rate data as a function of each of the investigated factors.

The MR analysis was performed using the statistical software SPSS[®] v. 11.0 for Windows. The robustness of the model was evaluated from the coefficient of multiple determination (R^2) and by examination of the residuals. In addition, a colinearity diagnostic was determined. Colinearity is a common complication in MR that can occur

when the effect of one independent variable on the dependent variable is contingent on the value of another independent variable (Philippi, 1993).

The greatest predictive capability (adjusted $R^2 = 0.953$, $P < 0.001$) was achieved when the data were left untransformed (i.e., linear regression) and activity was modeled rather than concentration in the cases of calcium and magnesium. The resulting regression yielded:

$$k = \beta_0 + \beta_1(t) + \beta_2(pCO_2) + \beta_3(I) + \beta_4(a_{Ca^{2+}}) + \beta_5(a_{Mg^{2+}}) \quad (16)$$

where t is °C, pCO_2 is given in bars, I is ionic strength and a_i are activities of calcium and magnesium. The unstandardized coefficients are provided in Table 13 for solving the surface area normalized rate constant (k). The calculated condition numbers for colinearity for each of the predictors were less than 20 and the variance inflation factors (VIF) less than 10, indicating that severe colinearity was not a factor (Freund and Littell, 1986; Chatterjee and Price, 1991). Since the predictors used in the model are measured in different units, the standardized coefficients (Table 13) are required to compare the relative effects of each of the predictors. The relative effects are $t \gg pCO_2 \approx I > a_{Ca^{2+}} \gg a_{Mg^{2+}}$. The results show that the ionic strength strongly correlates with a reduction in rate, and that the inhibitory effect of magnesium is small in these solutions. It also reveals that the calcium activity is positively correlated with the dissolution rate. Figure 23 illustrates the predictive capability of the model where the measured rate constants are plotted versus their predicted values.

Table 13. The coefficients derived from multiple regression analysis. These can be used to predict the rate constant from the predictors T °C, pCO_2 , I , $a_{Ca^{2+}}$ and $a_{Mg^{2+}}$.

Predictor	Coefficient	Unstandardized	Standardized
		$\times 10^3$	
Constant	β_0	-6.07	
t (°C)	β_1	1.42	0.879
pCO_2 (bar)	β_2	48.56	0.499
I (molal)	β_3	-10.97	-0.475
$a_{Ca^{2+}}$	β_4	127.45	0.259
$a_{Mg^{2+}}$	β_5	-58.54	-0.059

Figure 23. The measured rate constants versus the predicted values from equation 10. The lines represent the 95% confidence interval of the model prediction. The regression was fit to data obtained from dissolution rates using the rhombic calcite (solid square). The statistical model closely predicts previously measured rates obtained using powdered calcite (Gledhill and Morse, 2004) (open circle).

When we compare the dissolution rates measured using powdered calcite reported by Gledhill and Morse (2004) to those obtained using crushed rhombs, there are apparent gross dissimilarities. Specifically, although the powder rates generally decreased with increasing brine concentration, the net inhibition was relatively minor. In contrast, the crushed rhomb experiments reveal a stronger compositional effect at the same higher partial pressures. However, Figure 23 reveals that the MR model closely predicts the rates constants of the powdered calcite. It suggests that the limited inhibition observed by Gledhill and Morse (2004) using powdered calcite experiments is an artifact of the brine preparations. The median Ca:I ratio in the Gledhill and Morse (2004) experimental brines were about twice that of these experiments. Since the effects of calcium and ionic strength are inversely correlated, the subdued compositional inhibition observed in the powdered calcite experiments can be accounted for as a result of the calcium effect partially compensating for the inhibitory effect associated with ionic strength.

A common inhibitor of calcite reaction (dissolution/precipitation) kinetics in natural waters is the divalent anion sulfate (Akin and Lagerwerff, 1965; Sjöberg, 1978; Buhmann and Dreybrodt, 1987; Mucci et al., 1989). Sulfate present at seawater concentration has been demonstrated to reduce the dissolution rate constant by 40% in phosphate-free pseudo seawater (Sjöberg, 1978). In subsurface formation waters sulfate is often, but not always, a relatively minor component rarely exceeding 1 g L^{-1} compared with 2.7 g L^{-1} in seawater. Nevertheless, Sjöberg (1978) found that the effect of sulfate increases with increasing calcium and magnesium concentration and, thus, it could potentially be an even more potent inhibitor in brines. This could be related to the surface adsorption of calcium and magnesium, producing a more cationic surface that increases the adsorption of anions such as sulfate.

To test the effect, approximately 1 g L^{-1} ($\sim 0.01 \text{ m}$) of sulfate were added to each of the ‘model’ brines in the form of a concentrated Na_2SO_4 solution. The dissolution rates were measured in each solution at 25°C and $X_{\text{CO}_2} = 1$ and compared with its MR-model predicted rate. The higher CO_2 partial pressure was chosen since brines exhibited the greatest compositional sensitivity at this $p\text{CO}_2$. Figure 24 shows the increasing inhibitory effect of sulfate with increasing calcium and magnesium activity, consistent with Sjöberg’s (1978) findings. The equation fit to the data is purely an empirical construct, but does suggest that in the absence of calcium and magnesium the inhibitory effect of $1 \text{ g L}^{-1} \text{ SO}_4^{2-}$ would only be about 20%. In brines containing a TDS of 200 g L^{-1} the inhibition could be similar to that observed in seawater.

Summary: The calcite dissolution rate near equilibrium ($\Omega > 0.2$) in concentrated Na-Ca-Mg-Cl brines, equivalent to subsurface formation waters ranging from TDS 50 to 200 g L^{-1} , were measured. The rates can be described using first-order kinetics by the general rate equation: $R = k(1-\Omega)^n$, where $n = 1$ (first-order) and the rate constant k can be derived from the MR model:

$$k = \beta_0 + \beta_1(T) + \beta_2(p\text{CO}_2) + \beta_3(I) + \beta_4(a_{\text{Ca}^{2+}}) + \beta_5(a_{\text{Mg}^{2+}}).$$

The strongest influence on the rate is not salt content but temperature and CO_2 partial pressure. Surprisingly, ionic strength strongly correlates with an inhibition of rate of dissolution beyond the specific effects of calcium and magnesium. Magnesium showed only a minor inhibitory effect whereas increasing calcium actually increased the rate constant.

When SO_4^{2-} is present at concentrations typical of subsurface formation waters there is a strong inhibition effect similar to that observed previously in seawater. The influence of sulfate is also strongly sensitive to the concentrations of calcium and magnesium. Due to this relation, even though sulfate concentrations in subsurface formation waters are generally less than that in seawater, at TDS concentrations greater than 200 g L^{-1} , its effect on the rate may be of similar magnitude. It should be noted that these results are applicable to relatively high $p\text{CO}_2$ ($> 0.1 \text{ atm}$) waters where the pH is < 6.5 and they should be extrapolated with considerable caution to waters of lower $p\text{CO}_2$ and higher pH values as is typical of sediment pore waters.

Figure 24. The inhibitory effect of 1 g L⁻¹ sulfate in ‘model’ brines at 25 °C at X_{CO2} = 1.0. The measured rate constant (k) relative to the MR-model prediction (k₀) show that with increasing calcium and magnesium activity ($\Sigma = a_{Ca^{2+}} + a_{Mg^{2+}}$) the sensitivity to sulfate increases. The

equation of the line shown is: $1 - (k / k_0) = 0.20 + 4.68 \left(a_{Ca^{2+}}^2 + a_{Mg^{2+}}^2 \right)$, $r^2 > 0.99$.

Dissolution Kinetics References:

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4. Products and Technology Transfer

4.1. Papers in Scientific Journals

1. Seo, J. and Mamora, D.D.: “Experimental and Simulation Studies of Sequestration of Supercritical Carbon Dioxide in Depleted Gas Reservoirs,” *ASME J. Energy Resources Tech.*, vol. 127, Mar. 2005.
2. Nogueira, M. C. and Mamora, D.D.: “Effect of Flue Gas Impurities on the Process of Injection and Storage of CO₂ in Depleted Gas Reservoirs,” paper presented at SPE/DEA/DOE Exploration and Production Environmental conference, Galveston, Mar. 2005.
3. Gledhill, D.K., and J.W. Morse, 2004, Dissolution kinetics of calcite in NaCl-CaCl₂-MgCl₂ brines at 1 bar (0.1 MPa) pCO₂ and 25°C. *Aquatic Geochemistry*, **10**, 171-190.
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4.2. Talks and Posters at National and International Scientific Meetings

1. Mamora, D.D. and Seo, J.: “Enhanced Gas Recovery by Carbon Dioxide Sequestration in Depleted Gas Reservoirs,” paper SPE 77347 presented at SPE annual technical conference and exhibition, San Antonio, 29 Sept. Oct. 2, 2002

2. Nogueira, M. C. and Mamora, D.D.: "Effect of Flue Gas Impurities on the Process of Injection and Storage of CO₂ in Depleted Gas Reservoirs," paper presented at SPE/DEA/DOE Exploration and Production Environmental conference, Galveston, Mar. 2005.
3. Gledhill, D.K. and Morse, J.W., 2004, Calcite dissolution and solubility in NaCl-CaCl₂ brines up to 1 bar pCO₂ and 80°C. American Geophysical Union Annual Fall Meeting Abstracts .
4. Morse, J.W. and Gledhill, D.K., 2005, Geochemical considerations regarding the processes involved in mineral deposition in sedimentary rock-hosted veins. Invited paper, Abstracts AGU Annual Fall Meeting, San Francisco.

4.3. Graduate Degrees Awarded

1. Jeong Gyu Seo, PhD dissertation, May 2004: *Experimental and Simulation Studies of Sequestration of Supercritical Carbon Dioxide in Depleted Gas Reservoirs.*
2. Marjorie C. Nogueira, MS thesis, Aug. 2005: *Effect of Gas Impurities on the Process of Injection and Storage of Carbon Dioxide in Depleted Gas Reservoirs.*
3. Ekene O. Maduakor, MS thesis, Aug. 2006: *Effects of Carbon Dioxide Injection on the Displacement of Methane and Carbonate Dissolution in Sandstone Cores.*
4. Gledhill, Dwight K., PhD dissertation May 2005, *Calcite dissolution kinetics and solubility in Na-Ca-Mg-Cl brines of geologically relevant composition at 0.1 to 1 bar pCO₂ and 25 to 80 °C.*

4.4. Awards

1. Jeongyu Seo won second place in the PhD category of the international student paper contest held at the SPE/DEA/DOE Exploration and Production Environmental conference, Galveston, Mar. 2003.
2. Marjorie Nogueira won first place in the combined MS and PhD category of the international student paper contest held at the SPE/DEA/DOE Exploration and Production Environmental conference, Galveston, Mar. 2005.

Dissolution Kinetics of Calcite in NaCl–CaCl₂–MgCl₂ Brines at 25 °C and 1 bar pCO₂

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Abstract. Calcite dissolution rates were measured as a function of saturation state in NaCl–CaCl₂–MgCl₂ solutions at 1 bar (0.1 MPa) pCO₂ and 25 °C. Rates measured in phosphate- and sulfate-free pseudo-seawater (Ca²⁺:Mg²⁺ = 0.2, *I* = 0.7) were compared with those in synthetic brines. The brines were prepared by co-varying calcium and magnesium (Ca²⁺:Mg²⁺ = 0.9; 2.0; 2.8; 3.1; 4.8; 5.8) along with ionic strength (*I* = 0.9; 1.1; 1.6; 2.1; 3.0; 3.7; 4.4 m) to yield solutions approximating those of subsurface formation waters. The rate data were modeled using the equation, $R = k(1 - \Omega)^n$, where *k* is the empirical rate constant, *n* describes the order of the reaction and Ω is saturation state. For rates measured in the pseudo-seawater, *n* = 1.5 and $k = 4.7 \times 10^{-2} \text{ mol m}^{-2} \text{ hr}^{-1}$. In general, rates were not significantly faster in the synthetic brines ($n = 1.4 \pm 0.2$ and $k = 5.0 \pm 7 \times 10^{-2} \text{ mol m}^{-2} \text{ hr}^{-1}$). The rate coefficients agree within experimental error indicating that they are independent of ionic strength and Ca²⁺:Mg²⁺ over a broad range of brine compositions. These findings have important application to reaction-transport modeling because carbonate bearing saline reservoirs have been identified as potential repositories for CO₂ sequestration.

Key words: calcite, dissolution, kinetic, brine, CO₂ sequestration

1. Introduction

Carbonate minerals constitute ~20% of Phanerozoic sedimentary rock, and at least 60% of the world's known petroleum reserves occur in carbonate reservoirs (Morse and Mackenzie, 1990). Because calcite is a reactive common mineral, its precipitation and dissolution are of great importance in the creation and destruction of secondary porosity in the subsurface.

Although the importance of carbonate mineral dissolution during sediment diagenesis has been known since at least the late 1800s (e.g., Murray and Renard, 1891), experimental determination of dissolution rates as a function of solution composition did not receive considerable attention until the 1960s (e.g., Akin and Lagerwerff, 1965; Berner, 1967; Schmalz,

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1967; Terjesen et al., 1961; Weyl, 1958, 1967). Since that time, a large number of investigations have examined the influences of “foreign” ions, temperature, CO_2 partial pressure and other variables on calcite dissolution rates (see reviews of Morse, 1983; Morse and Arvidson, 2002; Plummer et al., 1979; Sjöberg and Rickard, 1983). Previous investigations sought to understand the behavior of calcite in solutions with ionic strengths that did not generally exceed that of seawater. Calcite reaction kinetics in concentrated solutions, typical of the subsurface, have received relatively little attention. Although recent observations included precipitation rates in high salinity waters (Zhang and Dawe, 1998), there are apparently no studies that have directly addressed dissolution kinetics in complex high ionic strength solutions.

Investigation of carbonate mineral dissolution as a function of saturation state requires accurate calculations of the carbonic acid system species distributions. Accurate determination of the activities of these species in high ionic strength solutions continue to be problematic. Investigations of the solubility of calcite coupled with the Pitzer parameterizations of the carbonic acid system in synthetic brines (He and Morse, 1983) have made such calculations more reliable.

In this study, we have determined the dissolution kinetics of calcite in saline waters with compositions approximating those in Northern Hemisphere reservoirs. Results have important applications to predictive chemical process models in carbonate cemented reservoirs and for carbon sequestration strategies.

2. Experimental

2.1. MATERIALS AND METHODS

The synthetic brines prepared in this study exhibited calcium and magnesium concentrations, and ionic strengths similar to subsurface brines and were based on the review of the composition of saline fluids in sedimentary basins by Hanor (1994). Each solution was prepared gravimetrically on the molal scale (m) from A.C.S. reagent grade NaCl , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as shown in Table I.

Solution concentrations of Cl^- were determined by AgNO_3 titration ($\pm 1.5\%$) using an Accumet silver ion selective electrode interfaced with a computer via an Orion 720A potentiometer. Calcium was analyzed by EGTA titration with calcium indicator Cal/Ver II[®], and Mg^{2+} concentrations were determined by EDTA titration with Erichrome Black (EBT). Endpoint detection was facilitated using a Brinkmann PC 800 colorimeter interfaced with a Brinkmann 682 titroprocessor. Precision was within 2% in most cases. The concentration of Na^+ was calculated from charge balance.

Table I. Initial solution composition of model brines prepared

Brine ID	~TDS (g l ⁻¹)	Ionic Strength (molal)	Ca ²⁺ (molal)	Mg ²⁺ (molal)	Na ²⁺ (molal)	Cl ⁻ (molal)
Pseudo-SW	35	0.73	0.0116	0.0593	0.5164	0.6426
Brine 1	41	0.86	0.0675	0.0720	0.4577	0.7005
Brine 2	56	1.14	0.0914	0.0456	0.7295	0.9971
Brine 3	77	1.60	0.1475	0.0532	0.9995	1.3960
Brine 4	105	2.13	0.2624	0.0858	1.1740	1.6880
Brine 5	134	2.99	0.4366	0.0903	1.4070	2.4580
Brine 6	158	3.70	0.6408	0.1112	1.4400	2.9410
Brine 7	179	4.43	0.9356	0.1624	1.1360	3.3300

Total alkalinity (TA) was determined by a Gran-type titration (Gran, 1952) using a Metrohm 655 Dosimat and an Orion 720A pH meter interfaced with a computer. Apparent sample pH was measured using a Corning Inc. semi-micro combination pH electrode calibrated via NBS 4 and 7 buffers. An HCl titrant and solutions of primary standard Na₂CO₃ were prepared in NaCl at ionic strengths identical to each of the brines. Precision ranged from $\pm 9\%$ for low concentrations to better than $\pm 0.3\%$ at high concentrations. The titrations were conducted at 25 ± 0.1 °C in a water-jacketed open cell into which CO₂ was continuously bubbled. Total dissolved inorganic carbon (TCO₂) was determined according to the method of Dickson and Goyet (1994) with a UIC Inc. Model 5011 CO₂ coulometer. Precision ranged from $\pm 3.7\%$ at low concentrations to better than $\pm 0.3\%$ for high concentrations.

A.C.S. reagent grade calcite (Fisher Scientific) was pretreated with dilute (0.1 N) HCl according to the methods of Sass et al. (1983). Mineralogy was verified as $> 99\%$ calcite by X-ray diffraction. Scanning electron microscopy (SEM) was used to characterize grain size and distribution. A geometric surface area calculated from SEM imaging ($0.87 \text{ m}^2 \text{ g}^{-1}$) was in good agreement with a separate determination by BET gas absorption ($0.95 \text{ m}^2 \text{ g}^{-1}$).

2.2. EQPITZER SOFTWARE

Using experimentally determined interaction parameters between the carbonic acid species (CO_{2(aq)}, HCO₃⁻, and CO₃²⁻) and the major ions Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻, the EQPITZER software makes calculations based on the Pitzer theory of electrolytes (Pitzer, 1973; Pitzer and Mayorga, 1973, 1974) and the ion-pairing model of Millero and Schreiber (1982). The software, developed by He and Morse (1993), incorporates into the model experimentally determined stoichiometric

Henry's law constants (K_H^*) and dissociation constants (K_1^* and K_2^*) for the carbonic acid system appropriate to a wide range of high ionic strength solutions. The program also includes the thermodynamic association constants of Reardon and Langmuir (1974) for the important ion pairs CaCO_3^0 , MgCO_3^0 and MgOH^+ . The software enables calculation of the thermodynamic properties of chemical species in complex electrolyte solutions (e.g., carbonic acid species). A *complete* description of the carbonic acid system (at constant temperature and pressure) can be obtained from at least two fundamental CO_2 system parameters (TA, TCO_2 , pCO_2 , and pH) and a solution's major ion composition.

2.3. DISSOLUTION RATE MEASUREMENT

An open system pH-free-drift method was employed in which the rate of CaCO_3 dissolution was determined by monitoring changes in solution pH as a function of time. The pH variations were converted to alkalinity concentration change using the EQPITZER software.

The 550 ml water-jacketed reaction vessel accommodated a gas feed, two electrodes, condenser/vent, temperature probe and sampling port. The solution was stirred at constant rate with a propeller shaft that passed through the top of the reaction vessel. Temperature was held constant at $25 \pm 0.1^\circ\text{C}$ using a Neslab[®] constant-temperature bath. The pCO_2 was maintained by bubbling commercially purified high grade CO_2 into the reaction vessel. A mass-flow controller interfaced with a computer assured constant flow rate. In order to minimize evaporation of experimental solutions, the gas was humidified by bubbling through sodium chloride solutions. The latter solutions were also maintained at $25 \pm 0.1^\circ\text{C}$ and had ionic strengths that were matched with the experimental solutions.

Solution pH was measured with an Orion 720A potentiometer using the modified approach of Knauss et al. (1990) in which a H^+ -selective electrode is coupled to a solid state Cl^- ion selective electrode. The method seeks to avoid the problems associated with pH measurement in high ionic strength solutions by avoiding a liquid junction. Although calibration of pH electrodes is commonly made with respect to NBS buffers, this approach is generally accurate for determination of pH only in dilute solutions. Since standard buffers are not readily available for solutions exhibiting the high ionic strengths used in this study, the electrodes were calibrated directly to the EQPITZER software from measurements of the initial and final TA and TCO_2 of the experimental solutions. Coupling these two carbonate system parameters with the solution composition, a "Pitzer scale" pH could be calculated using EQPITZER. The electrode response slope (S_x) was established using a two-point calibration from

$$S_x = \frac{E_f - E_i}{\text{pH}_i - \text{pH}_f} \quad (1)$$

where E is the emf and pH is the calculated “Pitzer pH”, initial (i) and final (f). Electrode response in the brines was within 15% of the ideal Nernst value (Table II). The Knauss method is internally consistent with the EQPITZER software since it was used in the CO₂-system Pitzer parameter determinations of He and Morse (1983).

The initial conditions of the brines prior to addition of calcite were established by bubbling with a 100% CO₂ gas stream followed by addition of a concentrated primary standard grade Na₂CO₃ solution sufficient to establish the CaCO₃ saturation state (Ω) at approximately 0.2. The solution was then equilibrated for several hours and the electrodes allowed to stabilize. The emf was recorded and a 10 ml aliquot was drawn for the initial determination of key parameters (Cl⁻, Ca²⁺, Mg²⁺, TA and TCO₂). Powdered calcite 200 mg in excess of its predicted consumption was then added to the reaction vessel and changes in solution pH were measured. To conserve system memory, the time interval (Δt) between the recorded measurements varied with saturation state; 5 s for $\Omega \ll 1$ and 40 s when $\Omega \cong 1$. Numerical differentiation was facilitated using a non-linear regression of the form

$$mV = a + bt + ct^2 + dt^3 + et^4 + \log(t). \quad (2)$$

However, due to the variable time interval this regression could not be applied directly. A cubic-spline smoothing routine had to first be applied that evenly distributed the mV -time data. Without the spline fitting, the regression would disproportionately weight the data for $\Omega \cong 1$ resulting in a poor fit when $\Omega \ll 1$. After 1 h the rate of change was typically too slow to resolve from electrode “noise”. A final emf value was then recorded and a second aliquot drawn and filtered through a Millipore 0.45 μm syringe filter for determination of final key parameters.

Following the rate measurement, the change in solution composition was measured by direct hourly sampling until, within experimental error, steady state was achieved. As a result of the high pCO₂ and use of high surface area calcite, the system typically achieved steady state within 6 h, whereupon equilibrium values for calcium and carbonate ion activities were calculated using EQPITZER.

2.4. CALCULATION OF CALCITE DISSOLUTION RATES

Mass and charge balance demands that in an open system the dissolution of 1 mol of calcite leads to a 2 mol change in TA as given by

Table II. Initial and steady-state carbonic acid system parameters. Alkalinity (TA) and total dissolved carbon (TCO₂) are given in molal concentrations and PCO₂ in MPa

Brine ID	pH _i	pH _{ss}	S _x ^b (%)	TA _i (molal)	TA _{ss} (molal)	TCO _{2i} (molal)	TCO _{2ss} (molal)	PCO ₂ ^c (MPa)
Pseudo-SW	5.794	6.059 ± 0.015	88	0.0157	0.0272 ± 0.0002	0.0443	0.0541 ± 0.0007	0.094 ± 0.003
Brine 1	5.523	5.803 ± 0.009	99	0.0076	0.0150 ± 0.0002	0.0328	0.0410 ± 0.0008	0.087 ± 0.002
Brine 2a	5.392	5.771 ± 0.017	94	0.0062	0.0142 ± 0.0001	0.0315	0.0383 ± 0.0009	0.089 ± 0.002
Brine 2b	5.368	5.737 ± 0.005	94	0.0060	0.0135 ± 0.0001	0.0320	0.0385 ± 0.0003	0.092 ± 0.003
Brine 3	5.289	5.661 ± 0.001	96	0.0049	0.0118 ± 0.0001	0.0277	0.0349 ± 0.0002	0.089 ± 0.000
Brine 4	5.187	5.599 ± 0.009	89	0.0038	0.0097 ± 0.0001	0.0244	0.0298 ± 0.0003	0.086 ± 0.001
Brine 5	5.071	5.481 ± 0.011	96	0.0028	0.0076 ± 0.0001	0.0208	0.0264 ± 0.0004	0.088 ± 0.004
Brine 6	5.054	5.433 ± 0.008	106	0.0023	0.0064 ± 0.0001	0.0170	0.0235 ± 0.0002	0.083 ± 0.009
Brine 7	4.733	5.399 ± 0.006	86	0.0012	0.0056 ± 0.0000	0.0176	0.0218 ± 0.0001	0.090 ± 0.000

^aThe subscript _i and _{ss} refer to initial and steady-state values, respectively.

^bElectrode response is reported in %Nernstian.

^cThe mean of the initial and at the time of electrode removal as calculated from TA and TCO₂.

Thus, the dissolution rate can be defined from the time dependent rate of change in TA:

$$\frac{d\text{CaCO}_3}{dt} = \frac{1}{2} \left(V \frac{d\text{TA}}{dt} \right), \quad (4)$$

where V is the mass of solvent since molal units are used. This requires that the pH–time data be converted to TA–time. Since pCO_2 remained near constant over the course of the reaction, TA could be solved for using EQPITZER by coupling pCO_2 and pH. TA–time data were differentiated numerically whereupon the dissolution rate, normalized to the CaCO_3 surface area, was calculated from equation (4).

As the calcite dissolved, the decrease in calcite surface area was included in the rate calculations. The calcite surface area at time t was estimated from

$$A_{r \times n} = (W_i - (1/2V(\text{F.W.})(\text{TA}_j - \text{TA}_i)))a_T, \quad (5)$$

where $A_{r \times n}$ is the calcite surface area (m^2) in the reaction vessel at time t , W_i is the initial calcite mass (g), V is mass of solvent (kg), F.W. is the molecular weight of calcite, and TA_j and TA_i are alkalinities at time t and $t = 0$. As a first order approximation, the term a_T is the mass specific surface area ($\text{m}^2 \text{g}^{-1}$) as initially determined by SEM and BET. However, since it is variable during dissolution, estimating a_T required an iterative procedure. The approach assumes a cubic geometry for each CaCO_3 grain and that the activity of each calcite grain is equivalent.

Prior to the experiments, SEM was used to image the calcite powder to characterize the distribution of grain size. A grain size frequency distribution was obtained by averaging the shortest and longest edge length (ℓ) of 125 grains. The initial geometric surface area ($a_{T_initial}$, $\text{m}^2 \text{g}^{-1}$) was calculated using the following equation:

$$(a_{T_initial}) = \sum \frac{a_j f_j}{m_T}, \quad (6)$$

where a_j is the area of grain size fraction (j) ($a_j = 6\ell_j^2$), f_j is the frequency of occurrence of the grain size fraction (j) and m_T is the total mass of the combined grain fractions as given by

$$m_T = \sum f_i \rho \left(\frac{a_i}{6} \right)^{3/2} \quad (7)$$

where ρ is the density of calcite (2.71 g cm^{-3}).

As a result of dissolution, the volume of each grain at time t (v_j^*) can be expected to vary approximately as follows:

$$v_j^* = v_j - R(\Delta t)6v_jv_m, \quad (8)$$

where v_j is the grain volume ($v_j = ((a_j)/(6))^{3/2}$, m^3) at $t-1$, R is the dissolution rate ($\text{mol m}^{-2} \text{h}^{-1}$) at time t , Δt is the time interval (hours) over which $d\text{CaCO}_3/dt$ was numerically differentiated, and v_m is the molar volume of calcite ($\text{m}^3 \text{mol}^{-1}$). A corrected grain surface area for a given grain can then be calculated ($a_j^* = 6(v_j^*)^{2/3}$), and the $A_{r \times n}$ and a_T terms recalculated from equations (5) to (6). The surface area normalized rate was then recalculated and the process iterated several times. The increase in specific surface area as the mass of calcite decreases tends to maintain a constant total surface area. The total decrease in surface area over an experimental run was typically about 30%.

3. Results

Table II lists the important CO_2 -related parameters at the start of each experiment and at steady state. Figure 1 shows the raw and fitted mV data and corresponding pH as a function of time for calcite dissolution in brine 5 (Table I). TA and the total ion activities of Ca^{2+} and CO_3^{2-} obtained from the experiment are presented in Figure 2. Both the EQPITZER generated and the corrected CO_3^{2-} total ion activities are shown (see Section 4). Results

Figure 1. Measured mV and calibrated "Pitzer Scale" pH change as a function of time for calcite dissolution in brine 5. (Δ) mV ; (—) Fit; (--) pH.

Figure 2. Key parameters as a function of time for calcite dissolution in brine 5. Converted values were derived from solution pH. (▲) TA (molal) — sample analysis; (■) EQPITZER Carbonate ion (activity) — sample analysis; (●) Ca (activity) — sample analysis; (□) Corrected carbonate ion (activity) — sample analysis; (Δ) TA (molal) — converted; (■) EQPITZER Carbonate ion (activity) — converted; (○) Ca (activity) — converted; (□) Corrected carbonate ion (activity) — converted.

from direct sampling illustrate the stability of the system at steady state. Within measurement error, calcium ion activity remains near constant, while TA and CO_3^{2-} exhibit initial rapid increases that asymptotically approach steady state values.

Rate data were interpreted using the general rate equation (see Morse and Arvidson, 2002, for discussion of application of different types of rate equations to calcite dissolution). The general rate equation is (GRE, equation (3), e.g., Morse and Berner, 1972):

$$R = -\frac{dm_{\text{calcite}}}{dt} = \left(\frac{A}{V}k\right)(1 - \Omega)^n \quad (9)$$

where R is the rate in $\text{mol m}^{-2} \text{h}^{-1}$, m the moles of calcite, t the time, A the calcite surface area, V the mass of solvent, k the empirical rate constant, and n is the reaction order.

The equation describes the rate as a function of saturation state (Ω) defined as

$$\Omega = \frac{a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}}}{K_{\text{cal}}} = \frac{\gamma_{\text{Ca}^{2+}}m_{\text{Ca}^{2+}}\gamma_{\text{CO}_3^{2-}}m_{\text{CO}_3^{2-}}}{K_{\text{cal}}}, \quad (10)$$

where

Table III. Calcite dissolution rate fitting parameters k ($\text{mol m}^{-2} \text{h}^{-1}$) and n for the general rate equation. $R = k(1 - \Omega)^n$

Brine ID	k	n	R^2
Pseudo-SW	0.047	1.51	0.999
Brine 1	0.040	1.16	0.993
Brine 2a	0.044	1.35	0.987
Brine 2b	0.059	1.53	0.999
Brine 3	0.046	1.39	0.999
Brine 4	0.062	1.63	0.997
Brine 5	0.046	1.28	1.000
Brine 6	0.050	1.22	0.999
Brine 7	0.049	1.58	1.000

$$K_{\text{cal}} = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}, \quad (11)$$

and a_i , γ_i and m_i are the activity, total ion activity coefficient and molal concentration of the i th species, respectively and $a_{(i)\text{eq}}$ is the activity of the i th species at equilibrium. The solubility product (K_{cal}) for calcite at 25 °C is $10^{-8.48}$ (Plummer and Busenberg, 1982). The extent of disequilibrium is then given by the difference between one and Ω (i.e., $1 - \Omega$) where values between 0 and 1 indicate undersaturation and values > 1 supersaturation. The necessary activity coefficients and carbonate ion concentrations were calculated using EQPITZER but a correction had to be applied to the carbonate ion activity coefficient as described in the following discussion. Table III gives the rate equation parameters obtained for each of the different solutions. The equations provided good fits ($R^2 > 0.99$) of the rate data over the modeled region (Figure 3).

4. Discussion

The classical pH-free-drift method employed in this study allows for rapid determination of dissolution rates over a broad range of saturation states. As with any pH dependent rate measurement, it is important that the thermodynamic model used to interpret changes in the carbonic acid system be reliable. EQPITZER calculations were evaluated by allowing the dissolution to proceed until steady state was achieved and comparing the steady-state ion activity product (IAP_{ss}) to K_{cal} . Selected experiments were allowed to proceed for greater than 70 h and deviations from the steady-state conditions were within experimental uncertainty. The EQPITZER calculated IAP was in reasonable agreement ($\pm 10\%$) with K_{cal} in pseudo-seawater and low concentration brines but with increasing brine concentration IAP_{ss} exceeded K_{cal} . To test

Figure 3. Calcite dissolution rates as a function of Ω in pseudo-seawater and synthetic brines. Rates modeled for $0.4 > \Omega > 0.8$ using the general rate equation $R = k(1-\Omega)^n$. The dashed line assumes first order kinetics where $n = 1$. ($\blacktriangle$) pseudo-SW; ($\triangleleft$) brine 1; ($\diamond$) brine 2a; (Δ) brine 2b; ($\circ$) brine 3; ($\square$) brine 4; ($\oplus$) brine 5; ($\triangleleft$) brine 6; ($\circ$) brine 7; (---) first order.

Figure 4. Steady-state Ω values as calculated using EQPITZER are close to unity for pseudo-seawater and low concentration brines but exceed unity for brines of increasing concentration. Solubility measurements made in Mg^{2+} -free brines also showed a similar trend. The error in Ω is most strongly correlated to the calcium activity. (▲) pseudo-SW; (⊖) brine 1; (◇) brine 2a; (△) brine 2b; (○) brine 3; (□) brine 4; (⊕) brine 5; (Δ) brine 6; (○) brine 7; (+) Mg-Free.

the possibility that this was the result of forming a more soluble magnesium-rich calcite phase a series of separate solubility experiments were performed in Mg^{2+} -free brines of similar ionic strength and Ca^{2+} concen-

Table IV. Steady-state calcium and carbonate ion concentrations with the EQPITZER calculated and corrected activity coefficient values.

Brine ID	Ca^{2+} (molal)	$\text{CO}_3^{2-} \times 10^5$ (molal)	$\gamma_{\text{Ca}^{2+}}$	$\gamma_{\text{CO}_3^{2-}}$	
				EQPITZER	Corrected
Pseudo-SW	0.0168	2.21	0.2080	0.0383	0.0424
Brine 1	0.0717	1.15	0.1855	0.0222	0.0215
Brine 2a	0.0962	1.08	0.1943	0.0199	0.0164
Brine 2b	0.1025	0.96	0.1931	0.0197	0.0174
Brine 3	0.1513	0.98	0.1936	0.0135	0.0115
Brine 4	0.2656	1.04	0.1698	0.0090	0.0070
Brine 5	0.4409	1.14	0.2098	0.0048	0.0031
Brine 6	0.6382	1.31	0.2156	0.0033	0.0018
Brine 7	0.9476	1.73	0.2193	0.0021	0.0009

tration. Even after 1 week the calculated IAP_{ss} still exhibited a similar trend that is strongly correlated with Ca^{2+} activity (Figure 4). Therefore, rather than an enhancement in solubility this has instead been interpreted as an uncertainty in the CO_3^{2-} ion activity coefficient perhaps related to errors in the Ca^{2+} interaction parameters with the carbonic acid system under these conditions. An empirical $\gamma_{CO_3^{2-}}$ correction was required to correct Ω values to unity at steady-state. This correction was derived from the equilibrium relationship

$$\Omega = 1 = \frac{a_{Ca^{2+}}(\gamma_{CO_3^{2-}} + \Delta)m_{CO_3^{2-}}}{K_{cal}}, \quad (12)$$

where $a_{Ca^{2+}}$ is the steady-state calcium activity, $\gamma_{CO_3^{2-}}$ the EQPITZER calculated carbonate ion activity coefficient, Δ is the empirical correction factor, and $m_{CO_3^{2-}}$ is the steady-state carbonate ion molal concentration. Rearrangement to solve for the empirical correction factor (Δ) yields

$$\Delta = \frac{K_{cal}}{(a_{Ca^{2+}})m_{CO_3^{2-}}} - \gamma_{CO_3^{2-}}. \quad (13)$$

The EQPITZER carbonate ion activity coefficients are compared with empirically corrected values in Table IV. The corrected ion activity coefficients were then used to recalculate Ω using equation (10) and the rate data were refit to the corrected $(1-\Omega)$.

The general rate equation was fit to the rate data using a non-linear least-squares regression fit that avoids disproportionate weighting of data near the terminus (as is the case with the commonly applied log-log method). Jeschke and Wolfgang (2002) showed that when rates are modeled by linear fits of $\log R$ vs. $\log (1-\Omega)$, small uncertainties of the IAP_{ss} can have a pronounced effect on the interpreted reaction order (n) and rate constant (k). Small errors can create nonlinearity in log-log plots. Such effects are particularly important under near equilibrium conditions.

Only rate data obtained between $0.4 < \Omega < 0.8$ were modeled. The analytical uncertainty in IAP_{ss} , combined with dmv/dt values within the “noise” of the electrodes, resulted in erratic rate measurement for $\Omega > 0.8$ (Figure 3). Rates obtained at $\Omega < 0.4$ were confined to approximately the first 4 min of each experiment during which time the system was recovering from an initial disruption related to the calcite powder being flushed into it. Also, there is a brief induction period for the calcite powder that may involve wetting of the calcite surface and the rapid dissolution of ultra-fine grained particles. Although the duration of the “induction” period was variable and

in some cases substantially less than 4 min, for the purpose of rate inter-comparisons, $\Omega = 0.4$ served as a conservative truncation point.

Calcite dissolution proceeds by both surface reaction and mass transport processes. Which of the two processes exhibits a dominant control on the observed rates can be determined by comparing the theoretical diffusion-controlled rate (R_D) to the measured rate (R). A similar approach, using the control index (q_D) of Nielsen and Toft (1984), was employed by Zhang and Dawe (1998) to evaluate the controlling mechanism of calcite growth in high salinity water.

$$q_D = \frac{R}{R_D}. \quad (14)$$

When $q_D \leq 0.1$ surface reactions dominate the dissolution, and when $q_D \geq 0.9$ diffusion dominates. Values between $0.1 < q_D < 0.9$ indicate a mixed kinetic regime where rates show intermediate behavior (Morse and Arudison, 2002). The theoretical diffusion-controlled rate (R_D) was estimated using the method of (Berner and Morse, 1972):

$$R_D = \frac{DA}{r} [(\bar{m}_{\text{HCO}_3^-} - m_{\text{HCO}_3^-}) + (\bar{m}_{\text{CO}_3^{2-}} - m_{\text{CO}_3^{2-}})], \quad (15)$$

Figure 5. Theoretical diffusion rates for dissolution (R_D) are 2 to 3 orders of magnitude greater than the experimental rates (R) indicating surface controlled kinetics. The upper limit of the range in the R_D is bounded by the pseudo-seawater R_D while the lower limit is bounded by the most concentrated brine (brine 7). Thus, the rate of theoretical diffusion decreases with increasing brine concentration.

where D is the diffusion coefficient (assumed $3.6 \times 10^{-5} \text{ m}^2 \text{ h}^{-1}$), A the surface area of the calcite, r the crystal particle radius ($\sim 3.5 \text{ } \mu\text{m}$), and $\bar{m}_i$ and m_i denote the concentration of the i th species in the solution layer adjacent to the crystal surface and in the bulk solution, respectively. The thickness of the stagnant boundary layer was not considered because the particle radius was $< 10 \text{ } \mu\text{m}$ and the low velocity of the crystal relative to the surrounding fluid makes convection negligible (Nielsen, 1964).

As a first-order approximation it was assumed that $\bar{m}_i$ was equivalent to the bulk concentration of equilibrium. While this will produce an overestimation for R_D , the approximation is appropriate in this case since, for all experiments, experimental rates (R) are two to three orders of magnitude less than theoretical diffusion rates (R_D) (Figure 5). Since $q_D \ll 1$ across the range of modeled saturation states, the dissolution is strongly surface controlled. From recent AFM observations that (a) no etch pit formation occurs for $\Omega > 0.4$ and (b) that dissolution occurs primarily at existing steps (Teng, 2004), surface controlled kinetics would be expected for the range of investigated saturation states. R_D rates were fastest for pseudo-seawater and decreased with increasing brine concentration. These slower diffusional rates are a consequence of the proportional decrease in equilibrium CO_3^{2-} concentration with increasing Ca^{2+} , resulting in smaller concentration gradients.

Previous investigations into the specific effects of calcium and magnesium on calcite kinetics have been conducted at many different saturation states and solution compositions and using differing techniques. Consequently, the results are often contradictory and not readily comparable. Berner (1967) and Weyl (1967) noted a marked inhibitory effect in the presence of Mg^{2+} on calcite dissolution rates at neutral to basic pH, while Alkattan et al. (2002) found no inhibition in the presence of Mg^{2+} at pH 1 and pH 3. Gutjahr et al., (1996b) also found no effect in the presence of Mg^{2+} under neutral to basic conditions over a broad range of saturation states including near equilibrium. This was attributed to the fact that upon dissolution no magnesium-rich calcite can be formed which agrees with our findings. Sjöberg and Rickard (1985) found no effect of Ca^{2+} in acidic solutions whereas in neutral to basic solutions Ca^{2+} was found to decrease the rate of the transport reaction making the dissolution more transport-controlled. Buhmann and Dreybrodt (1987) found that although the presence of Ca^{2+} and Mg^{2+} displace the calcite solution equilibria, the kinetics of the dissolution were hardly changed. Calcite dissolution experiments in these compositionally simple and generally dilute solutions were conducted under low pCO_2 and thus provide important insight into the kinetics from a “pure chemistry” standpoint but are of limited utility for subsurface waters where solutions are substantially

more complex and high $p\text{CO}_2$ usually prevails (Coudrain-Ribstein et al., 1998).

Given the extreme compositional variability of subsurface waters it might be anticipated that modeling the dissolution kinetics of calcite would be an insurmountable task. However, results from this study show that when Ca^{2+} , Mg^{2+} and ionic strength are co-varied in a geologically meaningful way at elevated $p\text{CO}_2$, the dissolution kinetics of calcite expressed as a function of saturation state are remarkably similar. Across the range of saturation states modeled in this study, the standard deviations of the rates do not exceed 20%, probably within the experimental uncertainty.

Dissolution rates of calcite in seawater modeled with the general rate equation typically yield reaction orders between 3 and 4 (Morse and Arvidson, 2000), which are considerably higher than the $n = 1.5$ observed for the pseudo-seawater in this study. Sjöberg (1979) reported a reaction order close to 2 for a pseudo-seawater prepared in a similar fashion to the one used here but containing sulfate. The disparities between these reaction orders may be related to the absence of sulfate and phosphate which are both prominent inhibitors present in seawater. The reaction orders observed in this study do agree well however with those of Gutjahr et al. (1996a) who examined the effect of modest amounts of calcium on the dissolution kinetics of calcite. Gutjahr also observed that dissolution rates increased with increasing Ca^{2+} concentration. Similarly, we find that in general the rates in the Ca^{2+} -rich brines are slightly faster than that of pseudo-seawater but the relationship is made more complex by the presence of Mg^{2+} . The rate constants observed in this study are about one order of magnitude faster than those reported by Gutjahr owing to the more acidic conditions of these experiments (pH 4.7–6.0) and the elevated $p\text{CO}_2$. Plummer et al. (1978) noted a strong $p\text{CO}_2$ dependence on dissolution rates for $\text{pH} > 4$ and the rates measured in this study are in good agreement with these early high $p\text{CO}_2$ studies.

5. Geological Relevance

An important carbon mitigation strategy under consideration is injection of CO_2 into geologic repositories. Possible formations that may serve as these repositories include deep saline aquifers, depleted oil and gas reservoirs, and coal seams. Saline aquifers are the most abundant making them the most logical long-term storage reservoirs. However, before large scale implementation of these technologies can occur key questions must be resolved with regards to the carbon mass exchange through interactions between the injected gas, formation minerals and the aquifer brines. Geochemical models must be devised describing the ultimate fate of the

injected carbon and its impact on formation integrity. Modeling such processes require the inclusion of rate kinetic terms such as those described in this study. Simulations describing the change in mineral saturation in the vicinity of injection wells have been offered (Shiraki and Dunn, 2000) that make use of general rate equations similar to the one modeled here but assume first order kinetics (i.e. $n = 1$) for mathematical simplicity. Considering the uncertainties with the other assumptions involved in these simple models, the assumption of first order kinetics is probably of minor consideration. The dashed line in Figure 3 shows a fit of the rate data for the equation $R = 0.049(1 - \Omega)$ where first order kinetics are assumed. This assumption would only over estimate the rates by approximately $5 \text{ mmol m}^{-2} \text{ h}^{-1}$ at a given Ω . Thermodynamic rather than kinetic considerations may prove the greater source of error. EQPITZER is arguably one of the better geochemical programs for predicting activity coefficients for the carbonic acid system in high ionic strength solutions and yet had considerable difficulty in predicting calcite solubility in these relatively simple brines even at 25°C and at a modest pCO_2 of 1 bar. Therefore, attempts to model these processes using software such as Geochemist's Workbench (GWBTM) and SOLMINEQ.88 at considerably higher temperatures, pressures and pCO_2 's would probably introduce considerably more error than the first order assumption.

6. Conclusion

An open-system pH-free-drift technique was employed to measure calcite dissolution in synthetic brines at 0.1 MPa pCO_2 for brines ranging in concentration from seawater (35 g l^{-1}) up to 179 g l^{-1} . Ionic strength and concentrations of Ca^{2+} and Mg^{2+} were allowed to co-vary in a geologically meaningful way. Dissolution rates were modeled using the general equation:

$$R = k(1 - \Omega)^n.$$

Observed rates were two to three orders of magnitude smaller than theoretical diffusional rates, over the range of saturation states modeled. Although rates measured in the more concentrated brines were generally faster than those of pseudo-seawater, they were not appreciably different. The mean rate constant (k) is $49 \pm 7 \text{ mmol m}^{-2} \text{ s}^{-1}$ and the mean reaction order (n) is 1.4 ± 0.2 . These parameters are in good agreement with previous studies under high pCO_2 conditions. The independence on composition of the rates and the near first-order reaction kinetics may prove beneficial to subsurface geochemical models. Experiments have been planned to extend this work to higher temperatures and pressures and investigate the effect of common inhibitors including phosphate and organics.

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Calcite solubility in Na–Ca–Mg–Cl brines

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Abstract

This study investigated calcite solubility approached from undersaturation in geologically relevant Na–Ca–Mg–Cl synthetic brines (35 to 200 g l⁻¹ TDS) at CO₂ partial pressures of ~0.1, 0.5 and 1.0 bar at 25 °C. Total carbon dioxide content, total alkalinity and total calcium content were measured and the carbonic acid species distribution and ion activities calculated using the Pitzer equation-based program EQPITZER. Stoichiometric (pK_{sp}^*) equilibrium constants ranged from 6.4 to 4.8, decreasing with increasing brine TDS. In general, good agreement was found between measured and predicted solubility data.

Evaluation of the Ca²⁺ and CO₃²⁻ activity coefficients with EQPITZER in brines <100 g l⁻¹ TDS yields a mean value of the thermodynamic pK_{sp} = 8.41 ± 0.12 in good agreement with literature data (8.48 ± 0.02). However, in more concentrated brines the values systematically decreased to 8.11 ± 0.02 in the most calcium-rich brines. The deviation was strongly correlated with calcium ion activity and was also observed in magnesium-free solutions. The error can be interpreted as the result of an uncertainty in the calculated activity of the carbonate ion, which occurs in exceedingly low concentrations in these calcium-rich, high pCO_2 brines. As a result, calculated calcite saturation states may erroneously suggest in excess of a 2-fold supersaturation in the most concentrated brines. This should be a consideration in kinetic studies where precise knowledge of near-equilibrium saturation states is critical in evaluating reaction rate constants and reaction orders.

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1. Introduction

Pore waters contained in sedimentary rocks can range in salinity by approximately five orders of magnitude (Hanor, 1994a), from dilute meteoric waters to waters with greater than 600 g l⁻¹ of dissolved salts (Case, 1945). There is growing interest in the geochemistry of these formation waters as reservoirs are being developed as possible repositories for waste

gases and fluids. Mineral–brine–waste interactions will impart a significant influence on processes affecting the post-injection development of secondary porosity, reservoir permeability and mass transport in the subsurface. Considerable progress has been made in predicting the solubility of many common reservoir minerals in high ionic strength solutions by applying the Pitzer virial-coefficient approach in estimating ion activities (Pitzer, 1973; Pitzer and Mayorga, 1973; Pitzer and Mayorga, 1974). However, predicting carbonate mineral solubility in solutions with ionic strengths greater than that of seawater has remained a formidable challenge outside of simple NaCl solutions (Millero et al., 1984).

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He and Morse (1993a) derived the Pitzer parameters for the interaction between species of the carbonic acid system and other ions in Na–K–Ca–Mg–Cl–SO₄ solutions. The resulting Pitzer equation-based model was used in the development of the EQPITZER geochemical software (He and Morse, 1993b). This software can be used to calculate the equilibrium distribution of the carbonate species in complex brines and predict carbonate mineral solubility. In this study, we investigate EQPITZER's ability to predict the solubility of calcite approached from undersaturation in Na–Ca–Mg–Cl brines of geologically relevant concentrations and under moderately high CO₂ partial pressures typical for the subsurface. The results of these experiments served as prelude to a series of kinetic experiments presented elsewhere (Gledhill and Morse, submitted for publication) and were necessary to evaluate the EQPITZER calculated calcite saturation state.

2. Experimental

2.1. Materials

Synthetic Na–Ca–Mg–Cl brines were prepared gravimetrically on the molal scale (m) from separate concentrated stock solutions of A.C.S. reagent grade NaCl, CaCl₂·2H₂O and MgCl₂·6H₂O. Phosphate measurements of the concentrated stock solutions were made according to the methods of Murphy and Riley (1962) and in all cases found to be below detection (<1 μM). A broad range of solution concentrations were investigated that ranged from that of seawater (TDS = 35 g l⁻¹) up to 200 g l⁻¹ with calcium concentrations ranging up to approximately 1m. In general, a multivariate approach was used such that the calcium, magnesium and ionic strength were co-varied as a function of TDS according to Hanor (1994b). Exceptions included cases where the specific effects of a given variable were explored. The initial compositions were verified by analytical determination of calcium, total hardness and chloride by the methods described below.

The brines were reacted with a variety of calcite substrates including A.C.S. reagent grade powder (Fisher Scientific) and two size fractions (32–63 μm and 63–125 μm) of crushed rhombic Iceland spar obtained from Ward's Scientific Inc. The reagent calcite was pretreated with dilute (0.1 N) HCl according to the methods of Sass et al. (1983). To relieve surface strain and to clean the grains of ultra-fine particles which can enhance solubility, the crushed material was sonicated in methanol for 1 h, re-sieved, briefly washed with milliQ®

(18.1 μΩ) water and freeze dried. The specific surface area of each of the calcite substrates was estimated from a geometric determination from scanning electron micrographs. The specific surface areas were 0.91 m² g⁻¹, 0.05 m² g⁻¹, 0.02 m² g⁻¹ for the powder, 32–63 μm and 63–125 μm for crushed Iceland Spar calcites, respectively. In addition, a BET determination was performed on the calcite powder and was in excellent agreement (<5%) with the geometric determination. BET determinations of the crushed Iceland Spar calcite were found to be suspect and may have been below the detection limit. The mineralogies of both the reagent grade calcite powder and crushed Iceland Spar calcites were verified by powder X-ray diffraction as being >99% calcite.

2.2. Kinetic and solubility reactors

A series of open-system free-drift experiments were performed to investigate the dissolution kinetics of calcite in these brines at CO₂ partial pressures of ~0.1, 0.5 and 1.0 bar at 25 °C. While the dissolution rates of these experiments are reported elsewhere (Gledhill and Morse, 2004; Gledhill and Morse, submitted for publication), the steady-state measurements that were obtained were in good agreement with those from separate closed-system solubility experiments and were therefore used to compliment the closed-system results. Both systems are discussed below.

The kinetic reactor (Gledhill and Morse, 2004) consisted of a 550ml water-jacketed vessel that accommodated a gas feed, two electrodes, vent, temperature probe, and sampling port. Commercially purified high-grade CO₂ and ultra-high purity N₂ were precisely mixed and their flow rate controlled using dual MKS® Type 1479A mass-flow regulators. The solution was stirred at constant rate with a propeller shaft that passed through the top of the reaction vessel and maintained at constant temperature (25 ± 0.01 °C) using a Neslab® RTE-8DD circulating bath. The system remained open during the duration of the experiment and evaporation was minimized by using gas humidifiers and a condenser. Once the system achieved steady state as observed by monitoring pH, multiple samples were drawn and filtered through a Millipore 0.45 μm syringe filter for analysis as described below.

The solubility reactor consisted of four specially modified glass 125ml serum bottles. Approximately 100ml of brine was added to each serum bottle that accommodated a pipette tip and small vent. A CO₂–N₂ gas mixture was then gently bubbled into the solution through the pipette tip. The serum bottles were then

inserted into water-jacketed vessels that were maintained at constant temperature ($25 \pm 0.01^\circ\text{C}$) using a Neslab® RTE-8DD circulating bath.

Following equilibration with the gas phase, 2 ml of concentrated primary standard grade Na_2CO_3 was added sufficient to establish approximately 20% saturation with respect to calcite. This was necessary to minimize the amount of calcite dissolution so as to limit changes in the solution Ca^{2+} concentration. Since a precise knowledge of the equilibrium concentrations was not initially known, the amount of sodium carbonate to be added could only be approximated based on EQPITZER predictions. After several attempts, much better estimates could be applied from trial and error. In the final experiments varying amounts of Na_2CO_3 were added to each of the four serum bottles so as to allow for a small range in final Ca^{2+} concentrations.

The solution was then allowed to reestablish equilibrium with the gas phase prior to the addition of approximately 1 g of calcite. Since the grinding action of magnetic stirrers has been known to produce enhanced solubility, the solutions were instead mixed by mounting the reactors on a Lab-line Instruments® orbit shaker which was oscillated continuously at 250 RPM. The calcite was allowed to react under the constant CO_2 – N_2 gas mixture for 7 h. The gas feed was then removed and the serum bottles sealed with a septum top. This reaction time generally brought the solution to within a few percent of equilibrium so that further consumption of CO_2 was minor. The calcite suspension was then permitted to react with the brine in the closed system for 1 week. The closed system eliminated evaporation of the brine for these extended duration experiments.

At the experiment completion, a nitrogen gas feed was inserted into the serum bottle septum. A minimal amount of nitrogen was used to displace fluid which was passed through a second syringe needle equipped with an in-line $0.45\ \mu\text{m}$ Acrodisk® filter. The filtered sample was collected into a 20-ml gas tight syringe. This method avoided any atmospheric exchange.

2.3. Post-equilibration analysis

Solution concentrations of Cl^- were determined by AgNO_3 titration ($\pm 1.5\%$) using an Accumet silver ion selective electrode interfaced with a computer via an Orion 720A potentiometer. Calcium was analyzed by EGTA titration with calcium indicator Cal/Ver II®, and Mg^{2+} concentrations were determined by EDTA titration with Erichrome Black (EBT). Endpoint detection was facilitated using a Brinkmann PC 800

colorimeter interfaced with a Brinkmann 682 titroprocessor. Precision was within 2% in most cases. The concentration of Na^+ was calculated from charge balance.

Total carbon dioxide (TCO_2) was immediately determined on the samples according to the method of [Dickson and Goyet \(1994\)](#) with a UIC Inc. Model 5011 CO_2 coulometer. Precision ranged from 3.7% at low concentrations to better than $\pm 0.3\%$ for high concentrations. Total alkalinity (TA) was determined by a Gran-type titration ([Gran, 1952](#)) using a Metrohm 655 Dosimat and an Orion 720A pH meter interfaced with a computer. Sample pH was measured using a Corning Inc. semi-micro combination pH electrode calibrated using NBS 4 and 7 buffers. Computer software was used to evaluate the inflection point. An HCl titrant and solutions of primary standard Na_2CO_3 were made in NaCl solutions at ionic strengths specific to each of the brines. The Na_2CO_3 standards were prepared gravimetrically under a nitrogen environment and their concentrations were verified by coulometric measurement of their TCO_2 concentrations. Four point calibration curves were made using weighted standards versus the volume at which the apparent inflection point occurred. Precision was better than $0.1\ \text{meq kg}^{-1}$. The titrations were conducted at $25 \pm 0.1^\circ\text{C}$ in a water-jacketed open cell into which CO_2 was continuously bubbled. The bubbling of CO_2 into the cell served to facilitate gas exchange and prevent the solution from becoming oversaturated with respect to CaCO_3 mineral phases as a result of degassing prior to the addition of the HCl titrant.

3. Results

The analytical results are presented in [Table 1](#) and indicate, as expected, a broad range in TA and TCO_2 for different electrolytes reacted with calcite under various CO_2 partial pressures at 25°C . The different substrates and size fractions used did not, however, impart a measurable effect. The species distributions of the carbonic acid system and ion activities were evaluated using EQPITZER software ([He and Morse, 1993b](#)) ([Table 2](#)). The program provides a complete description of the carbonic acid system using at least two fundamental CO_2 system parameters (TA, TCO_2 , $p\text{CO}_2$ and pH) and a solution major ion composition. The measured TA and TCO_2 were coupled to calculate $p\text{CO}_2$ ([Table 1](#)).

The measured TA and TCO_2 concentrations are generally in good agreement with those predicted by EQPITZER for a broad range of geologically relevant

Table 1

Solubility data for a broad range of Na–Ca–Mg–Cl brines reacted with calcite

ID	Ca ²⁺	Mg ²⁺	Na ⁺	Cl [−] (molal)	TA	TCO ₂	<i>I</i>	<i>p</i> CO ₂ (bar)	Area (m ² g ^{−1})
<i>Kinetic reactor experiments</i>									
PCO2_01a	0.0478	0.0245	0.7237	0.8759	0.0167	0.0432	0.9353	0.93	0.02
PCO2_01b	0.0432	0.0228	0.7128	0.8579	0.019	0.0445	0.927	0.89	0.05
PCO2_01c	0.0437	0.0218	0.7116	0.8591	0.0189	0.044	0.9258	0.88	0.91
PCO2_02a	0.1583	0.0661	1.577	2.212	0.0107	0.0301	2.365	0.86	0.02
PCO2_03a	0.348	0.124	1.555	2.193	0.0067	0.0222	3.8425	0.86	0.02
PCO2_03b	0.3626	0.118	2.217	3.633	0.0068	0.0216	3.8894	0.82	0.05
PCO2_03c	0.3639	0.1184	2.235	3.657	0.0066	0.0211	3.9138	0.82	0.91
PCO2_04a	0.042	0.022	1.561	2.194	0.0135	0.0264	0.9367	0.45	0.02
PCO2_05a	0.1656	0.0696	1.561	2.194	0.008	0.018	2.4913	0.46	0.02
PCO2_05b	0.1569	0.0703	1.67	2.364	0.0078	0.0178	2.353	0.45	0.02
PCO2_05c	0.1594	0.0672	1.567	2.223	0.008	0.018	2.3523	0.44	0.02
PCO2_06a	0.3625	0.1151	2.315	3.766	0.0046	0.0127	3.9979	0.46	0.02
PCO2_07a	0.0409	0.0232	0.7315	0.8935	0.0061	0.0084	0.9437	0.08	0.02
PCO2_08a	0.1573	0.0673	1.594	2.247	0.0035	0.0053	2.3714	0.08	0.02
PCO2_09a	0.3623	0.1136	2.316	3.767	0.0022	0.0036	3.9945	0.08	0.02
Mg_01a	0.1648	0.0217	1.75	2.35	0.0076	0.0175	2.4268	0.45	0.02
Mg_02a	0.1603	0.1173	1.49	2.236	0.0075	0.0176	2.4221	0.45	0.02
Ca_01a	0.0439	0.0707	1.912	2.391	0.0127	0.0222	2.3868	0.44	0.02
Ca_02a	0.3601	0.0658	1.091	2.056	0.006	0.0164	2.4283	0.45	0.02
L_01a	0.156	0.0685	0.2442	0.6992	0.0081	0.022	0.9248	0.47	0.02
L_02a	0.1641	0.0731	2.775	3.867	0.0059	0.0132	3.7988	0.42	0.02
XP_001C	0.017	0.059	0.5117	0.9128	0.0272	0.0544	0.7451	0.91	0.91
XP_001D	0.0148	0.0772	0.4864	0.6256	0.0284	0.0539	0.7542	0.86	0.91
AP_012A	0.0827	0.0747	0.5474	0.8166	0.0142	0.0394	1.0039	0.88	0.91
XP_009B	0.1021	0.0421	0.7476	1.03	0.0135	0.0385	1.1838	0.9	0.91
XP_005B	0.1475	0.0584	0.9992	1.4053	0.0116	0.0353	1.6193	0.92	0.91
XP_013A	0.2654	0.0903	1.17	1.697	0.009	0.0291	2.1498	0.85	0.91
XP_006B	0.4276	0.0889	1.4171	2.4464	0.0073	0.0274	2.9683	0.95	0.91
XP_006D	0.4411	0.0882	1.4111	2.467	0.0076	0.0266	3.0029	0.91	0.91
XP_010A	0.6381	0.1145	1.3705	2.8734	0.0064	0.0239	3.6433	0.89	0.91
XP_007C	0.9071	0.1264	1.2607	3.3263	0.0059	0.0217	4.3634	0.87	0.91
XP_007D	0.9475	0.1574	1.1213	3.3298	0.0056	0.0219	4.4518	0.9	0.91
<i>Solubility reactor experiments</i>									
KSP_Brine1_1	0.0434	0.021	0.7447	0.8594	0.0138	0.0285	0.9377	0.52	0.05
KSP_Brine1_2	0.0435	0.0213	0.7435	0.8581	0.0158	0.0321	0.9383	0.57	0.05
KSP_Brine1_3	0.0427	0.0229	0.7421	0.8564	0.0161	0.0334	0.9384	0.61	0.05
KSP_Brine1_4	0.0425	0.0219	0.7311	0.8438	0.0163	0.0327	0.9243	0.57	0.05
KSP_Brine2_1	0.1596	0.0679	1.8	2.252	0.009	0.02	2.4854	0.51	0.05
KSP_Brine2_2	0.159	0.0662	1.804	2.25	0.009	0.0195	2.482	0.49	0.05
KSP_Brine2_3	0.1599	0.0661	1.801	2.248	0.0088	0.0186	2.4811	0.45	0.05
KSP_Brine2_4	0.1589	0.0644	1.8	2.241	0.0091	0.0203	2.4716	0.52	0.05
KSP_Brine3_1	0.3648	0.1165	2.67	3.627	0.0056	0.0144	4.1137	0.53	0.05
KSP_Brine3_2	0.3621	0.1173	2.67	3.626	0.0057	0.0145	4.1093	0.53	0.05
KSP_Brine3_3	0.3636	0.1164	2.684	3.646	0.0057	0.0146	4.128	0.54	0.05
KSP_Brine3_4	0.3624	0.1158	2.665	3.62	0.0055	0.0146	4.1014	0.54	0.05
MgFree_1	0.023	0	3.0217	3.0428	0.0247	0.0412	3.0908	0.97	0.91
MgFree_2	0.154	0	2.5834	2.8806	0.0108	0.0285	3.0456	0.97	0.91
MgFree_3	0.9117	0	0.2371	2.0531	0.0071	0.0285	2.9712	0.97	0.91
MgFree_4	0.0234	0	3.0221	3.0433	0.0255	0.0418	3.0921	0.92	0.91
MgFree_5	0.1538	0	2.5834	2.881	0.0104	0.0285	3.0451	0.92	0.91

Molal values of total calcium (Ca²⁺), magnesium (Mg²⁺) and chloride (Cl[−]) were used to calculate total sodium (Na⁺) and ionic strength (*I*) from charge balance. The CO₂ partial pressure (*p*CO₂, bar) was calculate from molal concentrations of total alkalinity (TA) and total carbon dioxide (TCO₂) using EQPITZER. The specific geometric surface area (m² g^{−1}) of the calcite was estimated from scanning electron microscopy.

Table 2

The carbonate ion concentration (CO_3^{2-} , molal) along with the total ion activity coefficients for CO_3^{2-} and Ca^{2+} as derived using EQPITZER

ID	Ca ²⁺	CO ₃ [−]	
	γ _T	Molal	
Kinetic reactor experiments			
PCO2_01a	0.216	8.25e−06	0.035
PCO2_01b	0.213	1.13e−05	0.035
PCO2_01c	0.214	1.13e−05	0.035
PCO2_02a	0.264	1.14e−05	0.009
PCO2_03a	0.396	1.27e−05	0.003
PCO2_03b	0.401	1.44e−05	0.003
PCO2_03c	0.404	1.35e−05	0.003
PCO2_04a	0.216	1.23e−05	0.035
PCO2_05a	0.275	1.27e−05	0.008
PCO2_05b	0.261	1.15e−05	0.009
PCO2_05c	0.263	1.24e−05	0.009
PCO2_06a	0.428	1.25e−05	0.003
PCO2_07a	0.218	1.30e−05	0.035
PCO2_08a	0.265	1.31e−05	0.009
PCO2_09a	0.429	1.53e−05	0.003
Mg_01a	0.283	1.05e−05	0.010
Mg_02a	0.254	1.20e−05	0.008
Ca_01a	0.312	1.86e−05	0.015
Ca_02a	0.202	1.10e−05	0.006
L_01a	0.172	9.54e−06	0.015
L_02a	0.536	1.27e−05	0.005
XP_001C	0.208	2.21e−05	0.038
XP_001D	0.199	2.77e−05	0.035
XP_012A	0.183	1.09e−05	0.021
XP_009B	0.193	9.41e−06	0.019
XP_005B	0.194	9.37e−06	0.014
XP_013A	0.170	9.09e−06	0.009
XP_006B	0.210	9.73e−06	0.005
XP_006D	0.210	1.14e−05	0.005
XP_010A	0.216	1.31e−05	0.003
XP_007C	0.226	1.84e−05	0.002
XP_007D	0.219	1.73e−05	0.002
Solubility reactor experiments			
KSP_Brine1_1	0.208	9.84e−06	0.036
KSP_Brine1_2	0.208	1.19e−05	0.036
KSP_Brine1_3	0.208	1.15e−05	0.035
KSP_Brine1_4	0.208	1.24e−05	0.036
KSP_Brine2_1	0.243	1.28e−05	0.010
KSP_Brine2_2	0.243	1.31e−05	0.010
KSP_Brine2_3	0.242	1.37e−05	0.010
KSP_Brine2_4	0.242	1.26e−05	0.010
KSP_Brine2_1	0.353	1.30e−05	0.003
KSP_Brine2_2	0.354	1.33e−05	0.003
KSP_Brine2_3	0.357	1.33e−05	0.003
KSP_Brine2_4	0.353	1.23e−05	0.004
MgFree_1	0.362	1.75e−05	0.027
MgFree_2	0.313	9.24e−06	0.010
MgFree_3	0.131	1.58e−05	0.004
MgFree_4	0.362	1.90e−05	0.027
MgFree_5	0.313	8.46e−06	0.010

Fig. 1. Comparison between the measured and EQPITZER predicted total alkalinity (TA) (A) and total carbon dioxide content (TCO_2) (B) of a broad range of geologically relevant Na–Ca–Mg–Cl synthetic brines (35 to 200 g l^{-1} TDS) equilibrated with calcite at CO_2 partial pressures of ~ 0.1 (solid triangle), 0.5 (open square) and 1.0 bar (solid square) at 25 °C.

Na–Ca–Mg–Cl synthetic brines (35 to 200 g l^{-1} TDS) equilibrated with calcite at CO_2 partial pressures of ~ 0.1 (solid triangle), 0.5 (open square) and 1.0 bar (solid square) at 25 °C (Fig. 1).

4. Discussion

The stoichiometric equilibrium constants ($\text{p}K_{\text{sp}}^*$) for each of the solutions was calculated from the concentration products as

$$\text{p}K_{\text{sp}}^* = -\log(m_{\text{Ca}^{2+}} m_{\text{CO}_3^{2-}}) \quad (1)$$

and shows a broad range of over nearly two orders of magnitude in the apparent solubility of calcite in these solutions generally increasing (a.k.a. decreasing pK_{sp}^*) with increasing TDS (Fig. 2A). Perhaps surprisingly, the actual carbonate carrying capacity of these solutions, although exceedingly small in all cases, actually slightly increases with increasing brine concentration despite an increase in calcium activity (Fig. 3).

The negative logarithms of the ion activity products (pK_{sp}) where

$$pK_{sp} = -\log(\gamma_{Ca^{2+}}\gamma_{CO_3^{2-}}m_{Ca^{2+}}m_{CO_3^{2-}}) \quad (2)$$

yield values in reasonable agreement ($\pm 10\%$) with K_c ($-\log K_c = 8.480 \pm 0.020$, Plummer and Busenberg, 1982) in brines less than 100 g l^{-1} TDS. However, with increasing concentration there is what appears to be systematic increase in thermodynamic solubility product (i.e. decreasing pK_{sp}).

Although a multivariate approach was applied in which calcium, magnesium and ionic strength were all co-varied with increasing TDS, there is a strong relation between the variability and calcium activity (Fig. 2B). Even experiments performed in Mg^{2+} -free solutions exhibit the same behavior implying that this is not due to the formation of a more soluble Mg^{2+} -rich surface phase. Nor is it specifically related to ionic strength, since in the Mg^{2+} -free solutions the ionic strength was

Fig. 3. The Ω values calculated using EQPITZER from the analytical results of this study compared with values calculated from literature data. Open scatter points are experimental data from this study. Open squares were measured in Na–Ca–Mg–Cl brines, while open circles were measured in Mg^{2+} -free brines. Solid triangles are from Millero et al. (1984). Solid circles are from Wolf et al. (1989). The inset figure expands the region investigated in this study as denoted by the dashed box. The solid line represents thermodynamic equilibrium within the uncertainty depicted by the dashed lines (Plummer and Busenberg, 1982).

fixed ($I=3 \text{ m}$) by balancing with NaCl. It should also be noted that in these solutions the Mg/Ca ratio was always <0.5 . This is much lower than in seawater where an

Fig. 2. The negative logarithms of the stoichiometric (pK_{sp}^* , triangles) and thermodynamic (pK_{sp} , squares) equilibrium constants for calcite measured in a broad range of geologically relevant Na–Ca–Mg–Cl synthetic brines (35 to 200 g l^{-1} TDS). Solid scatter points are experimental data from kinetic experiments measured at steady state. Open scatter points were measured in closed system solubility experiments and are in good agreement. The solid line represents the thermodynamic equilibrium constant of Plummer and Busenberg (1982).

~8% Mg-calcite can form at an Mg/Ca ratio of ~5 (Mucci and Morse, 1984). The simplest explanation for this apparent deviation from K_c is that there is a small error associated with the EQPITZER calculated carbonate ion activity coefficient ($\gamma_{\text{CO}_3^{2-}}$) in the most calcium-rich brines.

This error would have little consequence in many geochemical contexts, such as in the case of mineral mass transport since the carbonate carrying capacity of these calcium-rich brines is rather small and the difference between the predicated and observed TA and TCO_2 is very minor (Fig. 1). However, it may become important when modeling the reaction kinetics of these minerals when the degree of disequilibrium is used as a key term in the rate equation. An example of this would be the commonly applied general rate equation (e.g., Morse and Berner, 1972) used to describe the rate of calcite dissolution:

$$R = -\frac{dm_{\text{calcite}}}{dt} = \left(\frac{A}{V}\right)k(1-\Omega)^n \quad (3)$$

where t is time, A is the surface area of the solid, V is the volume of solution (or mass of solvent in cases where molal units are used), k is the rate constant and n is the OrderOf the reaction. The saturation state (Ω) is the ratio of the ion activity product of calcium and carbonate (IAP) to K_c , as given by

$$\Omega = \frac{\gamma_{\text{Ca}^{2+}}m_{\text{Ca}^{2+}}\gamma_{\text{CO}_3^{2-}}m_{\text{CO}_3^{2-}}}{K_c} \quad (4)$$

If $\Omega=1$, then the solution is in equilibrium with respect to calcite; if $\Omega<1$ the solution is undersaturated; and if $\Omega>1$ the solution is supersaturated. EQPITZER reports saturation states increasingly greater than one with increasing calcium concentration. In this study, brines that contained calcium concentrations nearing 1 molal yielded EQPITZER predicted saturation states more than twice saturated (e.g., $\Omega>2$, Fig. 3).

Millero et al. (1984) measured the solubility of calcite in NaCl solutions up to 6 m. In these experiments the $m_{\text{Ca}^{2+}}$ did not exceed $0.6 \text{ mmol kg}^{-1} \text{ H}_2\text{O}$. Based on the reported solution compositions and coupling TA and TCO_2 to solve for the carbonic acid system, analogous to the approach used with the analytical data from this study, the derived Ω values using EQPITZER closely approximated 1 (Fig. 3, solid triangles). This indicates that EQPITZER is quite capable of predicting equilibrium up to high ionic strengths in the absence of large amounts of calcium. The same approach was applied to the data reported by Wolf et al. (1989) in which calcite dissolution was measured in highly concentrated CaCl_2

solutions (up to 3 m Ca^{2+}). In this case a near exponential deviation with increasing $m_{\text{Ca}^{2+}}$ was observed with an apparent supersaturation in excess of 20 times for the most concentrated case (Fig. 3, solid circles).

Although these errors may seem dramatic, one has to consider that not only does the carbonate ion occur in very low concentration (<15 micromolal), but also its predicted activity coefficient decreases to $\sim 3 \times 10^{-3}$ in the most concentrated brines. Because carbonate ion activities are on the order of 10^{-8} in these brines, it is not surprising that such errors in the calculated saturation state arise. In fact, it is rather remarkable how well the current model holds up under these extreme conditions.

5. Conclusion

Although EQPITZER reasonably predicts equilibrium ($\pm 10\%$) with respect to calcite in relatively low concentration brines ($<100 \text{ g l}^{-1} \text{ TDS}$), with increasing brine concentration a systematic increase in the calculated saturation state is observed, yielding at steady state more than an apparent 2-fold supersaturation in the most calcium-rich brine. The error is not specifically related to magnesium concentration suggesting that it is not the result of the formation of an enhanced solubility Mg-rich phase. Instead, it strongly correlates with increases in calcium activity. We cannot be certain that the apparent increase in steady-state IAP is not related to a complex interaction between the calcite surface and these highly concentrated brines, but perhaps the simplest explanation is that the apparent IAP increase represents minor uncertainty in the carbonate ion activity coefficient. Although this minor error would have little consequence in many geochemical contexts, such as in the case of mineral mass transport, it can impart significant error to kinetic rate models that empirically describe the rate of dissolution as a function of the degree of disequilibrium ($1-\Omega$). Jeschke and Dreybrodt (2002) showed that when rates are modeled by linear fits of $\log R$ versus $\log (1-\Omega)$, small uncertainties in Ω can have a pronounced effect on the interpreted reaction order (n) and rate constant (k). Small errors can create nonlinearity in log–log plots. Such effects are particularly important under near equilibrium conditions. It is therefore advised that although the program EQPITZER performs well for moderately concentrated brines ($<100 \text{ g l}^{-1} \text{ TDS}$) caution should be taken well applied to more concentrated calcium-rich systems when a precise knowledge of saturation state is required.

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Calcite solubility in Na–Ca–Mg–Cl brines

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Abstract

This study investigated calcite solubility approached from undersaturation in geologically relevant Na–Ca–Mg–Cl synthetic brines (35 to 200 g l⁻¹ TDS) at CO₂ partial pressures of ~0.1, 0.5 and 1.0 bar at 25 °C. Total carbon dioxide content, total alkalinity and total calcium content were measured and the carbonic acid species distribution and ion activities calculated using the Pitzer equation-based program EQPITZER. Stoichiometric (pK_{sp}^{*}) equilibrium constants ranged from 6.4 to 4.8, decreasing with increasing brine TDS. In general, good agreement was found between measured and predicted solubility data.

Evaluation of the Ca²⁺ and CO₃²⁻ activity coefficients with EQPITZER in brines <100 g l⁻¹ TDS yields a mean value of the thermodynamic pK_{sp}=8.41±0.12 in good agreement with literature data (8.48±0.02). However, in more concentrated brines the values systematically decreased to 8.11±0.02 in the most calcium-rich brines. The deviation was strongly correlated with calcium ion activity and was also observed in magnesium-free solutions. The error can be interpreted as the result of an uncertainty in the calculated activity of the carbonate ion, which occurs in exceedingly low concentrations in these calcium-rich, high pCO₂ brines. As a result, calculated calcite saturation states may erroneously suggest in excess of a 2-fold supersaturation in the most concentrated brines. This should be a consideration in kinetic studies where precise knowledge of near-equilibrium saturation states is critical in evaluating reaction rate constants and reaction orders.

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Keywords: Calcite; Brine; Solubility; Carbonate; Carbon sequestration

1. Introduction

Pore waters contained in sedimentary rocks can range in salinity by approximately five orders of magnitude (Hanor, 1994a), from dilute meteoric waters to waters with greater than 600 g l⁻¹ of dissolved salts (Case, 1945). There is growing interest in the geochemistry of these formation waters as reservoirs are being developed as possible repositories for waste

gases and fluids. Mineral–brine–waste interactions will impart a significant influence on processes affecting the post-injection development of secondary porosity, reservoir permeability and mass transport in the subsurface. Considerable progress has been made in predicting the solubility of many common reservoir minerals in high ionic strength solutions by applying the Pitzer virial-coefficient approach in estimating ion activities (Pitzer, 1973; Pitzer and Mayorga, 1973; Pitzer and Mayorga, 1974). However, predicting carbonate mineral solubility in solutions with ionic strengths greater than that of seawater has remained a formidable challenge outside of simple NaCl solutions (Millero et al., 1984).

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He and Morse (1993a) derived the Pitzer parameters for the interaction between species of the carbonic acid system and other ions in Na–K–Ca–Mg–Cl–SO₄ solutions. The resulting Pitzer equation-based model was used in the development of the EQPITZER geochemical software (He and Morse, 1993b). This software can be used to calculate the equilibrium distribution of the carbonate species in complex brines and predict carbonate mineral solubility. In this study, we investigate EQPITZER's ability to predict the solubility of calcite approached from undersaturation in Na–Ca–Mg–Cl brines of geologically relevant concentrations and under moderately high CO₂ partial pressures typical for the subsurface. The results of these experiments served as prelude to a series of kinetic experiments presented elsewhere (Gledhill and Morse, submitted for publication) and were necessary to evaluate the EQPITZER calculated calcite saturation state.

2. Experimental

2.1. Materials

Synthetic Na–Ca–Mg–Cl brines were prepared gravimetrically on the molal scale (m) from separate concentrated stock solutions of A.C.S. reagent grade NaCl, CaCl₂·2H₂O and MgCl₂·6H₂O. Phosphate measurements of the concentrated stock solutions were made according to the methods of Murphy and Riley (1962) and in all cases found to be below detection (<1 μM). A broad range of solution concentrations were investigated that ranged from that of seawater (TDS = 35 g l⁻¹) up to 200 g l⁻¹ with calcium concentrations ranging up to approximately 1m. In general, a multivariate approach was used such that the calcium, magnesium and ionic strength were co-varied as a function of TDS according to Hanor (1994b). Exceptions included cases where the specific effects of a given variable were explored. The initial compositions were verified by analytical determination of calcium, total hardness and chloride by the methods described below.

The brines were reacted with a variety of calcite substrates including A.C.S. reagent grade powder (Fisher Scientific) and two size fractions (32–63 μm and 63–125 μm) of crushed rhombic Iceland spar obtained from Ward's Scientific Inc. The reagent calcite was pretreated with dilute (0.1 N) HCl according to the methods of Sass et al. (1983). To relieve surface strain and to clean the grains of ultra-fine particles which can enhance solubility, the crushed material was sonicated in methanol for 1 h, re-sieved, briefly washed with milliQ®

(18.1 μΩ) water and freeze dried. The specific surface area of each of the calcite substrates was estimated from a geometric determination from scanning electron micrographs. The specific surface areas were 0.91 m² g⁻¹, 0.05 m² g⁻¹, 0.02 m² g⁻¹ for the powder, 32–63 μm and 63–125 μm for crushed Iceland Spar calcites, respectively. In addition, a BET determination was performed on the calcite powder and was in excellent agreement (<5%) with the geometric determination. BET determinations of the crushed Iceland Spar calcite were found to be suspect and may have been below the detection limit. The mineralogies of both the reagent grade calcite powder and crushed Iceland Spar calcites were verified by powder X-ray diffraction as being >99% calcite.

2.2. Kinetic and solubility reactors

A series of open-system free-drift experiments were performed to investigate the dissolution kinetics of calcite in these brines at CO₂ partial pressures of ~0.1, 0.5 and 1.0 bar at 25 °C. While the dissolution rates of these experiments are reported elsewhere (Gledhill and Morse, 2004; Gledhill and Morse, submitted for publication), the steady-state measurements that were obtained were in good agreement with those from separate closed-system solubility experiments and were therefore used to compliment the closed-system results. Both systems are discussed below.

The kinetic reactor (Gledhill and Morse, 2004) consisted of a 550 ml water-jacketed vessel that accommodated a gas feed, two electrodes, vent, temperature probe, and sampling port. Commercially purified high-grade CO₂ and ultra-high purity N₂ were precisely mixed and their flow rate controlled using dual MKS® Type 1479A mass-flow regulators. The solution was stirred at constant rate with a propeller shaft that passed through the top of the reaction vessel and maintained at constant temperature (25 ± 0.01 °C) using a Neslab® RTE-8DD circulating bath. The system remained open during the duration of the experiment and evaporation was minimized by using gas humidifiers and a condenser. Once the system achieved steady state as observed by monitoring pH, multiple samples were drawn and filtered through a Millipore 0.45 μm syringe filter for analysis as described below.

The solubility reactor consisted of four specially modified glass 125 ml serum bottles. Approximately 100 ml of brine was added to each serum bottle that accommodated a pipette tip and small vent. A CO₂–N₂ gas mixture was then gently bubbled into the solution through the pipette tip. The serum bottles were then

inserted into water-jacketed vessels that were maintained at constant temperature ($25 \pm 0.01^\circ\text{C}$) using a Neslab® RTE-8DD circulating bath.

Following equilibration with the gas phase, 2 ml of concentrated primary standard grade Na_2CO_3 was added sufficient to establish approximately 20% saturation with respect to calcite. This was necessary to minimize the amount of calcite dissolution so as to limit changes in the solution Ca^{2+} concentration. Since a precise knowledge of the equilibrium concentrations was not initially known, the amount of sodium carbonate to be added could only be approximated based on EQPITZER predictions. After several attempts, much better estimates could be applied from trial and error. In the final experiments varying amounts of Na_2CO_3 were added to each of the four serum bottles so as to allow for a small range in final Ca^{2+} concentrations.

The solution was then allowed to reestablish equilibrium with the gas phase prior to the addition of approximately 1 g of calcite. Since the grinding action of magnetic stirrers has been known to produce enhanced solubility, the solutions were instead mixed by mounting the reactors on a Lab-line Instruments® orbit shaker which was oscillated continuously at 250 RPM. The calcite was allowed to react under the constant CO_2 – N_2 gas mixture for 7 h. The gas feed was then removed and the serum bottles sealed with a septum top. This reaction time generally brought the solution to within a few percent of equilibrium so that further consumption of CO_2 was minor. The calcite suspension was then permitted to react with the brine in the closed system for 1 week. The closed system eliminated evaporation of the brine for these extended duration experiments.

At the experiment completion, a nitrogen gas feed was inserted into the serum bottle septum. A minimal amount of nitrogen was used to displace fluid which was passed through a second syringe needle equipped with an in-line $0.45\text{ }\mu\text{m}$ Acrodisc® filter. The filtered sample was collected into a 20-ml gas tight syringe. This method avoided any atmospheric exchange.

2.3. Post-equilibration analysis

Solution concentrations of Cl^- were determined by AgNO_3 titration ($\pm 1.5\%$) using an Accumet silver ion selective electrode interfaced with a computer via an Orion 720A potentiometer. Calcium was analyzed by EGTA titration with calcium indicator Cal/Ver II®, and Mg^{2+} concentrations were determined by EDTA titration with Erichrome Black (EBT). Endpoint detection was facilitated using a Brinkmann PC 800

colorimeter interfaced with a Brinkmann 682 titroprocessor. Precision was within 2% in most cases. The concentration of Na^+ was calculated from charge balance.

Total carbon dioxide (TCO_2) was immediately determined on the samples according to the method of Dickson and Goyet (1994) with a UIC Inc. Model 5011 CO_2 coulometer. Precision ranged from 3.7% at low concentrations to better than $\pm 0.3\%$ for high concentrations. Total alkalinity (TA) was determined by a Gran-type titration (Gran, 1952) using a Metrohm 655 Dosimat and an Orion 720A pH meter interfaced with a computer. Sample pH was measured using a Corning Inc. semi-micro combination pH electrode calibrated using NBS 4 and 7 buffers. Computer software was used to evaluate the inflection point. An HCl titrant and solutions of primary standard Na_2CO_3 were made in NaCl solutions at ionic strengths specific to each of the brines. The Na_2CO_3 standards were prepared gravimetrically under a nitrogen environment and their concentrations were verified by coulometric measurement of their TCO_2 concentrations. Four point calibration curves were made using weighted standards versus the volume at which the apparent inflection point occurred. Precision was better than 0.1 meq kg^{-1} . The titrations were conducted at $25 \pm 0.1^\circ\text{C}$ in a water-jacketed open cell into which CO_2 was continuously bubbled. The bubbling of CO_2 into the cell served to facilitate gas exchange and prevent the solution from becoming oversaturated with respect to CaCO_3 mineral phases as a result of degassing prior to the addition of the HCl titrant.

3. Results

The analytical results are presented in Table 1 and indicate, as expected, a broad range in TA and TCO_2 for different electrolytes reacted with calcite under various CO_2 partial pressures at 25°C . The different substrates and size fractions used did not, however, impart a measurable effect. The species distributions of the carbonic acid system and ion activities were evaluated using EQPITZER software (He and Morse, 1993b) (Table 2). The program provides a complete description of the carbonic acid system using at least two fundamental CO_2 system parameters (TA, TCO_2 , $p\text{CO}_2$ and pH) and a solution major ion composition. The measured TA and TCO_2 were coupled to calculate $p\text{CO}_2$ (Table 1).

The measured TA and TCO_2 concentrations are generally in good agreement with those predicted by EQPITZER for a broad range of geologically relevant

Table 1
Solubility data for a broad range of Na–Ca–Mg–Cl brines reacted with calcite

ID	Ca ²⁺	Mg ²⁺	Na ⁺	Cl [−] (molal)	TA	TCO ₂	<i>I</i>	<i>p</i> CO ₂ (bar)	Area (m ² g ^{−1})
<i>Kinetic reactor experiments</i>									
PCO2_01a	0.0478	0.0245	0.7237	0.8759	0.0167	0.0432	0.9353	0.93	0.02
PCO2_01b	0.0432	0.0228	0.7128	0.8579	0.019	0.0445	0.927	0.89	0.05
PCO2_01c	0.0437	0.0218	0.7116	0.8591	0.0189	0.044	0.9258	0.88	0.91
PCO2_02a	0.1583	0.0661	1.577	2.212	0.0107	0.0301	2.365	0.86	0.02
PCO2_03a	0.348	0.124	1.555	2.193	0.0067	0.0222	3.8425	0.86	0.02
PCO2_03b	0.3626	0.118	2.217	3.633	0.0068	0.0216	3.8894	0.82	0.05
PCO2_03c	0.3639	0.1184	2.235	3.657	0.0066	0.0211	3.9138	0.82	0.91
PCO2_04a	0.042	0.022	1.561	2.194	0.0135	0.0264	0.9367	0.45	0.02
PCO2_05a	0.1656	0.0696	1.561	2.194	0.008	0.018	2.4913	0.46	0.02
PCO2_05b	0.1569	0.0703	1.67	2.364	0.0078	0.0178	2.353	0.45	0.02
PCO2_05c	0.1594	0.0672	1.567	2.223	0.008	0.018	2.3523	0.44	0.02
PCO2_06a	0.3625	0.1151	2.315	3.766	0.0046	0.0127	3.9979	0.46	0.02
PCO2_07a	0.0409	0.0232	0.7315	0.8935	0.0061	0.0084	0.9437	0.08	0.02
PCO2_08a	0.1573	0.0673	1.594	2.247	0.0035	0.0053	2.3714	0.08	0.02
PCO2_09a	0.3623	0.1136	2.316	3.767	0.0022	0.0036	3.9945	0.08	0.02
Mg_01a	0.1648	0.0217	1.75	2.35	0.0076	0.0175	2.4268	0.45	0.02
Mg_02a	0.1603	0.1173	1.49	2.236	0.0075	0.0176	2.4221	0.45	0.02
Ca_01a	0.0439	0.0707	1.912	2.391	0.0127	0.0222	2.3868	0.44	0.02
Ca_02a	0.3601	0.0658	1.091	2.056	0.006	0.0164	2.4283	0.45	0.02
L_01a	0.156	0.0685	0.2442	0.6992	0.0081	0.022	0.9248	0.47	0.02
L_02a	0.1641	0.0731	2.775	3.867	0.0059	0.0132	3.7988	0.42	0.02
XP_001C	0.017	0.059	0.5117	0.9128	0.0272	0.0544	0.7451	0.91	0.91
XP_001D	0.0148	0.0772	0.4864	0.6256	0.0284	0.0539	0.7542	0.86	0.91
AP_012A	0.0827	0.0747	0.5474	0.8166	0.0142	0.0394	1.0039	0.88	0.91
XP_009B	0.1021	0.0421	0.7476	1.03	0.0135	0.0385	1.1838	0.9	0.91
XP_005B	0.1475	0.0584	0.9992	1.4053	0.0116	0.0353	1.6193	0.92	0.91
XP_013A	0.2654	0.0903	1.17	1.697	0.009	0.0291	2.1498	0.85	0.91
XP_006B	0.4276	0.0889	1.4171	2.4464	0.0073	0.0274	2.9683	0.95	0.91
XP_006D	0.4411	0.0882	1.4111	2.467	0.0076	0.0266	3.0029	0.91	0.91
XP_010A	0.6381	0.1145	1.3705	2.8734	0.0064	0.0239	3.6433	0.89	0.91
XP_007C	0.9071	0.1264	1.2607	3.3263	0.0059	0.0217	4.3634	0.87	0.91
XP_007D	0.9475	0.1574	1.1213	3.3298	0.0056	0.0219	4.4518	0.9	0.91
<i>Solubility reactor experiments</i>									
KSP_Brine1_1	0.0434	0.021	0.7447	0.8594	0.0138	0.0285	0.9377	0.52	0.05
KSP_Brine1_2	0.0435	0.0213	0.7435	0.8581	0.0158	0.0321	0.9383	0.57	0.05
KSP_Brine1_3	0.0427	0.0229	0.7421	0.8564	0.0161	0.0334	0.9384	0.61	0.05
KSP_Brine1_4	0.0425	0.0219	0.7311	0.8438	0.0163	0.0327	0.9243	0.57	0.05
KSP_Brine2_1	0.1596	0.0679	1.8	2.252	0.009	0.02	2.4854	0.51	0.05
KSP_Brine2_2	0.159	0.0662	1.804	2.25	0.009	0.0195	2.482	0.49	0.05
KSP_Brine2_3	0.1599	0.0661	1.801	2.248	0.0088	0.0186	2.4811	0.45	0.05
KSP_Brine2_4	0.1589	0.0644	1.8	2.241	0.0091	0.0203	2.4716	0.52	0.05
KSP_Brine3_1	0.3648	0.1165	2.67	3.627	0.0056	0.0144	4.1137	0.53	0.05
KSP_Brine3_2	0.3621	0.1173	2.67	3.626	0.0057	0.0145	4.1093	0.53	0.05
KSP_Brine3_3	0.3636	0.1164	2.684	3.646	0.0057	0.0146	4.128	0.54	0.05
KSP_Brine3_4	0.3624	0.1158	2.665	3.62	0.0055	0.0146	4.1014	0.54	0.05
MgFree_1	0.023	0	3.0217	3.0428	0.0247	0.0412	3.0908	0.97	0.91
MgFree_2	0.154	0	2.5834	2.8806	0.0108	0.0285	3.0456	0.97	0.91
MgFree_3	0.9117	0	0.2371	2.0531	0.0071	0.0285	2.9712	0.97	0.91
MgFree_4	0.0234	0	3.0221	3.0433	0.0255	0.0418	3.0921	0.92	0.91
MgFree_5	0.1538	0	2.5834	2.881	0.0104	0.0285	3.0451	0.92	0.91

Molal values of total calcium (Ca²⁺), magnesium (Mg²⁺) and chloride (Cl[−]) were used to calculate total sodium (Na⁺) and ionic strength (*I*) from charge balance. The CO₂ partial pressure (*p*CO₂, bar) was calculate from molal concentrations of total alkalinity (TA) and total carbon dioxide (TCO₂) using EQPITZER. The specific geometric surface area (m₂ g^{−1}) of the calcite was estimated from scanning electron microscopy.

Table 2

The carbonate ion concentration (CO_3^{2-} , molal) along with the total ion activity coefficients for CO_3^{2-} and Ca^{2+} as derived using EQPITZER

ID	Ca ²⁺	CO ₃ ²⁻	
	γ _T	Molal	
Kinetic reactor experiments			
PCO2_01a	0.216	8.25e−06	0.035
PCO2_01b	0.213	1.13e−05	0.035
PCO2_01c	0.214	1.13e−05	0.035
PCO2_02a	0.264	1.14e−05	0.009
PCO2_03a	0.396	1.27e−05	0.003
PCO2_03b	0.401	1.44e−05	0.003
PCO2_03c	0.404	1.35e−05	0.003
PCO2_04a	0.216	1.23e−05	0.035
PCO2_05a	0.275	1.27e−05	0.008
PCO2_05b	0.261	1.15e−05	0.009
PCO2_05c	0.263	1.24e−05	0.009
PCO2_06a	0.428	1.25e−05	0.003
PCO2_07a	0.218	1.30e−05	0.035
PCO2_08a	0.265	1.31e−05	0.009
PCO2_09a	0.429	1.53e−05	0.003
Mg_01a	0.283	1.05e−05	0.010
Mg_02a	0.254	1.20e−05	0.008
Ca_01a	0.312	1.86e−05	0.015
Ca_02a	0.202	1.10e−05	0.006
L_01a	0.172	9.54e−06	0.015
L_02a	0.536	1.27e−05	0.005
XP_001C	0.208	2.21e−05	0.038
XP_001D	0.199	2.77e−05	0.035
XP_012A	0.183	1.09e−05	0.021
XP_009B	0.193	9.41e−06	0.019
XP_005B	0.194	9.37e−06	0.014
XP_013A	0.170	9.09e−06	0.009
XP_006B	0.210	9.73e−06	0.005
XP_006D	0.210	1.14e−05	0.005
XP_010A	0.216	1.31e−05	0.003
XP_007C	0.226	1.84e−05	0.002
XP_007D	0.219	1.73e−05	0.002
Solubility reactor experiments			
KSP_Brine1_1	0.208	9.84e−06	0.036
KSP_Brine1_2	0.208	1.19e−05	0.036
KSP_Brine1_3	0.208	1.15e−05	0.035
KSP_Brine1_4	0.208	1.24e−05	0.036
KSP_Brine2_1	0.243	1.28e−05	0.010
KSP_Brine2_2	0.243	1.31e−05	0.010
KSP_Brine2_3	0.242	1.37e−05	0.010
KSP_Brine2_4	0.242	1.26e−05	0.010
KSP_Brine2_1	0.353	1.30e−05	0.003
KSP_Brine2_2	0.354	1.33e−05	0.003
KSP_Brine2_3	0.357	1.33e−05	0.003
KSP_Brine2_4	0.353	1.23e−05	0.004
MgFree_1	0.362	1.75e−05	0.027
MgFree_2	0.313	9.24e−06	0.010
MgFree_3	0.131	1.58e−05	0.004
MgFree_4	0.362	1.90e−05	0.027
MgFree_5	0.313	8.46e−06	0.010

Fig. 1. Comparison between the measured and EQPITZER predicted total alkalinity (TA) (A) and total carbon dioxide content (TCO_2) (B) of a broad range of geologically relevant Na–Ca–Mg–Cl synthetic brines (35 to 200 g l^{-1} TDS) equilibrated with calcite at CO_2 partial pressures of ~ 0.1 (solid triangle), 0.5 (open square) and 1.0 bar (solid square) at 25 °C.

Na–Ca–Mg–Cl synthetic brines (35 to 200 g l^{-1} TDS) equilibrated with calcite at CO_2 partial pressures of ~ 0.1 (solid triangle), 0.5 (open square) and 1.0 bar (solid square) at 25 °C (Fig. 1).

4. Discussion

The stoichiometric equilibrium constants ($\text{p}K_{\text{sp}}^*$) for each of the solutions was calculated from the concentration products as

$$\text{p}K_{\text{sp}}^* = -\log(m_{\text{Ca}^{2+}}m_{\text{CO}_3^{2-}}) \quad (1)$$

and shows a broad range of over nearly two orders of magnitude in the apparent solubility of calcite in these solutions generally increasing (a.k.a. decreasing pK_{sp}^*) with increasing TDS (Fig. 2A). Perhaps surprisingly, the actual carbonate carrying capacity of these solutions, although exceedingly small in all cases, actually slightly increases with increasing brine concentration despite an increase in calcium activity (Fig. 3).

The negative logarithms of the ion activity products (pK_{sp}) where

$$pK_{sp} = -\log(\gamma_{Ca^{2+}}\gamma_{CO_3^{2-}}m_{Ca^{2+}}m_{CO_3^{2-}}) \quad (2)$$

yield values in reasonable agreement ($\pm 10\%$) with K_c ($-\log K_c = 8.480 \pm 0.020$, Plummer and Busenberg, 1982) in brines less than 100 g l^{-1} TDS. However, with increasing concentration there is what appears to be systematic increase in thermodynamic solubility product (i.e. decreasing pK_{sp}).

Although a multivariate approach was applied in which calcium, magnesium and ionic strength were all co-varied with increasing TDS, there is a strong relation between the variability and calcium activity (Fig. 2B). Even experiments performed in Mg^{2+} -free solutions exhibit the same behavior implying that this is not due to the formation of a more soluble Mg^{2+} -rich surface phase. Nor is it specifically related to ionic strength, since in the Mg^{2+} -free solutions the ionic strength was

Fig. 3. The Ω values calculated using EQPITZER from the analytical results of this study compared with values calculated from literature data. Open scatter points are experimental data from this study. Open squares were measured in Na–Ca–Mg–Cl brines, while open circles were measured in Mg^{2+} -free brines. Solid triangles are from Millero et al. (1984). Solid circles are from Wolf et al. (1989). The inset figure expands the region investigated in this study as denoted by the dashed box. The solid line represents thermodynamic equilibrium within the uncertainty depicted by the dashed lines (Plummer and Busenberg, 1982).

fixed ($I=3 \text{ m}$) by balancing with NaCl. It should also be noted that in these solutions the Mg/Ca ratio was always <0.5 . This is much lower than in seawater where an

Fig. 2. The negative logarithms of the stoichiometric (pK_{sp}^* , triangles) and thermodynamic (pK_{sp} , squares) equilibrium constants for calcite measured in a broad range of geologically relevant Na–Ca–Mg–Cl synthetic brines (35 to 200 g l^{-1} TDS). Solid scatter points are experimental data from kinetic experiments measured at steady state. Open scatter points were measured in closed system solubility experiments and are in good agreement. The solid line represents the thermodynamic equilibrium constant of Plummer and Busenberg (1982).

~8% Mg-calcite can form at an Mg/Ca ratio of ~5 (Mucci and Morse, 1984). The simplest explanation for this apparent deviation from K_c is that there is a small error associated with the EQPITZER calculated carbonate ion activity coefficient ($\gamma_{\text{CO}_3^{2-}}$) in the most calcium-rich brines.

This error would have little consequence in many geochemical contexts, such as in the case of mineral mass transport since the carbonate carrying capacity of these calcium-rich brines is rather small and the difference between the predicated and observed TA and TCO_2 is very minor (Fig. 1). However, it may become important when modeling the reaction kinetics of these minerals when the degree of disequilibrium is used as a key term in the rate equation. An example of this would be the commonly applied general rate equation (e.g., Morse and Berner, 1972) used to describe the rate of calcite dissolution:

$$R = -\frac{dm_{\text{calcite}}}{dt} = \left(\frac{A}{V}\right)k(1-\Omega)^n \quad (3)$$

where t is time, A is the surface area of the solid, V is the volume of solution (or mass of solvent in cases where molal units are used), k is the rate constant and n is the OrderOf the reaction. The saturation state (Ω) is the ratio of the ion activity product of calcium and carbonate (IAP) to K_c , as given by

$$\Omega = \frac{\gamma_{\text{Ca}^{2+}}m_{\text{Ca}^{2+}}\gamma_{\text{CO}_3^{2-}}m_{\text{CO}_3^{2-}}}{K_c} \quad (4)$$

If $\Omega=1$, then the solution is in equilibrium with respect to calcite; if $\Omega<1$ the solution is undersaturated; and if $\Omega>1$ the solution is supersaturated. EQPITZER reports saturation states increasingly greater than one with increasing calcium concentration. In this study, brines that contained calcium concentrations nearing 1 molal yielded EQPITZER predicted saturation states more than twice saturated (e.g., $\Omega>2$, Fig. 3).

Millero et al. (1984) measured the solubility of calcite in NaCl solutions up to 6 m. In these experiments the $m_{\text{Ca}^{2+}}$ did not exceed $0.6\text{ mmol kg}^{-1}\text{ H}_2\text{O}$. Based on the reported solution compositions and coupling TA and TCO_2 to solve for the carbonic acid system, analogous to the approach used with the analytical data from this study, the derived Ω values using EQPITZER closely approximated 1 (Fig. 3, solid triangles). This indicates that EQPITZER is quite capable of predicting equilibrium up to high ionic strengths in the absence of large amounts of calcium. The same approach was applied to the data reported by Wolf et al. (1989) in which calcite dissolution was measured in highly concentrated CaCl_2

solutions (up to 3 m Ca^{2+}). In this case a near exponential deviation with increasing $m_{\text{Ca}^{2+}}$ was observed with an apparent supersaturation in excess of 20 times for the most concentrated case (Fig. 3, solid circles).

Although these errors may seem dramatic, one has to consider that not only does the carbonate ion occur in very low concentration (<15 micromolal), but also its predicted activity coefficient decreases to $\sim 3 \times 10^{-3}$ in the most concentrated brines. Because carbonate ion activities are on the order of 10^{-8} in these brines, it is not surprising that such errors in the calculated saturation state arise. In fact, it is rather remarkable how well the current model holds up under these extreme conditions.

5. Conclusion

Although EQPITZER reasonably predicts equilibrium ($\pm 10\%$) with respect to calcite in relatively low concentration brines (<100 g l^{-1} TDS), with increasing brine concentration a systematic increase in the calculated saturation state is observed, yielding at steady state more than an apparent 2-fold supersaturation in the most calcium-rich brine. The error is not specifically related to magnesium concentration suggesting that it is not the result of the formation of an enhanced solubility Mg-rich phase. Instead, it strongly correlates with increases in calcium activity. We cannot be certain that the apparent increase in steady-state IAP is not related to a complex interaction between the calcite surface and these highly concentrated brines, but perhaps the simplest explanation is that the apparent IAP increase represents minor uncertainty in the carbonate ion activity coefficient. Although this minor error would have little consequence in many geochemical contexts, such as in the case of mineral mass transport, it can impart significant error to kinetic rate models that empirically describe the rate of dissolution as a function of the degree of disequilibrium ($1-\Omega$). Jeschke and Dreybrodt (2002) showed that when rates are modeled by linear fits of $\log R$ versus $\log (1-\Omega)$, small uncertainties in Ω can have a pronounced effect on the interpreted reaction order (n) and rate constant (k). Small errors can create nonlinearity in log–log plots. Such effects are particularly important under near equilibrium conditions. It is therefore advised that although the program EQPITZER performs well for moderately concentrated brines (<100 g l^{-1} TDS) caution should be taken well applied to more concentrated calcium-rich systems when a precise knowledge of saturation state is required.

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Effect of Flue Gas Impurities on the Process of Injection and Storage of CO₂ in Depleted Gas Reservoirs

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Our previous coreflood experiments - injecting pure CO₂ into carbonate cores - showed that the process is a win-win technology, sequestering CO₂ while recovering a significant amount of hitherto unrecoverable natural gas that could help defray the cost of CO₂ sequestration. In this paper, we report our findings on the effect of “impurities”

in flue gas - N_2 , O_2 , H_2O , SO_2 , NO_2 , and CO - on the displacement of natural gas during CO_2 sequestration. Results show that injection of CO_2 with approximately less than 1 mole % “impurities” would result in practically the same volume of CO_2 being sequestered as injecting pure CO_2 . This gas would have the advantage of being a cheaper separation process compared to pure CO_2 as not all the “impurities” are removed. Although separation of CO_2 out of flue gas is a costly process, it appears this is necessary to maximize CO_2 sequestration volume, reduce compression costs of N_2 (approximately 80% of the stream), and improve sweep efficiency and gas recovery in the reservoir.

Introduction

Geologic sequestration of CO_2 appears to be a reasonable pathway to reducing carbon emissions and consequently CO_2 levels in the atmosphere. Four main options have been identified for geological sequestration of carbon dioxide: (1) aquifers, (2) oil reservoirs, (3) depleted gas fields, and (4) coal beds. The various options must be evaluated for cost, safety, and environmental effects.

Our ongoing study is evaluating CO_2 storage in depleted gas reservoirs. The principal motivation for injecting CO_2 in geologic formations has been enhancing hydrocarbon recovery. This is the case of CO_2 injection in depleted oil reservoirs and

unmineable coal beds. Two current examples of geologic sequestration of CO₂ are the EOR project in the Weyburn field in Saskatchewan and the CO₂ injection into the overlying Utsira aquifer from the Sleipner Vest gas field in the North Sea [1,2].

CO₂ injection into gas reservoirs has been proposed but not tested. CO₂ could be used for pressure maintenance or for condensate vaporization, but the cost of purchasing CO₂ makes this approach uneconomical in the absence of incentives for CO₂ storage [1]. Given a depleted natural gas reservoir and a depleted oil reservoir with the same hydrocarbon pore volume, the depleted natural gas reservoir will store significantly more CO₂ [3]. In addition to the larger storage capacity of depleted gas reservoirs, another advantage is that all CO₂ - resulting from the combustion of natural gas produced from the reservoir - could be stored in the same reservoir, with additional storage capacity. Therefore, CO₂ injection could be replaced for a mixture of CO₂, N₂ and impurities resulting from the partial separation of flue gas [1].

Unfortunately, CO₂ sources are rarely pure; the most likely CO₂ source is usually a stream extracted from the flue gas of a power plant [4]. A typical flue-gas composition of an electric power plant based on a combustion calculation for a Powder River Basin (PRB) coal, in a 500 MW plant with 20% excess air is shown in **Table 1**. The main components of flue gas are N₂ (71 mole %), CO₂ (12 mole %), H₂O (12 mole %), O₂ (5

mole %), and also impurities such as SO₂, NO₂, and CO.* Flue gas may be treated in order to obtain a stream rich in CO₂ for sequestration purposes.

According to the International Environmental Agency (IEA), the total cost of CO₂ capture and storage ranges from \$50 to \$100/tonne of CO₂. This cost can be split into cost of capture, transportation and storage. Current estimates for large-scale capture systems (including CO₂ pressurization, excluding transportation and storage) are \$25 to \$50/tonne of CO₂. Transportation costs are approximately \$1 to \$5/tonne of CO₂ per 100 km, and storage costs are \$1 to \$2/tonne of CO₂ [5,6]. Unquestionably, the cost of separating CO₂ out of flue gas is significantly higher than that of transporting and injecting CO₂ in reservoirs. Due to the high cost of CO₂ capture, the purpose of this study is to understand and model the displacement of natural gas by flue gas and compare it with the displacement by pure CO₂.

Previous coreflood experiments injecting pure CO₂ into carbonate rocks showed that the process is a win-win technology, sequestering CO₂ while recovering a significant amount of hitherto unrecoverable natural gas that could help defray the cost of CO₂ sequestration[3,7,8].

* Electronic communication with D. Chuck, EPRI-Continuous and Predictive Emissions Monitoring Group (22 July 2003).

Experimental Apparatus and Procedure

Two types of flue gas were used in our experiments: dehydrated flue gas with 13.574 mole % CO₂ (Gas A), and treated flue gas with 99.433 mole % CO₂ (Gas B) as presented in **Table 1**. Gas A results from dehydrating flue gas and Gas B results from removing N₂, O₂ and water. Both types of flue gas are used in the displacement experiments. The phase envelopes of the two gases were obtained from the company *Specialty Gas Products* that provided these gases to our laboratory, and are presented in **Fig. 1**. No critical point was observed for Gas A.

The equipment used in our experiments consists of four main components: the injection system, coreflood cell, Universal System HD 350 X-ray CT scanner, and the production and data recording system. **Fig. 2** shows the experimental apparatus, which is briefly described in the following.

The injection system consists of two sets of one-liter *Temco* accumulators. One is connected to a *Micromeritics* 760 HPLC pump to displace the CO₂ gas mixture into the cell, and the other one is connected to a Ruska pump to displace methane into the cell. After introducing the gas into the accumulator, the gas pressure is slowly increased to the desired level by injecting water below the piston in the accumulator.

The coreflood cell (**Fig. 3**), measuring 21 in. (0.533 m) long with an OD of 3.75 in. (0.0953 m) and wall thickness of 0.75 in. (0.0191 m), is constructed of aluminum (transparent to X-ray CT scanning), and is machined out of a solid cylindrical block of aluminum 7075-T6 to withstand the high temperature and pressure. A carbonate core measuring 1 ft (0.305 m) long and 1 in. (0.0254 m) in diameter is inserted into a Viton Hassler sleeve with both ends secured to plungers in the cell. The cell is placed inside a *Precision* mechanical convection incubator for an accurate temperature control. The system is pressurized with nitrogen to test for leaks and then displaced to methane.

The Universal System HD 350 is a fourth generation X-ray CT scanner that provides precise determination of core porosity and fluid saturation. The CT scanner performs with a maximum tube rating of 140 kV and 400 mA, a speed up to 1 rev/sec, and a resolution of 6 to 9 line pairs/cm. The scanner generates slices that have 512 by 512 elements. This overall dimension is set by two parameters on the scanner: the scanning mode (full=48 cm, and half usually 24 cm), and the field of view 120 to 140 mm. For example, if 240 mm is selected, then $240/512$ gives a field of view of approximately 0.47 mm. The best slice thickness (dz dimension) the scanner can do is 0.5 mm. To process, analyze and visualize CT scanner images, two softwares are used: VoxelCalc & 3D Petro, Copyright of KehlCo, Inc.1999 ([www. kehlco.com](http://www.kehlco.com))

The produced gas volume and composition are measured using a wet test meter and a *Hewlett Packard* 5890 Series II gas chromatograph with a *Hewlett Packard* 3396A integrator, respectively. The cell outlet pressure is set to the desired level with the aid of a *Temco* backpressure regulator. Pressure and temperature readings are recorded in 30-second intervals using a *Hewlett Packard* 34970A data logger in conjunction with a personal computer.

A typical experiment is conducted as follows. With the backpressure regulator closed, the coreflood cell is slowly charged up with methane from the accumulator until the desired pressure is reached. While injecting methane into the cell, high-temperature *Mobil DTE 26* hydraulic oil is injected into the Hassler sleeve-inner cell wall annulus to maintain an overburden pressure differential of about 2.07 MPa (300 psi). The CO₂ gas mixture is then injected into the cell at a constant rate of 0.25 mL/min. A run is terminated when the methane composition in the produced gas is negligible.

Experimental Results

A total of 5 runs at 10.44 MPa (1,500 psig) and 343 K are reported in **Table 2**; three runs injecting Gas A (one of them with initial water saturation of 20% in the core), and two runs injecting Gas B with zero initial core water saturation.

Prior to every run, core porosity was determined using the CT-scanner. An average porosity of 21% was calculated using the VoxelCalc software. A 3D porosity profile was created using 3D Petro software to better understand the porosity distribution inside the core (**Fig. 4**). Porosity was used to calculate the pore volume, and consequently the OGIP with **Eq.1** and gas recovery at breakthrough for every run.

$$OGIP = \frac{V_p (1 - S_{wi})}{1,000 B_g} \quad (1)$$

The coefficients of dispersion of gases A and B were estimated using the convection-dispersion equation as follows:

$$K_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (2)$$

where C is the concentration of gases A or B at location x at time t , K_L is the coefficient of longitudinal dispersion, and v is the interstitial velocity. **Eq. 2** may be expressed in dimensionless form as follows.

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D} \quad (3)$$

where:

$$x_D = \frac{x}{L}, \quad \text{dimensionless distance, where } L \text{ is length of core,}$$

$$t_D = \frac{tv}{L}, \quad \text{dimensionless time, and}$$

$$P_e = \frac{vL}{K_L}, \quad \text{Peclet number (ratio of convection to dispersion).}$$

Since the carbon dioxide injection inlet is at $x = 0$, then

Initial condition: $C = 0$ at $t_D = 0, \quad 0 < x_D < \infty$

Boundary conditions: $C = 1$ at $x_D = 0, \quad t_D > 0$

$$C \rightarrow 0 \quad \text{at} \quad x_D \rightarrow \infty, \quad t_D > 0$$

Solution to **Eq. 3** is presented below.

$$C = \frac{1}{2} \left\{ \operatorname{erfc} \left(\frac{x_D - t_D}{2\sqrt{t_D / P_e}} \right) + e^{P_e x_D} \operatorname{erfc} \left(\frac{x_D + t_D}{2\sqrt{t_D / P_e}} \right) \right\} \quad (4)$$

The longitudinal dispersion coefficient was varied to yield the best agreement between experimental data and analytical solution. Calculated profiles of concentration of gases A and B are presented as “best fit” in **Fig. 5**. The coefficients of dispersion obtained for each run are presented in **Table 2**. These values are, in general, relatively small, ranging from 0.13 to 0.25 cm²/min.

Comparing our results to those presented by Seo and Mamora [3,8] corresponding to experiments with pure CO₂, the following observations can be pointed out. First, the dispersion coefficient of pure CO₂ at 343 K and 10.44 MPa is approximately 0.15 cm²/min. This value is in good agreement with the dispersion coefficient of Gas B, 0.13 to 0.15 cm²/min, which contains 99.433 mole % CO₂. Displacement efficiency of Gas B and pure CO₂ are very similar.

Second, the dispersion coefficients for Gas A, 0.18 to 0.25 cm²/min, is consistently higher than that for pure CO₂ and for Gas B. This result can be better understood by looking at the densities and viscosities of pure CO₂ and Gas A, as well as the phase envelopes at the conditions of the experiment. **Fig. 6** and **Fig. 7** show densities and viscosities estimated with the software *PVTsim* version 13.0.2. Pure CO₂ exhibits

higher density and higher viscosity than Gas A. The phase behavior of pure CO₂ in this miscible displacement exhibits less fingering and bypassing than Gas A due to a greater viscosity, and thus is more efficient displacing methane in the experiment. In addition, the phase envelope of Gas A (**Fig. 1**) does not exhibit a critical point, indicating that at 343 K and 10.44 MPa the fluid is in vapor phase, different from CO₂ that is in supercritical phase.

Breakthrough times vary from 0.78 to 0.89 pore volumes injected (102.5 to 140 min) for runs with zero initial water saturation, despite the fact that the water HPLC pump (displacing gases A and B in the accumulator) was set constant to 0.25 mL/min for all runs. This is probably due to cell pressure variations resulting from continuous adjustment of the backpressure regulator during each run. For the run with 20% initial water saturation, the breakthrough time was significantly lower, 0.60 pore volumes (88.5 min), due to the reduction in hydrocarbon pore volume compared to zero initial water saturation.

Recovery of methane is lower for Gas A (79-81% OGIP) than for Gas B (88-90% OGIP) and pure CO₂ (ca. 86% OGIP) [3]. These results indicate that Gas A exhibits the poorest displacement efficiency, in line with the fact that its longitudinal dispersion coefficient is the largest.

Conclusions

Main conclusions arising from our study to-date may be summarized as follows:

1. Displacement of methane by Gas A (dehydrated flue gas with CO₂ concentration of 13.574 mole %) at the conditions studied exhibits larger dispersion coefficients, 0.18-0.25 cm²/min, than displacement by pure CO₂, ca. 0.15 cm²/min.
2. Impurities appear to have a negligible effect in the displacement of methane by Gas B (CO₂ concentration of 99.433 mole %). Dispersion coefficient of Gas B is 0.13-0.15 cm²/min.
3. Recovery of methane at breakthrough is higher for Gas B (88-90% OGIP) and pure CO₂ (86% OGIP) than for Gas A (79-81% OGIP). Gas recovery from injection of Gas A is lowest due to the large concentration of N₂ in the gas, resulting in the largest dispersion coefficient of the three injection gases studied.
4. It appears therefore that injection of CO₂ with approximately less than 1 mole % “impurities” would result in practically the same volume of CO₂ being sequestered as injecting pure CO₂. Gas B would have the advantage of being a

cheaper separation process compared to pure CO₂ as not all the “impurities” are removed in the case of Gas B.

5. Although separation of CO₂ out of flue gas is a costly process, it appears that this is necessary to maximize CO₂ sequestration volume, reduce compression costs of N₂ (approximately 80% of the stream), and improve sweep efficiency and gas recovery in the reservoir.

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Nomenclature

B_g = formation volume factor of gas (C₁), vol/vol

C = concentration of Gas A or Gas B, mole%

K_L = coefficient of longitudinal dispersion, cm²/min

$OGIP$ = original gas (C₁)-in-place, std. Liter

P = pressure, MPa

P_e = Peclet number, dimensionless

S_{wi} = initial water saturation, fraction

t = time, min

t_D = dimensionless time, defined in **Eq. 3**

T = temperature, K

V_p = pore volume, cm³

v = interstitial velocity, cm/min

x = distance from core injection point, cm

x_D = dimensionless distance, defined in **Eq. 3**

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VITAE

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FIGURES

Fig. 1 – Phase envelopes of the two gases injected (Gas A and Gas B) in coreflood experiments compared to the vapor pressure line for pure CO₂.

Fig. 2 – Photograph showing main components of the experimental apparatus.

Fig. 3 – Longitudinal section of coreflood cell with maximum operating conditions of 34.58 MPa (5,000 psig) and 366 K. Scale approximately 1: 3.

Fig. 4 – Isosurface images of 3D porosity profiles using *Petro3D*. These images are very helpful for understanding the porosity distribution in the core.

Fig. 5 – Concentration of produced gas versus injected pore volume for runs at 10.44 MPa (1,500 psig) and 343K. Best-fit lines represent analytical solution for the best value of the coefficient of longitudinal dispersion. Earlier breakthrough time for Gas A when the initial water saturation is 20%.

Fig. 6 – Density diagram with respect to pressure at 343°C as calculated using *PVTSim* 13.0.2.

Fig. 7 - Viscosity diagram with respect to pressure at 343K as calculated using *PVTSim* 3.0.2. Viscosity of CO₂ is higher than that of Gas A at pressures higher than 6.90 MPa (1,000 psia).

TABLES

Table 1 – Composition of flue gas, Gas A and Gas B.

	Composition, mole %		
Component	Flue Gas	Gas A	Gas B
Nitrogen, N ₂	70.726	80.370	---
Water, H ₂ O	12.000	---	---
Carbon dioxide, CO ₂	11.945	13.574	99.433
Oxygen, O ₂	5.258	5.975	---
Sulfur dioxide, SO ₂	0.045	0.051	0.368
Nitrogen oxide, NO ₂	0.016	0.018	0.129
Carbon monoxide, CO	0.010	0.012	0.070
Total	100.000	100.000	100.000

Table 2 – Summary of coreflood experiments at 10.44 MPa (1,500 psig) and 343 K.

Gas A (13.574% CO₂) shows higher longitudinal dispersion coefficients and lower C₁ recovery at breakthrough than Gas B (99.433% CO₂).

Injection gas	S_{wi}	OGIP, std L	C ₁ recovery at breakthrough, %OGIP	Breakthrough, Pore Volume	K_L , cm ² /min
Gas A	0.0	3.967	80.66	0.79	0.18
	0.0	4.027	79.46	0.79	0.19
	0.2	3.227	74.36	0.60	0.25
Gas B	0.0	3.982	89.90	0.89	0.15
	0.0	3.060	88.16	0.78	0.13

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Experimental and Simulation Studies of Sequestration of Supercritical Carbon Dioxide in Depleted Gas Reservoirs

This paper presents experimental and simulation studies to evaluate the feasibility of sequestering supercritical CO₂ in depleted gas reservoirs. Experimental results were simulated to obtain gas-liquid relative permeability curves used in the field simulation study. A 3D simulation model of one-eighth of a five-spot pattern was constructed to evaluate injection of supercritical CO₂ under typical field conditions.

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Introduction

Carbon dioxide emission from burning fossil fuels has been identified as the major contributor to the increase in atmospheric CO₂ levels that can potentially lead to global climate change [1]. During the last decade, worldwide concern has focused on possible global warming caused by heat being trapped by CO₂ in the upper atmosphere (the greenhouse effect). In 1993, the European Commission began the Joule II Non-nuclear Energy Research Program, which studied sequestration of industrially produced carbon dioxide [2,3]. Injection of carbon dioxide into depleted gas reservoirs has the potential to enhance gas recovery, while simultaneously sequestering a greenhouse gas.

As discussed in the Joule II Non-nuclear Energy Research Program, for maximum storage capacity, carbon dioxide has to be stored as a supercritical fluid, which requires reservoirs deeper than 800 m.

Consequently, at pressures and temperatures typically encountered in the field, carbon dioxide will behave as a supercritical fluid. CO₂ in this form is transported via surface pipelines from states, such as New Mexico, to west Texas for injection into oil reservoirs to enhance oil recovery [4]. However, displacement of natural gas by supercritical CO₂ has not been done in the field and is not well understood. To better understand this, we have conducted experimental and simulation studies of sequestering supercritical CO₂ in depleted gas reservoirs.

Experimental Apparatus and Procedure

The experimental apparatus consists of five main components: the injection system, coreflood cell, HD 200 x-ray CT scanner, production system, and data recording system (Fig. 1) [5]. The systems are briefly described in the following.

The injection system consists of two sets of a one-liter *Temco* accumulator connected to a ISCO syringe pump, one set for each of the gases—methane and carbon dioxide. After introducing the gas into the accumulator, the gas pressure is slowly increased to the desired level by injecting water below the piston in the accumulator.

The coreflood cell, measuring 21 in. (53.3 cm) long with an OD of 3.75 in. (9.53 cm) and wall thickness of 0.75 in. (1.91 cm), is constructed of aluminum (transparent to x-ray CT scanning) and is machined out of a solid cylindrical block of aluminum 7075-T6 to withstand the high temperature and pressure. A carbonate core

measuring 1 ft (30.48 cm) long and 1 in. (2.54 cm) in diameter is inserted into a viton Hassler sleeve with both ends secured to plungers in the cell. The cell is placed inside an aluminum trough that is fixed in a horizontal position to the moveable CT scanner sample table. The trough is adjusted so that the cell lies in the center of the scanner gantry aperture. The cell and trough are wrapped with 4 in. (10.2 cm) thick *Fiberfrax* insulation. Hot air from a temperature-regulated blower is piped in at one end of the trough. In this manner, the desired cell temperature can be obtained. The system is pressurized with nitrogen to test for leaks and then displaced to methane.

The x-ray CT scanner is a Universal System HD200 with 760 diode detectors, giving a cross-sectional resolution of about 0.3 mm by 0.3 mm. Cross-sectional CT scans of the cell are made three times during an experimental run: at start of the run, at carbon dioxide breakthrough, and at the end of the run. The CT scan images provide core porosity data and help corroborate the dispersion and displacement of methane as inferred from gas compositional data and analysis. Figure 2 shows CT images of porosity profile with the aid of *Voxelcalc* image processing software. In color scale, minimum value of porosity is about 0.1, maximum value is about 0.28, and average value of porosity is 0.23.

Produced gas volume and composition are measured using a wet test meter and a *Carle SX* gas chromatograph with a *Spectra Physics* SP4100 integrator, respectively. The cell outlet pressure is set to the desired level with the aid of a *Temco* backpressure regulator. Pressure and temperature readings are recorded in 10 s intervals using a HP 34970A data logger in conjunction with a personal computer.

A typical experiment is conducted as follows. With the backpressure regulator closed, the coreflood cell is slowly charged up with methane from the accumulator until the desired pressure is reached. While injecting methane into the cell, high-temperature Mobil DTE 26 hydraulic oil is injected into the Hassler sleeve inner-cell wall annulus to maintain an overburden pressure differential of 300 psig (2.170 MPa). Carbon dioxide is then injected into the cell at a constant rate of 0.25 ml/min. A run is terminated when the produced gas is practically 100% carbon dioxide.

Simulation Model

Carbon dioxide will behave as a supercritical fluid at pressures and temperatures typically encountered in the field. Supercritical fluids have liquidlike densities, gaslike diffusivities, and could be liquid or gas dependent on pressure and temperature change in the field.

To conduct the simulation study, we first determined gas-liquid relative permeability curves used in the field simulation study by

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Fig. 1 Schematic diagram of supercritical carbon dioxide coreflood apparatus

history-matching the experimental results (Figs. 3 and 4). A 1D 96 grid-cell model was used to represent the physical cell.

A 3D simulation model of one-eighth of a five-spot pattern was constructed to model injection of supercritical CO₂ under two typical field conditions (Table 1). Two pattern areas at a depth of 7000 ft (2133.6 m) were modeled, 40 acres (1.619 × 10⁵ m²) [150 ft (45.72 m) thickness: 15 ft (4.572 m) × 10 layers], and 80 acres (3.237 × 10⁵ m²) [300 ft (91.44 m) thickness: 15 ft (4.572 m) × 20 layers]. To model fluid flow more accurately, smaller grids are made near the injector and producer than far from the wells, and grids are parallel to the diagonal between the injector and producer (Fig. 5). The injector is perforated on the bottommost layer, and the producer is perforated on the topmost layer.

Porosity is 0.23 in both cases, which is calculated from CT scanner. We assumed direction permeability is the same as y-direction permeability (50 md), z-direction permeability is 5 md, and initial water saturation is 0. Also, we assumed an original reservoir pressure of 3045 psia (20.99 MPa) from hydrostatic pressure gradient [0.435 psia/ft (9840 Pa/m) × 7000 ft (2133.6 m)]. The reservoir temperature is taken as 152°F (66.7°C) from geothermal gradient [75°F (23.9°C) + 0.011°F/ft (0.02006°C/m) × 7000 ft (2133.6 m)]. Injection pressure of supercritical CO₂

Fig. 3 Gas mass rate vs. time from experimental and simulation results to calculate gas-liquid relative permeability curves

[3245 psia (22.37 MPa)] is 200 psia (1.379 MPa) higher than the original reservoir pressure [3045 psia (20.99 MPa)]. When CO₂ is detected in the producer, we will shut off the producer and continue to inject supercritical CO₂ until field reaches the original reservoir pressure [3045 psia (20.99 MPa)]. At this pressure, CO₂ injection into gas field will be terminated.

Experimental Results

A total of 17 runs have been made (Table 2): nine runs at 20°C (68°F) and eight at 40–60°C (104–140°F). For each temperature, the cell pressure is varied, ranging from 500 psig (3.55 MPa) to 3000 psig (20.79 MPa).

The coefficient of dispersion of carbon dioxide may be estimated from the convection-dispersion equation as follows:

$$K_l \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (1)$$

where C is the carbon-dioxide concentration at location x at time t , K_l is the coefficient of longitudinal dispersion, and v is the interstitial velocity. Equation (1) may be expressed in dimensionless form as follows:

Fig. 2 CT images of porosity profile using Voxelfalc software

Fig. 4 Gas-liquid relative permeability curves

Table 1 Properties of two case simulation models

Property	Units	Case 1	Case 2
Five-spot pattern area	m ²	1.619E+05	3.237E+05
One-eighth of five spot area	m ²	2.024E+04	4.046E+04
Thickness	m	45.72	91.44
Layers	—	10	20
Pore volume	m ³	2.128E+05	8.511E+05
Porosity	fraction	0.23	0.23
X,Y-direction permeability	md	50	50
Z-direction permeability	md	5	5
Initial water saturation	—	0	0
Reservoir temperature	°C	66.7	66.7
Original reservoir pressure	MPa	20.99	20.99

Fig. 5 Schematic of one-eighth of 5-spot and simulation model

$$\frac{1}{Pe} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D} \quad (2)$$

where

$$x_D = \frac{x}{L}, \quad \text{dimensionless distance, where } L \text{ is length of core;}$$

$$t_D = \frac{tv}{L}, \quad \text{dimensionless time; and}$$

$$Pe = \frac{vL}{K_l}, \quad \text{Peclet number (ratio of convection to dispersion)}$$

Since the carbon dioxide injection inlet is at $x=0$, then

$$\text{initial condition: } C=0 \text{ at } t_D=0, 0 < x_D < \infty$$

$$\text{boundary conditions: } \left. \begin{array}{l} C=1 \text{ at } x_D=0 \\ C \rightarrow 0 \text{ at } x_D \rightarrow \infty \end{array} \right\} t_D > 0$$

Solution to Eq. (2) may be shown to be as follows:

$$C = \frac{1}{2} \left\{ \operatorname{erfc} \left(\frac{x_D - t_D}{2\sqrt{t_D/Pe}} \right) + e^{Pe x_D} \operatorname{erfc} \left(\frac{x_D + t_D}{2\sqrt{t_D/Pe}} \right) \right\} \quad (3)$$

A computer program was written to calculate carbon-dioxide concentration per Eq. (3) in which the dispersion coefficient K_l is varied to yield the best agreement between data and the analytical solution. In the program, $\operatorname{erfc}(y)$ is calculated using the following approximation [6].

$$\operatorname{erfc}(y) = (a_1 z + a_2 z^2 + a_3 z^3 + a_4 z^4 + a_5 z^5) e^{-y^2} \quad (4)$$

where

$$z = \frac{1}{1 + 0.3275911y}, \quad a_1 = 0.254829592$$

$$a_2 = -0.284496736, \quad a_3 = 1.421413741$$

$$a_4 = -1.453152027, \quad a_5 = 1.061405429$$

The recovery factors and coefficients of dispersion obtained for each run are shown in Table 2. The dispersion coefficient values are relatively small, ranging from 0.01 to 0.12 cm²/min. As a result of the stable displacement by carbon dioxide, the methane recovery at carbon dioxide breakthrough is high, ranging from 73% to 87% of OGIP.

Table 2 Estimation of recovery factors and coefficients of dispersion

Run no.	Temperature °C	Pressure MPa	C ₁ production at CO ₂ SL	breakthrough %OGIP	Dispersion coefficient cm ² /min
9	20	7.18	3.135	85.1	0.100
10	20	13.89	5.660	73.0	0.025
14	20	7.00	2.755	77.0	0.100
15	20	7.00	2.620	73.1	0.100
16	20	13.89	5.950	77.0	0.028
17	20	13.89	5.635	72.9	0.032
18	20	20.79	9.125	79.9	0.010
19	20	20.79	9.185	80.4	0.011
20	40	18.72	7.840	84.5	0.021
21	60	18.72	7.145	85.8	0.040
22	40	15.27	6.280	82.9	0.030
23	60	15.27	5.925	87.2	0.060
24	40	11.82	4.935	86.2	0.070
25	60	11.82	4.515	86.8	0.120
26	40	8.38	3.350	84.5	0.120
27	60	8.38	3.130	86.8	0.200
28	20	3.55	1.400	82.4	0.150

Fig. 6 C_1 recovery factor vs. injection rates for cases 1 and 2

Fig. 9 CO_2 injection end vs. injection rates for cases 1 and 2

Fig. 7 CO_2 breakthrough time at various injection rates for cases 1 and 2

Fig. 10 C_1 recovery factor vs. abandoned reservoir pressure for cases 1 and 2

Fig. 8 Amounts of CO_2 sequestered vs. injection rates for cases 1 and 2

Fig. 11 CO_2 breakthrough time at various abandoned reservoir pressures for cases 1 and 2

Simulation Results

To evaluate the effect of injection rate and abandoned (initial) reservoir pressure on gas recovery factor, CO_2 breakthrough time, and the amount of CO_2 sequestered, we simulated two cases: case 1 [40 acres ($1.619 \times 10^5 \text{ m}^2$)] and case 2 [80 acres ($3.237 \times 10^5 \text{ m}^2$)]. First, for each case, we fixed abandoned (initial) reservoir pressure to 500 psia (3.55 MPa) to find the effect of injection

rate on recovery factor, breakthrough time, and the amount of CO_2 sequestered.

Figure 6 shows methane recovery factor at CO_2 breakthrough for various injection rates at the two cases. Recovery factor is increased as injection rate is increased until a maximum recovery factor is obtained. The corresponding injection rates are: 400 bbl/d ($127.2 \text{ m}^3/\text{d}$) (case 1) and 800 bbl/d ($63.6 \text{ m}^3/\text{d}$) (case 2). C_1 sweep is explained by perforation. Our results for methane recovery factor are similar to Clemens and Wit's results [7]. Figure 7

Fig. 12 Amounts of CO₂ sequestered vs. abandoned reservoir pressures for cases 1 and 2

Fig. 13 CO₂ injection end vs. abandoned reservoir pressures for cases 1 and 2

shows CO₂ breakthrough time versus various injection rates in the two cases. CO₂ breakthrough time is decreased as injection rate is increased.

The amounts of CO₂ sequestered in the gas field for different injection rates are shown in Fig. 8. The amounts of CO₂ sequestered are almost the same, independent of injection rate because the amounts of CO₂ sequestered are directly proportional to the pore volume. Because the pore volume of case 2 is four times bigger than that of case 1, the amount of CO₂ sequestered in case 2 is exactly four times bigger than that of case 1. At lower injection rate, time of injection end is longer. This relationship is shown in Fig. 9.

Through above procedure, we found optimum injection rate to maximize both recovery factor and the amount of CO₂ sequestered. To find the effect of abandoned (initial) reservoir pressure on recovery factor, breakthrough time, and the amount of CO₂ sequestered, we simulated the two cases with fixed injection rates [case 1: 400 bbl/d (63.6 m³/d) and case 2: 800 bbl/d (127.2 m³/d)].

Figure 10 shows recovery factor at various abandoned reservoir pressures for the two cases. The recovery factor in the more depleted and smaller gas field is bigger. Breakthrough time versus abandoned reservoir pressures is shown in Fig. 11.

Figure 12 shows the relationship between the amount of CO₂ sequestered and abandoned reservoir pressures. The amount of CO₂ sequestered in more depleted and larger gas reservoir is bigger. The time of CO₂ injection ends versus abandoned reservoir pressures is shown in Fig. 13.

Conclusions

Main conclusions arising from this study may be summarized as follows. A large amount of CO₂ is sequestered: about 1.2 million tons in 29 years (case 1), and about 4.8 million tons in 56 years (case 2). The amount of CO₂ sequestered in more depleted and larger gas reservoir is larger. However, injection rate does not affect the amounts of CO₂ sequestered. A significant amount of natural gas is also produced: about 1.3 BSCF (36.81 × 10⁶ m³) or 74% OGIP (case 1) and about 4.9 BSCF (138.75 × 10⁶ m³) or 68% OGIP (case 2).

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Nomenclature

- C = concentration of CO₂, mole%
- K_l = coefficient of longitudinal dispersion, cm²/min
- L = length of core, cm
- OGIP = original gas (C₁)-in-place, std. Liter
- Pe = Peclet number, dimensionless
- SL = volume in liter at standard conditions
- t = time, min
- t_D = dimensionless time as defined for Eq. (2)
- v = interstitial velocity, cm/min
- x = distance from core injection point, cm
- x_D = dimensionless distance as defined for Eq. (2)
- z = gas compressibility factor, dimensionless
- K_{rg} = relative permeability to gas
- K_{rlg} = relative permeability to liquid

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Enhanced Gas Recovery by Carbon Dioxide Sequestration in Depleted Gas Reservoirs

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Abstract

A depleted natural gas reservoir can store significantly more gas than a depleted oil reservoir (with the same initial hydrocarbon pore volume) for two reasons. First, ultimate gas recovery (about 65% of gas initially-in-place) is typically about twice that of oil (average 35% of oil initially-in-place). Second, gas is some 30 times more compressible than oil or water. CO₂ has a critical temperature of 31°C (88°F) and a critical pressure of 7.38 MPa (1070 psia). Consequently, at pressures and temperatures typically encountered in the field, carbon dioxide will behave as a supercritical fluid. However, displacement of natural gas by supercritical CO₂ has not been done in the field and is not well understood.

As part of a CO₂ sequestration study, we have conducted experimental and analytical studies to evaluate the feasibility of displacing natural gas with supercritical CO₂. The experiments involved injecting supercritical CO₂ into an aluminum Hassler core-holder containing a 1-ft long by 1-in. diameter carbonate core initially saturated with methane. Rate and composition of the produced gas were measured, enabling determination of mole fraction of produced CO₂ as a function of time. In addition, the core holder was CT scanned to determine core porosity, and CO₂ and methane saturation. Experiments have been conducted for core pressures in the range, 500-3000 psig at 70°-140°F. Results indicate that some 73%-87% of the gas initially-in-place is recovered at CO₂ breakthrough, with a low CO₂ dispersion coefficient of 0.01-0.12 cm²/min.

We can tentatively conclude that CO₂ injection into depleted or abandoned gas reservoirs would not only sequester CO₂ but would also re-pressurize the reservoir, and most

likely result in effective displacement of the gas. Thus, production of hitherto unrecoverable gas reserves could help defray the cost of CO₂ sequestration: in short, a possible win-win technology.

Introduction

In 1996 the Norwegian state oil company, Statoil, started the first large-scale underground disposal of CO₂ in the North Sea.^{1,2} Some 1 million tonnes per year of CO₂ - separated out of the natural gas produced from the Sleipner Vest field - has been injected into the overlying Utsira aquifer. A similar project is being planned for the Natuna gas field in Indonesia. The field contains some 1.4×10⁶ m³ (50 TSCF) gas, about 70% by volume of which is carbon dioxide. The Natuna project, to be undertaken by a consortium of companies, would involve liquefying the sales gas (LNG) while the carbon dioxide would be injected into an aquifer.

Underground disposal of CO₂ - emitted by industrial sources such as fossil fuel-fired power plants - has not been undertaken. In the last decade, however, there has been worldwide concern on possible global warming caused by heat being trapped by CO₂ in the upper atmosphere (the greenhouse effect). In 1993, the European Commission began the Joule II Non-nuclear Energy Research Program, which studied sequestration of industrially produced CO₂.^{2,3}

The Joule II study concluded that (i) shallow reservoirs do not provide sufficient storage for carbon dioxide because it would be in gaseous form, (ii) for maximum storage capacity, carbon dioxide has to be stored as a supercritical fluid - which requires reservoirs deeper than 800 m (2,600 ft), (iii) such deep reservoirs could be depleted oil or gas reservoirs or structures containing aquifers, (iv) if carbon dioxide is stored in aquifers, then to avoid contaminating shallower potable water sources, carbon dioxide would be sequestered in aquifers deep below the North Sea, (v) if carbon dioxide is injected into a limestone reservoir, carbonate dissolution could occur around the injection wells causing subsidence, and (vi) the cost of carbon dioxide separation out of flue gas is significantly higher than that of transporting and injecting carbon dioxide in reservoirs.

As part of the Joule II project, Pearce *et al.* (1996)⁴ conducted hydrothermal experiments to determine the effect of carbon dioxide (as supercritical fluid or saturated in water)

on anhydrites, mudstones, and sandstones. These experiments were restricted to observation of changes to the physical properties and chemical composition of the rocks after carbon dioxide was passed through the rock samples. Reaction kinetic parameters were not measured. Excluded from the study were carbonate rocks – these would have been more reactive to carbon dioxide.

Carbon dioxide sequestration is a very recent development. Uncertainties still exist with respect to the process of injecting carbon dioxide into depleted gas and oil reservoirs or aquifers. To gain further insight into the process, we have reviewed literature on two somewhat similar processes, namely, the storage of natural gas in the U.S., and enhanced coalbed methane recovery using carbon dioxide injection.

Natural Gas Storage in the U.S. The process of storing piped natural gas in depleted gas reservoirs in summer, and subsequently producing the gas in winter, began in the U.S. in 1915.^{5,6} Since then, the underground gas storage industry has developed into a mature industry. By 1979, about $211 \times 10^9 \text{ m}^3$ (7.437 TSCF) of natural gas was stored in 399 reservoirs in 26 states with seasonal gas withdrawal of $1.1 \times 10^9 \text{ m}^3$ (39.7 BSCF). About 80% of the storage capacity was provided by *depleted gas reservoirs* and 20% by injecting natural gas into aquifer-filled structures. Storage reservoir pressures ranged from 2.07 to 27.6 MPa (300 to 4,000 psi).

A depleted natural gas reservoir (containing mainly methane) can store significantly more gas than a depleted oil reservoir, if each reservoir has the same initial hydrocarbon pore volume. This is due to two reasons. First, ultimate gas recovery (about 65% of initial gas-in-place) is typically about twice that of oil (average 35% of initial oil-in-place). Also, gas density - in-situ gradient about 1.81 kPa/m (0.08 psi/ft) - is significantly less than that of oil, which is typically about 6.11 kPa/m (0.27 psi/ft). There is therefore less remaining hydrocarbon mass in a gas reservoir than in an oil reservoir. Secondly, gas is some 30 times more compressible than oil or water. At 13.8 MPa (2000 psia), isothermal compressibility of natural gas is typically about $72.5 \times 10^{-6} \text{ kPa}^{-1}$ ($500 \times 10^{-6} \text{ psi}^{-1}$) versus $2.2 \times 10^{-6} \text{ kPa}^{-1}$ ($15 \times 10^{-6} \text{ psi}^{-1}$) for oil and $0.4 \times 10^{-6} \text{ kPa}^{-1}$ ($3 \times 10^{-6} \text{ psi}^{-1}$) for water. As borne out by natural gas storage in the U.S., a depleted gas reservoir would appear to be best suited for carbon dioxide sequestration.

We then evaluated the possible gain in producing additional natural gas resulting from gas reservoirs being re-pressurized by carbon dioxide injection. Using the 1979 AGA data, the average storage capacity per reservoir for the 399 gas storage depleted reservoirs is $0.53 \times 10^9 \text{ m}^3$ (18.64 BSCF). Assuming conservatively that this is equal to the initial gas-in-place volume per reservoir, and a recovery factor of 65%, the hitherto unrecoverable gas reserves amount to about $0.35 \times 0.53 \times 10^9 \text{ m}^3$, i.e. $0.19 \times 10^9 \text{ m}^3$ (6.52 BSCF). If carbon dioxide were injected into such a reservoir, re-pressurizing it and displacing the natural gas, the potential value of the gas could be as high as \$12 million, assuming a gas price of

\$1.90/MSCF (6.71 cents/ m^3). For a reservoir with, say, ten times larger initial gas-in-place or where ten of such reservoirs are in close proximity to one another and therefore be treated as a single carbon dioxide sequestration point, then the potential value of the produced gas ($1.9 \times 10^9 \text{ m}^3$ or 65.2 BSCF) could be as high as \$120 million. These gas revenues could be used to offset the costs of carbon dioxide transportation, injection wells, etc. Further, the production of natural gas has the benefit of providing additional storage space for carbon dioxide.

Enhanced Coalbed Methane Recovery Using Carbon Dioxide. Methane is conventionally produced from coal seams by pressure depletion that causes methane to desorb from the coalbed. Injected carbon dioxide is preferentially adsorbed by coal causing desorption and thus production of methane. In 1995, Burlington Resources commenced carbon dioxide injection into the Allison Unit coalbed in the San Juan Basin, New Mexico, to enhance coalbed methane recovery.⁷ This world's first CO_2 enhanced coalbed methane (CO_2 -ECBM) pilot consisted of a 4-injector/7-producer pattern. CO_2 was supplied from a nearby pipeline that transports the gas at 13.8 MPa (2000 psi) from a carbon dioxide field in Colorado for injection into oil fields in West Texas to enhance oil recovery.

Some $85 \times 10^3 \text{ m}^3/\text{D}$ (3 MMSCF/D) of carbon dioxide was injected, with gas production enhanced by up to 150% over the conventional pressure-depletion method. As of 1998, more than $57 \times 10^6 \text{ m}^3$ (2 BSCF) carbon dioxide has been sequestered at the Allison pilot project. Pilot results indicate CO_2 -ECBM would be profitable in the San Juan Basin at wellhead gas prices above 6.18 cents/ m^3 (\$1.75/MSCF), possibly adding as much as $3.7 \times 10^{11} \text{ m}^3$ (13 TSCF) methane production – a resource value of \$22.8 billion.

Coalbed methane development in the San Juan basin accounts for 75% of world coalbed methane production. Stevens and Riemer (1998)⁷ also estimated that possible commercial CO_2 -ECBM worldwide could be as high as $1.93 \times 10^{12} \text{ m}^3$ (68 TSCF) with about 7.1 billion metric tonnes carbon dioxide sequestration potential.

Sequestration of Supercritical Carbon Dioxide in Depleted Gas Fields. Carbon dioxide has a critical temperature of 31°C (88°F) and a critical pressure of 7.38 MPa (1070 psia). Thus, at pressures and temperatures encountered in the field, CO_2 will behave as a supercritical fluid. CO_2 in this form is transported via surface pipelines from states such as New Mexico to West Texas for injection into oil reservoirs to enhance oil recovery.⁸ However, displacement of natural gas in a reservoir by supercritical CO_2 has not been done because there has been no compelling reason to do so, except for injection of CO_2 to enhance coalbed methane production.

Research Objectives

The overall objective of this study was to understand and model the displacement of natural gas by supercritical CO_2 in

a depleted carbonate porous medium. To achieve this objective, coreflood experiments were conducted in which C_1 in the core would be displaced by CO_2 at pressures and temperatures encountered in the field, 500-3000 psig (3.55-20.79 MPa) and 68°-140°F (20°-60°C), respectively. From analytical modeling of the experimental results, the following would be determined.

- the rate of diffusion of supercritical carbon dioxide in gas-bearing carbonate reservoirs, and
- displacement mechanisms of natural gas by supercritical carbon dioxide in carbonate reservoirs.

Experimental Apparatus and Procedure

The experimental apparatus consists of four main components, the injection system, coreflood cell, HD 200 x-ray CT scanner, production system, and data recording system (Figs. 1 and 2). The systems are briefly described in the following.

The injection system consists of two sets of one-liter *Temco* accumulator connected to a *Beckman* HPLC water pump, one set for each of the gases, methane and carbon dioxide. After introducing the gas into the accumulator, the gas pressure is slowly increased to the desired level by injecting water below the piston in the accumulator.

The coreflood cell, measuring 21 in. (53.3 cm) long with an OD of 3.75 in. (9.53 cm) and wall thickness of 0.75 in. (1.91 cm), is constructed of aluminum (transparent to x-ray CT scanning), and is machined out of a solid cylindrical block of aluminum 7075-T6 to withstand the high temperature and pressure. A carbonate core measuring 1 ft (30.5 cm) long and 1 in. (2.54 cm) in diameter is inserted into a viton Hassler sleeve with both ends secured to plungers in the cell. The cell is placed inside an aluminum trough that is fixed in a horizontal position to the moveable CT scanner sample table. The trough is adjusted so that the cell lies in the center of the scanner gantry aperture. The cell and trough are wrapped with 4 inch- thick *Fiberfrax* insulation. Hot air from a temperature-regulated blower is piped at one of the trough. In this manner, the desired cell temperature can be obtained. The system is pressurized with nitrogen to test for leaks and then displaced to methane.

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Produced gas volume and composition are measured using a wet test meter and a *Carle* SX gas chromatograph with a *Spectra Physics* SP4100 integrator, respectively. The cell outlet pressure is set to the desired level with the aid of a *Temco* backpressure regulator. Pressure and temperature readings are recorded in 10-second intervals using a *HP* 34970A data logger in conjunction with a personal computer.

A typical experiment is conducted as follows. With the

backpressure regulator closed, the coreflood cell is slowly charged up with methane from the accumulator until the desired pressure is reached. While injecting methane into the cell, high-temperature *Mobil DTE 26* hydraulic oil is injected into the Hassler sleeve-inner cell wall annulus to maintain an overburden pressure differential of 300 psi. Carbon dioxide is then injected into the cell at a constant rate of 0.25 ml/min. A run is terminated when the produced gas is practically 100% carbon dioxide.

Experimental Results

A total of 17 runs have been made (Table 1): nine runs at 20°C (68°F) and eight at 40°-60°C (104°-140°F). For each temperature, the cell pressure is varied, ranging from 500 psig (3.55 MPa) to 3000 psig (20.79 MPa).

Fig. 3 graphs the mole percent of carbon dioxide as a function of time for the nine runs at 20°C - where carbon dioxide is either liquid (runs 9-19) or gas (run 28) depending on the pressure. Fig. 4 shows similar graphs for the eight runs at higher temperatures and pressures where the carbon dioxide is at supercritical conditions. From the graphs of carbon dioxide concentration versus time data, breakthrough time of carbon dioxide may be inferred by visual inspection. The coefficient of dispersion of carbon dioxide may be estimated from the convection-dispersion equation as follows.

$$K_l \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (1)$$

where C is the carbon dioxide concentration at location x at time t , K_l is the coefficient of longitudinal dispersion, and v is the interstitial velocity. Eq. 1 may be expressed in dimensionless form as follows.

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D}, \quad (2)$$

where:

$x_D = \frac{x}{L}$, dimensionless distance, where L is length of core,

$t_D = \frac{tv}{L}$, dimensionless time, and

$P_e = \frac{vL}{K_l}$, Peclet number (ratio of convection to dispersion).

Since the carbon dioxide injection inlet is at $x = 0$, then

initial condition: $C = 0$ at $t_D = 0$, $0 < x_D < \infty$;

boundary conditions: $C = 1$ at $x_D = 0$, $t_D > 0$,

$C \rightarrow 0$ as $x_D \rightarrow \infty$, $t_D > 0$.

Solution to Eq. 2 may be shown to be as follows.

$$C = \frac{1}{2} \left\{ \operatorname{erfc} \left(\frac{x_D - t_D}{2\sqrt{t_D / P_e}} \right) + e^{P_e x_D} \operatorname{erfc} \left(\frac{x_D + t_D}{2\sqrt{t_D / P_e}} \right) \right\}, \quad (3)$$

A computer program was written to calculate carbon dioxide concentration per Eq. 3 in which the dispersion coefficient K_l is varied to yield the best agreement between data and the analytical solution. In the program, $\operatorname{erfc}(y)$ is calculated using the following approximation.⁹

$$\operatorname{erfc}(y) = (a_1 z + a_2 z^2 + a_3 z^3 + a_4 z^4 + a_5 z^5) e^{-y^2} \quad (4)$$

where:

$$z = \frac{1}{1 + 0.3275911y}, \quad a_1 = 0.254829592$$

$$a_2 = -0.284496736, \quad a_3 = 1.421413741$$

$$a_4 = -1.453152027, \quad a_5 = 1.061405429$$

Calculated profiles of carbon dioxide concentration versus time are shown as “best fit” lines for each run in **Figs. 3 and 4**. The coefficients of dispersion obtained for each run are shown in **Table 1**. The values are relatively small, ranging from 0.01 to 0.12 cm²/min. As a result of the stable displacement by carbon dioxide, the methane recovery at carbon dioxide breakthrough is high, ranging from 73% to 87% of OGIP.

Breakthrough times. **Figs. 3 and 4** indicate that the breakthrough times of CO₂ vary from 55 min to 170 min. **Fig. 5** shows a typical set of CT scan images indicating that at breakthrough, CO₂ concentration in the core is quite uniform, corroborating analytical results of low dispersion. Breakthrough times appear to increase with pressure for each run temperature (**Fig. 6**), despite the fact that the water syringe pump (displacing the CO₂ in the accumulator) was set to 0.25 ml/min for all runs. This probably means that the CO₂ injection rate varies in each run due to cell pressure variation resulting from continuous adjustment of the backpressure regulator during a run. The actual CO₂ has thus been estimated as follows, using run 9 as an example.

Remaining C₁ vol. (at cell conditions) at CO₂ b/t
= vol. at std. conditions $\times z \times (T/520) \times (14.7/P)$
= 548 ml $\times 0.865 \times (528^\circ\text{R} / 520^\circ\text{R}) \times (14.7 \text{ psia} / 1041.7 \text{ psia})$
= 6.8 ml

Pore vol. = 10.3 ml (dead vol.) + $\pi (2.54/2)^2 \text{ cm}^2$
 $\times 30.48 \text{ cm} \times 0.23$ (porosity from CT scan)
= 45.8 ml

C₁ saturation in cell at CO₂ b/t, $S_g = 6.8 \text{ ml} / 45.8 \text{ ml} = 15\%$

CO₂ P.V. at b/t = P.V. $\times (1 - S_g) = 45.8 \text{ ml} \times (1 - 0.15)$
= 38.9 ml

Ave. CO₂ injection rate = 38.9 ml / 125 min = 0.31 ml/min

Thus, CO₂ b/t time = 38.9 ml / (0.31 ml/min) = 125 min

The calculated CO₂ breakthrough times for all runs are listed in **Table 2** and compared against observed values in **Fig. 7**.

Good agreement is obtained between calculated and observed CO₂ breakthrough times. The saturation of C₁ in the cell at CO₂ breakthrough time, S_g , varies. For runs at 20°C, S_g lies in the range 15%-27% of pore volume; 14%-17% at 40°C; and 12%-14% at 60°C. The results indicate that S_g generally decreases with increase in temperature – i.e. sweep of C₁ increases as CO₂ becomes more supercritical (and thus more dense).⁸ This favorable supercritical property of CO₂ also explains the observed increase of C₁ recovery at CO₂ breakthrough from 73%-85% OGIP at 20°C, to 83%-86% OGIP at 40°C, to 86%-87% OGIP at 60°C. The favorable displacement by CO₂ results in 100% C₁ recovery at the end of each run (**Fig. 8**).

Conclusions and Recommendations

Findings and recommendations arising from this study may be summarized as follows.

1. Displacement of methane by CO₂ – whether CO₂ is a gas, liquid, or a supercritical fluid – appears to be a very efficient process. Dispersion coefficient of CO₂ in methane is relatively low, 0.01- 0.12 cm²/min.
2. The recovery of methane at CO₂ breakthrough time is high, 73%-87% of OGIP. In the field, this could translate into production of hitherto unrecoverable gas reserves – through improving sweep efficiency and reservoir repressurization - from depleted/abandoned gas fields into which supercritical CO₂ is being sequestered. The gas revenue would help defray the cost of CO₂ sequestration.
3. This study has been restricted to one-dimensional horizontal displacement of C₁ by CO₂. In practice, gravity segregation would increase displacement stability and thus help recovery of natural gas during sequestration of CO₂.
4. This study has been performed using a carbonate core. Similar studies using sandstone cores are recommended.
5. In practice, “impurities” such as CO and NO_x are present in flue gas to be sequestered. Effect of these “impurities” on CO₂ displacement efficiency needs to be investigated.

Nomenclature

b/t	=	breakthrough
C	=	concentration of CO ₂ , mole%
K_l	=	coefficient of longitudinal dispersion, cm ² /min
L	=	length of core, cm
OGIP	=	original gas (C ₁)-in-place, std. Liter
P	=	pressure, psia
P_e	=	Peclet number, dimensionless
P.V.	=	pore volume of core plus dead volume, ml
S_g	=	saturation of C ₁ in the core
SL	=	volume in liter at standard conditions
t	=	time, min
T	=	temperature, °R
t_D	=	dimensionless time as defined for Eq. 2
v	=	interstitial velocity, cm/min
x	=	distance from core injection point, cm
x_D	=	dimensionless distance as defined for Eq. 2
z	=	gas compressibility factor, dimensionless

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Table 1 – Summary of experimental runs

Run no.	Temp., °C	Press., psig	Properties of C ₁				C ₁ prod. at CO ₂ b/t		CO ₂ b/t, min	Dispers. coeff., cm ² /min
			P_{pr}	T_{pr}	z	OGIP,SL	SL	% OGIP		
9	20	1027	1.56	1.54	0.865	3.683	3.135	85.1	125	0.010
10	20	2000	3.02	1.54	0.795	7.749	5.660	73.0	160	0.025
14	20	1000	1.52	1.54	0.870	3.579	2.755	77.0	120	0.010
15	20	1001	1.52	1.54	0.870	3.582	2.620	73.1	120	0.010
16	20	2000	3.02	1.54	0.800	7.727	5.950	77.0	150	0.020
17	20	2000	3.02	1.54	0.800	7.727	5.635	72.9	155	0.020
18	20	3000	4.51	1.54	0.810	11.420	9.125	79.9	170	0.021
19	20	3000	4.51	1.54	0.810	11.420	9.185	80.4	170	0.016
20	40	2700	4.06	1.64	0.840	9.283	7.840	84.5	155	0.021
21	60	2700	4.06	1.75	0.880	8.330	7.145	85.8	135	0.030
22	40	2200	3.32	1.64	0.840	7.573	6.280	82.9	130	0.030
23	60	2200	3.32	1.75	0.880	6.795	5.925	87.2	120	0.030
24	40	1700	2.57	1.64	0.860	5.727	4.935	86.2	100	0.070
25	60	1700	2.57	1.75	0.890	5.202	4.515	86.8	90	0.080
26	40	1200	1.82	1.64	0.880	3.965	3.350	84.5	65	0.120
27	60	1200	1.82	1.75	0.910	3.604	3.130	86.8	55	0.060
28	20	500	0.77	1.54	0.930	1.698	1.400	82.4	105	0.040

Table 2 – Estimation of gas saturation and breakthrough time

Run	Remaining C ₁ vol. at CO ₂ b/t, ml		S _g (%)	CO ₂ P.V. at b/t, ml	CO ₂ inj. ml/min	CO ₂ b/t time, min	
	Std. cond.	Cell cond.				Calc.	Actual
9	548	6.8	15	38.9	0.31	126	125
10	2089	12.3	27	33.4	0.21	159	160
14	824	10.6	23	35.3	0.29	122	120
15	962	12.3	27	33.4	0.28	119	120
16	1777	10.5	23	35.3	0.24	147	150
17	2092	12.4	27	33.4	0.22	152	155
18	2295	9.2	20	36.6	0.22	167	170
19	2235	9.0	20	36.6	0.22	167	170
20	1443	7.1	16	38.5	0.23	167	155
21	1185	6.5	14	39.4	0.29	136	135
22	1293	7.8	17	38.0	0.29	131	130
23	870	5.5	12	40.3	0.33	122	120
24	792	6.3	14	39.4	0.39	101	100
25	687	6.1	13	39.8	0.44	91	90
26	615	7.1	16	38.5	0.60	64	65
27	474	6.0	13	39.8	0.72	55	55
28	298	8.0	18	37.6	0.36	104	105

Fig. 1 - Schematic diagram of supercritical carbon dioxide coreflood apparatus.

Fig. 2 - Photograph showing main components of the coreflood apparatus. The Ruska pump (foreground) is used to inject the CO₂ into the coreholder placed in the CT scanner (background).

Fig. 3 – Produced CO₂ concentration versus time for runs at 20°C. Injected CO₂ is in liquid form except for run 28 (gas). Best-fit lines represent analytical solution for the best value of the coefficient of dispersion of carbon dioxide.

Fig. 4 – Produced carbon dioxide concentration versus time for runs at 40°C and 60°C (CO_2 at supercritical conditions). Best-fit lines represent analytical solution for the best value of the coefficient of dispersion of carbon dioxide.

Fig. 5 – Typical CT scan images of core at breakthrough of liquid CO_2 (red/yellow, bright), with residual methane gas in green (dark). The CT scanner was an invaluable tool for determination of core porosity and saturation and in providing insight into the displacement mechanisms.

Fig. 6 – Increase of CO₂ breakthrough time with pressure, indicating improved sweep of C₁ with increasing pressure. Improved sweep may be attributed to CO₂ becoming denser with pressure, providing a greater density contrast at the CO₂-C₁ interface.

Fig. 8 – Practically all of C₁ initially in the core is displaced by CO₂ at the end of each run.

Fig. 7 – Comparison of observed and calculated CO₂ breakthrough times. The good agreement between the two sets of values confirms the accuracy of the core porosity value (0.23) measured with the aid of the CT scanner.

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Effect of Flue Gas Impurities on the Process of Injection and Storage of CO₂ in Depleted Gas Reservoirs

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Abstract

Our previous coreflood experiments - injecting pure CO₂ into carbonate cores - showed that the process is a win-win technology, sequestering CO₂ while recovering a significant amount of hitherto unrecoverable natural gas that could help defray the cost of CO₂ sequestration. In this paper, we report our findings on the effect of “impurities” in flue gas - N₂, O₂, H₂O, SO₂, NO₂, and CO - on the displacement of natural gas during CO₂ sequestration. Coreflood experiments were conducted at 1,500 psig and 70°C, in which a flue gas was injected into a carbonate core containing initially methane. Two types of flue gas were injected: dehydrated flue gas with 13.574 mole % CO₂ (Gas A), and treated flue gas (N₂, O₂ and water removed) with 99.433 mole % CO₂ (Gas B).

Main results of our study to-date are as follows. First, during displacement of methane, the dispersion coefficient increases with concentration of the “impurities”. Gas A exhibits the largest dispersion coefficients, 0.18 - 0.25 cm²/min, compared to 0.13 - 0.15 cm²/min for Gas B, and 0.15 cm²/min for pure CO₂. Second, for all cases, recovery of methane at breakthrough is relatively high, ranging from 86% OGIP for pure CO₂, 74-90% OGIP for Gas B, and 79-81% for Gas A. Lastly, injection of Gas A would sequester the least amount of CO₂ as it contains about 80 mole % nitrogen. From the view point of sequestration, Gas A would be least desirable (though the cheapest separation process). Gas B (flue gas with N₂, O₂ and water removed) appears to be the most desirable as separation cost would probably be cheaper than that for pure CO₂ while natural gas recovery are similar in both cases.

Introduction

One of the foundations of the world economy is the reliability of low cost energy. In 2003, the United States consumed 2.6 kilowatt-hours of energy for each dollar of economic activity

and 86% of that energy came from fossil fuels.¹ CO₂ emissions from burning fossil fuels have been identified as the major contributor to the increase in atmospheric CO₂ levels and associated to global temperature rise. The average concentration of CO₂ in the lower atmosphere has increased by 30% after the industrial revolution to levels up to 370 ppm, and the concentration is increasing steadily at a rate of 1 to 2 ppm per year as shown in Fig. 1.² Estimates of energy consumption, population and economic growth, and greenhouse gas emissions associated with energy use indicate that CO₂ level in the atmosphere will continue to increase unless significant efforts are aimed towards its reduction.^{3,4} Projections by U.S. DOE point to an increase of fossil fuel consumption by 40% over the next 20 years and greenhouse gas emissions by 33% in the United States.²

Worldwide environmental concerns are causing new regulations to come and higher standards to be enforced. Under the Kyoto protocol, developed countries are committed to reduce emissions of greenhouse gases by an average of 5.2% below the 1990 levels by 2008 to 2012.⁵ Under the Rio Treaty, the United States and other 160 countries target to stabilize greenhouse gas concentrations in the atmosphere within a time frame sufficient to allow ecosystems to adapt, to ensure food production and to enable a sustainable economic development.⁶ On November 2003, U.S. DOE proposed General Guidelines for the voluntary reporting of greenhouse gas emissions and emission reductions, scheduled for release in fall 2004. In the future, greenhouse gas emission reporting will be mandatory; hence, a more efficient use of energy and the development of new technologies will be required to meet the challenge of stabilizing CO₂ concentrations in the atmosphere.

Geologic sequestration of CO₂ appears to be a reasonable pathway to stabilization. Fig. 2 summarizes different storage sites for CO₂. The various options must be evaluated for cost, safety, and environmental effects. Our ongoing study is evaluating CO₂ storage in depleted gas reservoirs. The principal motivation for injecting CO₂ in geologic formations has been enhancing hydrocarbon recovery. This is the case of CO₂ injection in depleted oil reservoirs and unmineable coal beds. The first large-scale project specifically aimed at CO₂ underground disposal was started in 1996 by Statoil in the North Sea.^{4,7} Approximately 1x10⁶ tonnes per year of CO₂ from the Sleipner Vest field are separated out of the produced natural gas and injected into the overlying Utsira aquifer. This project demonstrated the feasibility of sequestering CO₂ in

saline aquifers. More recently, a combined EOR and CO₂-sequestration project has been undertaken, in which CO₂ generated at a coal-gasification plant in North Dakota is transported by pipeline to the Weyburn field in Saskatchewan to be injected.⁸ This is the first attempt to sequester CO₂ in an oil reservoir.

CO₂ injection into gas reservoirs has been proposed but not tested. CO₂ could be used for pressure maintenance or for condensate vaporization, but the cost of purchasing CO₂ makes this approach uneconomical in the absence of incentives for CO₂ storage.⁴ Given a depleted natural gas reservoir and a depleted oil reservoir with the same hydrocarbon pore volume, the depleted natural gas reservoir will store significantly more CO₂. This is due to the high compressibility of natural gas (approximately 30 times more compressible than oil and water), and the fact that the ultimate hydrocarbon recovery in a gas reservoir is typically about twice as large as that in an oil reservoir.⁹ In addition to the larger storage capacity of depleted gas reservoirs, another advantage is that all CO₂ - resulting from the combustion of natural gas produced from the reservoir - could be stored in the same reservoir, with additional storage capacity. For each mole of C₁ combusted, one mole of CO₂ is produced, and the molar volume of CO₂ is smaller than that of C₁ at the same field temperature and pressure. Therefore, CO₂ injection could be replaced for a mixture of CO₂, N₂ and impurities resulting from the partial separation of flue gas.⁴

Unfortunately, CO₂ sources are rarely pure; the most likely CO₂ source is usually a stream extracted from the flue gas of a power plant.¹⁰ Flue-gas composition from typical electric power generation plants depends on the fuel type (bituminous coal, natural gas, wet feed of slurry coal), amount of excess air, and power generation scheme (boiler, steam, and gas turbine types). A typical flue-gas composition of an electric power plant based on a combustion calculation for a Powder River Basin (PRB) coal, in a 500 MW plant with 20% excess air is shown in **Table 1**. The main components of flue gas are N₂ (71 mole %), CO₂ (12 mole %), H₂O (12 mole %), O₂ (5 mole %), and also impurities such as SO₂, NO₂, and CO.* Flue gas may be treated in order to obtain a stream rich in CO₂ for sequestration purposes.

According to the International Environmental Agency (IEA), the total cost of CO₂ capture and storage ranges from \$50 to \$100/tonne of CO₂. This cost can be split into cost of capture, transportation and storage. Current estimates for large-scale capture systems (including CO₂ pressurization, excluding transportation and storage) are \$25 to \$50/tonne of CO₂. Transportation costs are approximately \$1 to \$5/tonne of CO₂ per 100 km, and storage costs are \$1 to \$2/tonne of CO₂.^{11,12} Unquestionably, the cost of separating CO₂ out of flue gas is significantly higher than that of transporting and injecting CO₂ in reservoirs.¹³

Due to the high cost of CO₂ capture, the purpose of this study is to understand and model the displacement of natural gas by flue gas and compare it with the displacement by pure CO₂. Results will determine if flue gas displacement

efficiency will enhance gas recovery, and if flue gas sequestration in depleted gas reservoirs is an alternative for reducing CO₂ levels in the atmosphere.

Previous coreflood experiments injecting pure CO₂ into carbonate rocks showed that the process is a win-win technology, sequestering CO₂ while recovering a significant amount of hitherto unrecoverable natural gas that could help defray the cost of CO₂ sequestration.^{9,14,15} A summary of the experimental results is presented in **Table 2**, and will be used as a reference to compare flue gas displacement efficiency reported in this paper with that of pure CO₂.

Experimental Apparatus and Procedure

Two types of flue gas were used in our experiments: dehydrated flue gas with 13.574 mole % CO₂ (Gas A), and treated flue gas with 99.433 mole % CO₂ (Gas B) as presented in **Table 1**. The phase envelopes of the two gases were obtained from the company *Specialty Gas Products* that provided these gases to our laboratory, and are presented in **Fig. 3**. No critical point was observed for Gas A.

The equipment used in our experiments consists of four main components: the injection system, coreflood cell, Universal System HD 350 x-ray CT scanner, and the production and data recording system. **Fig. 4** shows the experimental apparatus, which is briefly described in the following.

The injection system consists of two sets of one-liter *Temco* accumulators. One is connected to a *Micromeritics* 760 HPLC pump to displace the CO₂ gas mixture into the cell, and the other one is connected to a Ruska pump to displace methane into the cell. After introducing the gas into the accumulator, the gas pressure is slowly increased to the desired level by injecting water below the piston in the accumulator.

The coreflood cell (**Fig. 5**), measuring 21 in. (53.3 cm) long with an OD of 3.75 in. (9.53 cm) and wall thickness of 0.75 in. (1.91 cm), is constructed of aluminum (transparent to x-ray CT scanning), and is machined out of a solid cylindrical block of aluminum 7075-T6 to withstand the high temperature and pressure. A carbonate core measuring 1 ft (30.5 cm) long and 1 in. (2.54 cm) in diameter is inserted into a viton Hassler sleeve with both ends secured to plungers in the cell. The cell is placed inside a *Precision* mechanical convection incubator for an accurate temperature control. The system is pressurized with nitrogen to test for leaks and then displaced to methane.

The Universal System HD 350 x-ray CT scanner provides precise determination of core porosity and fluid saturation. CT scanner performs with a speed up to 1 rev/sec and resolution of 6 to 9 line pairs/cm.

Produced gas volume and composition are measured using a wet test meter and a *Hewlett Packard* 5890 Series II gas chromatograph with a *Hewlett Packard* 3396A integrator, respectively. The cell outlet pressure is set to the desired level with the aid of a *Temco* backpressure regulator. Pressure and temperature readings are recorded in 30-second intervals using a *Hewlett Packard* 34970A data logger in conjunction with a personal computer.

A typical experiment is conducted as follows. With the backpressure regulator closed, the coreflood cell is slowly charged up with methane from the accumulator until the

* Electronic communication with D. Chuck, EPRI-Continuous and Predictive Emissions Monitoring Group (22 July 2003).

desired pressure is reached. While injecting methane into the cell, high-temperature *Mobil DTE 26* hydraulic oil is injected into the Hassler sleeve-inner cell wall annulus to maintain an overburden pressure differential of about 300 psi. The CO₂ gas mixture is then injected into the cell at a constant rate of 0.25 ml/min. A run is terminated when the methane composition in the produced gas is negligible.

Experimental Results

A total of 5 runs at 1,500 psig and 70°C are reported in **Table 3**. Three runs injecting Gas A (one of them with initial water saturation of 20% in the core), and two runs injecting Gas B with zero initial core water saturation.

Prior to every run, core porosity was determined using the CT-scanner. An average porosity of 21% was calculated using the *Voxcalc* software as presented in **Fig. 6**. A 3D porosity profile was created using *3D-Petro* software to better understand the porosity distribution inside the core (**Fig. 7**). Porosity was used to calculate the pore volume, and consequently the OGIP with Eq.1 and gas recovery at breakthrough for every run.

$$OGIP = \frac{V_p(1 - S_{wi})}{1,000 B_g} \quad (1)$$

The coefficients of dispersion of gases A and B were estimated using the convection-dispersion equation as follows:

$$K_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (2)$$

where C is the concentration of gases A or B at location x at time t , K_L is the coefficient of longitudinal dispersion, and v is the interstitial velocity. **Eq. 2** may be expressed in dimensionless form as follows.

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D}, \quad (3)$$

where:

$x_D = \frac{x}{L}$, dimensionless distance, where L is length of core,

$t_D = \frac{tv}{L}$, dimensionless time, and

$P_e = \frac{vL}{K_L}$, Peclet number (ratio of convection to dispersion).

Since the carbon dioxide injection inlet is at $x = 0$, then

Initial condition: $C = 1$ at $t_D = 0$,

Boundary conditions: $C = 1$ at $x_D = 0$, $t_D > 0$

$C \rightarrow 0$ as $x_D \rightarrow \infty$, $t_D > 0$

Solution to **Eq. 3** is presented below.

$$C = \frac{1}{2} \left\{ \operatorname{erfc} \left(\frac{x_D - t_D}{2\sqrt{t_D / P_e}} \right) + e^{P_e x_D} \operatorname{erfc} \left(\frac{x_D + t_D}{2\sqrt{t_D / P_e}} \right) \right\}, \quad (4)$$

The longitudinal dispersion coefficient was varied to yield the best agreement between experimental data and analytical solution. Calculated profiles of concentration of gases A and B are presented as “best fit” in **Fig. 8**. The coefficients of dispersion obtained for each run are presented in **Table 3**. These values are, in general, relatively small, ranging from 0.13 to 0.25 cm²/min.

Comparing our results to those presented in Table 2 corresponding to experiments with pure CO₂, the following observations can be pointed out. First, the dispersion coefficient of pure CO₂ at 70°C and 1,500 psig, estimated with linear interpolation from the values presented in table 2 is approximately 0.15 cm²/min. This value is in good agreement with the dispersion coefficient of Gas B, 0.13 to 0.15 cm²/min, which contains 99.433 mole % CO₂. Displacement efficiency of Gas B and pure CO₂ are very similar.

Second, the dispersion coefficients for Gas A, 0.18 to 0.25 cm²/min, is consistently higher than that for pure CO₂ and for Gas B. This result can be better understood by looking at the densities and viscosities of pure CO₂ and Gas A, as well as the phase envelopes at the conditions of the experiment. **Fig. 9** and **Fig. 10** show densities and viscosities estimated with the software *PVTsim* version 13.0.2. Pure CO₂ exhibits higher density and higher viscosity than Gas A. The phase behavior of pure CO₂ is more liquid-like than Gas A, and thus is more efficient displacing methane in the experiment. In addition, the phase envelope of Gas A (**Fig. 3**) does not exhibit a critical point, indicating that at 70°C and 1,500 psig the fluid is in vapor phase, different from CO₂ that is in supercritical phase.

Breakthrough times vary from 102.5 to 140 min for runs with zero initial water saturation, despite the fact that the water HPLC pump (displacing gases A and B in the accumulator) was set constant to 0.25 ml/min for all runs. This is probably due to cell pressure variations resulting from continuous adjustment of the backpressure regulator during each run. For the run with 20% initial water saturation, the breakthrough time was significantly lower, 88.5 min, due to the reduction in hydrocarbon por volume compared to zero initial water saturation.

Recovery of methane is lower for Gas A (79-81% OGIP) than for Gas B (88-90% OGIP) and pure CO₂ (ca. 86% OGIP). These results indicate that Gas A exhibits the poorest displacement efficiency, in line with the fact that its longitudinal dispersion coefficient is the largest.

Conclusions

Main conclusions arising from our study to-date may be summarized as follows.

1. Displacement of methane by Gas A (dehydrated flue gas with CO₂ concentration of 13.574 mole %) at the conditions studied exhibits larger dispersion coefficients, 0.18-0.25 cm²/min, than displacement by pure CO₂, ca. 0.15 cm²/min.
2. Impurities appear to have a negligible effect in the displacement of methane by Gas B (CO₂ concentration of

99.433 mole %). Dispersion coefficient of Gas B is 0.13-0.15 cm²/min.

3. Recovery of methane at breakthrough is higher for Gas B (88-90% OGIP) and pure CO₂ (86% OGIP) than for Gas A (79-81% OGIP). Gas recovery from injection of Gas A is lowest due to the large concentration of N₂ in the gas, resulting in the largest dispersion coefficient of the three injection gases studied.
4. It appears therefore that injection of CO₂ with approximately less than 1 mole % “impurities” would result in practically the same volume of CO₂ being sequestered as injecting pure CO₂. Gas B would have the advantage of being a cheaper separation process compared to pure CO₂ as not all the “impurities” are removed in the case of Gas B.
5. Although separation of CO₂ out of flue gas is a costly process, it appears this is necessary to maximize CO₂ sequestration volume, reduce compression costs of N₂ (approximately 80% of the stream), improve sweep efficiency and gas recovery in the reservoir.

Nomenclature

B_g = formation volume factor of gas (C₁), vol/vol
 C = concentration of Gas A or Gas B, mole%
 K_L = coefficient of longitudinal dispersion, cm²/min
 $OGIP$ = original gas (C₁)-in-place, std. Liter
 P = pressure, psi
 P_e = Peclet number, dimensionless
 S_{wi} = initial water saturation, fraction
 t = time, min
 t_D = dimensionless time, defined in Eq. 3
 T = temperature, °C
 V_p = pore volume, cm³
 v = interstitial velocity, cm/min
 x = distance from core injection point, cm
 x_D = dimensionless distance, defined in Eq. 3

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Fig. 1 – Daily average concentration of CO₂ in the atmosphere during the last 30 Years from the Mauna Loa Observatory in Hawaii, NOAA.³

Fig. 2 – Storage sites for CO₂ in geologic formations and the deep sea.

Table 1 – Composition of flue gas from an electric power generation plant burning Powder River Basin coal. Gas A results from dehydrating flue gas and Gas B results from removing N₂, O₂ and water. Both types of flue gas are used in the displacement experiments.

Component	Composition, mole %		
	Flue Gas	Gas A	Gas B
Nitrogen, N ₂	70.726	80.370	---
Water, H ₂ O	12.000	---	---
Carbon dioxide, CO ₂	11.945	13.574	99.433
Oxygen, O ₂	5.258	5.975	---
Sulfur dioxide, SO ₂	0.045	0.051	0.368
Nitrogen oxide, NO ₂	0.016	0.018	0.129
Carbon monoxide, CO	0.010	0.012	0.070
Total	100.000	100.000	100.000

Table 2 – Experimental data reported by Mamora and Seo using supercritical CO₂ in coreflood experiments.^{9,14}

P, psig	T, °C	S_{wi}	OGIP, std L	C ₁ recovery at breakthrough, %OGIP	Breakthrough, min	K_L , cm ² /min
1,200	60	0.0	3.604	86.80%	55.0	0.06
1,200	80	0.0	2.850	84.60%	30.0	0.30
1,700	60	0.0	5.202	86.80%	90.0	0.08
1,700	80	0.0	4.045	83.90%	60.0	0.17
1,700	80	0.2	3.739	61.80%	55.0	0.15

Fig. 3 – Phase envelopes of the two gases injected (Gas A and Gas B) in coreflood experiments compared to the vapor pressure line for pure CO₂.

Fig. 4 – Photograph showing main components of the experimental apparatus.

Fig. 5 – Longitudinal section of coreflood cell with maximum operating conditions of 5,000 psig and 200°F. Scale approximately 1: 3.

Fig. 6 – CT scan images of porosity profile using *Voxcalc* software. The core average porosity is 21% as observed in the scale above.

Fig. 7 – Isosurface images of 3D porosity profiles using *Petro3D*. These images are very helpful to understand the porosity distribution in the core.

Table 3 – Summary of coreflood experiments at 1,500 psig and 70°C. Gas A (13.574% CO₂) shows higher longitudinal dispersion coefficients and lower C₁ recovery at breakthrough than Gas B (99.433% CO₂).

Injection gas	S_{wi}	OGIP, std L	C ₁ recovery at breakthrough, %OGIP	Breakthrough, min	K_{Lj} , cm ² /min
Gas A	0.0	3.967	80.66%	121.5	0.18
	0.0	4.027	79.46%	102.5	0.19
	0.2	3.227	74.36%	88.5	0.25
Gas B	0.0	3.982	89.90%	112	0.15
	0.0	3.060	88.16%	140	0.13

Fig. 8 – Concentration of the produced gas versus time for runs at 1,500 psig and 70°C. Best-fit lines represent analytical solution for the best value of the coefficient of longitudinal dispersion. Earlier breakthrough time for Gas A when the initial water saturation is 20%.

Fig. 9 – Density diagram with respect to pressure at 160°C as calculated using *PVTSim* 13.0.2.

Fig. 10 - Viscosity diagram with respect to pressure at 160°C as calculated using *PVTSim* 3.0.2. Viscosity of CO₂ is higher than that of Gas A for pressures higher than 1,000 psia.

Initial responses of carbonate-rich shelf sediments to rising atmospheric $p\text{CO}_2$ and “ocean acidification”: Role of high Mg-calcites

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Abstract

Carbonate-rich sediments at shoal to shelf depths (<200 m) represent a major CaCO_3 reservoir that can rapidly react to the decreasing saturation state of seawater with respect to carbonate minerals, produced by the increasing partial pressure of atmospheric carbon dioxide ($p\text{CO}_2$) and “acidification” of ocean waters. Aragonite is usually the most abundant carbonate mineral in these sediments. However, the second most abundant (typically ~24 wt%) carbonate mineral is high Mg-calcite (Mg-calcite) whose solubility can exceed that of aragonite making it the “first responder” to the decreasing saturation state of seawater. For the naturally occurring biogenic Mg-calcites, dissolution experiments have been used to predict their “stoichiometric solubilities” as a function of mol% MgCO_3 . The only valid relationship that one can provisionally use for the metastable stabilities for Mg-calcite based on composition is that for the synthetically produced phases where metastable equilibrium has been achieved from both under- and over-saturation. Biogenic Mg-calcites exhibit a large offset in solubility from that of abiotic Mg-calcite and can also exhibit a wide range of solubilities for biogenic Mg-calcites of similar Mg content. This indicates that factors other than the Mg content can influence the solubility of these mineral phases. Thus, it is necessary to turn to observations of natural sediments where changes in the saturation state of surrounding waters occur in order to determine their likely responses to the changing saturation state in upper oceanic waters brought on by increasing $p\text{CO}_2$. In the present study, we investigate the responses of Mg-calcites to rising $p\text{CO}_2$ and “ocean acidification” by means of a simple numerical model based on the experimental range of biogenic Mg-calcite solubilities as a function of Mg content in order to bracket the behavior of the most abundant Mg-calcite phases in the natural environment. In addition, observational data from Bermuda and the Great Bahama Bank are also presented in order to project future responses of these minerals. The numerical simulations suggest that Mg-calcite minerals will respond to rising $p\text{CO}_2$ by sequential dissolution according to mineral stability, progressively leading to removal of the more soluble phases until the least soluble phases remain. These results are confirmed by laboratory experiments and observations from Bermuda. As a consequence of continuous increases in atmospheric CO_2 from burning of fossil fuels, the average composition of contemporary carbonate sediments could change, i.e., the average Mg content in the sediments may slowly decrease. Furthermore, evidence from the Great Bahama Bank indicates that the amount of abiotic carbonate production is likely to decline as $p\text{CO}_2$ continues to rise.

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1. Introduction

The partial pressure of carbon dioxide ($p\text{CO}_2$) in the atmosphere is rising at an increasing rate due to human activities such as burning of fossil fuels. This increase in

atmospheric CO_2 would be even more rapid if the global ocean were not capable of relatively rapidly acting as a sink for currently about half the “excess” CO_2 that has been produced by fossil fuel combustion. As the rate of CO_2 emissions continues to rise, and in turn the oceans take up larger amounts of CO_2 , there also will be increasing impacts on the chemistry of the oceans and marine life. Among the most important of these impacts on seawater chemistry will be the lowering of the pH and saturation

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state of seawater with respect to calcium carbonate minerals, generally referred to as the process of “acidification” of ocean waters (e.g., Kleypas et al., 1999, 2006; Andersson et al., 2005; Orr et al., 2005).

Consequently, considerable attention has been focused on the problem of declining surface seawater carbonate mineral saturation state due to past and future rising atmospheric CO₂ concentrations and the effects on marine calcifying organisms. It has been shown in experimental situations for both single calcifying species of corals, foraminifera, coccolithophores, and coralline algae and carbonate communities that as seawater carbonate saturation decreases, the rate of calcification decreases (see for example Gattuso et al., 1999; Riebesell et al., 2000; Langdon et al., 2000; Orr et al., 2005). These results, along with the predicted rising temperatures of the future and other stresses, suggest the potential of devastating effects on coral reef and other carbonate ecosystems (Kleypas et al., 2006), including those currently exposed to cold waters – the “cold-water” carbonates (e.g., Alexandersson, 1979; James and Clarke, 1997). Our knowledge of the effects of ocean acidification on the Mg-calcite calcifiers is limited because of the problems involving the basic thermodynamic and kinetic properties of these phases. For the naturally occurring biogenic phases, only a kinetic “equilibrium”, expressed as an ion activity product (IAP) mainly obtained from the extrapolation of data acquired in dissolution experiments, has formed the foundation for the “solubilities” of these phases.

In addition to reducing biogenic marine carbonate mineral production, the lowered saturation state of seawater will lead to an increase in carbonate mineral dissolution. In fact, the dissolution of carbonate minerals will play an increasing important role in the future in modifying changes to ocean chemistry and the ability of the oceans to take up atmospheric CO₂ (e.g., Garrels and Mackenzie, 1980; Andersson et al., 2003, 2005). Simply put, biogenic carbonate minerals may act as the ocean’s “anti-acid tablet” via the schematic reaction that increases the total alkalinity of seawater:

In considering this reaction, it is important to note that, rather counter intuitively, precipitation of calcium carbonate raises $p\text{CO}_2$, whereas its dissolution lowers it (e.g., Smith, 1985; Frankignoul et al., 1994; Lerman and Mackenzie, 2005).

Biogenic high (generally taken as >3–4 mol% MgCO₃; Reeder, 1983; Mackenzie et al., 1983) Mg-calcites have been found to exceed the solubility of aragonite at approximately 12 mol% MgCO₃ (e.g., Bischoff et al., 1983, 1987; Walter and Morse, 1984). In tropical and subtropical shoal and shelf carbonate-rich sediments, most Mg-calcites have >12 mol% MgCO₃ (Chave, 1954), and thus are presumably the most soluble metastable carbonate minerals in contact with relatively shallow ocean water. They have consequently been widely considered to likely be the ocean’s “first

responders” to a falling saturation state associated with increasing atmospheric $p\text{CO}_2$.

This paper examines the several major issues that contribute to the complexity, controversy, and mysteries still surrounding the solubility of Mg-calcites and if indeed the concept of thermodynamic solubility is even meaningful for this group of carbonate minerals. In doing so, we caution that this examination is definitely not intended as a comprehensive review of the large number of papers that have been written regarding Mg-calcites (see e.g., Mackenzie et al., 1983; Morse and Mackenzie, 1990). We then use the Mg-calcite solubility discussion to form the foundation for discussion of the chemistry of the shoal-water CO₂–carbonic acid–carbonate system and ocean acidification in the past and future, using a simple numerical model, laboratory experiments, and observations from what are reasonably representative carbonate-rich sedimentary environments on the Great Bahama Bank and the Bermuda Platform, where we and our associates have been carrying out research on the interactions between sedimentary carbonates and the waters of these areas for decades.

2. Mg-calcite solubility and related chemistry

2.1. General considerations

Calcite occurs in the marine environment with a wide variety of coprecipitated cationic and anionic components. Most of these components are generally found only at minor-to-trace concentrations (<1 mol%) in calcite and generally exert minor influences on the chemical behavior of the bulk mineral, such as its solubility, reaction kinetics, and surface chemistry. An important exception is Mg²⁺ which is found to occur in both biogenic and abiotic marine calcites over a wide range of concentrations, typically up to about 20 mol% MgCO₃ (Fig. 1). Pelagic biogenic calcite, from organisms such as coccolithophores and foraminifera, has <1 mol% MgCO₃, whereas the calcite in tropical and subtropical carbonate-rich sediments typically averages about 13–15 mol% MgCO₃ (Garrels and Wollast, 1978; Agegian and Mackenzie, 1989), with the magnesium content of specific taxa contributing to the sediments generally decreasing with decreasing sea surface temperature polewards (Chave, 1954). It has become customary to divide marine calcites into low and high Mg-calcites based on a boundary of a few mol% MgCO₃ (~3–4 mol% MgCO₃), which is representative of the least soluble Mg-calcite phase (e.g., Reeder, 1983; Mackenzie et al., 1983). High Mg-calcites are often denoted simply as Mg-calcite.

It is the general practice, as was done in the preceding paragraph, to consider the Mg(II) in Mg-calcites to be present as MgCO₃. However, the mineral magnesite (MgCO₃) does not form at near Earth surface temperatures from aqueous solutions except in highly saline solutions (e.g., Lippmann, 1973). Hydrated forms of MgCO₃

Fig. 1. The relative frequencies of occurrence of calcites containing different mol% MgCO₃ for marine cements (open bars; Morse and Mackenzie, 1990) and mid-depth bank carbonate sands (solid bars; Alegian and Mackenzie, 1989).

precipitate from solution, such as nesquehonite (MgCO₃ · 3H₂O), hydromagnesite (Mg₄(CO₃)₃(OH)₂ · 3H₂O), and artinite (Mg₂CO₃(OH)₂ · 3H₂O). The many possible end members for the Mg-calcite solid solutions, in addition to the above minerals, include ordered phases, such as dolomite, proto-dolomite, and huntite (CaMg₃(CO₃)₄). This lack of a critical end member has led to extensive theoretical controversy (e.g., Busenberg and Plummer, 1989; Lippmann, 1991; Glynn and Reardon, 1992a,b; Königsberger and Gamsjäger, 1992; Arvidson and Mackenzie, 1999).

The studies of Bischoff et al. (1983, 1985, 1987) and Gaffey (1988) indicated that biogenic calcites, even with low Mg(II) content, contain variable amounts of water and it is possible that H₂O, and perhaps OH⁻, should be considered additional solid-phase components in biogenic calcites. Raman spectra studies (Bischoff et al., 1985) and dissolution enthalpy measurements (Bischoff, 1998) of Mg-calcites indicate that biogenic Mg-calcites have more carbonate and cation disordering than synthetic Mg-calcites. A further complication is that Mg-calcites derived from at least some organisms, such as red algae (e.g., *Goniolithon*), contain brucite (Mg(OH)₂) (Moberly, 1968) and, consequently, their Mg content determined by X-ray diffraction can indicate a substantially lower mol% MgCO₃ than that measured by direct chemical analysis (see Walter and Morse, 1984, for discussion). In their extensive review of Mg-calcite chemistry, Morse and Mackenzie (1990; also see Mackenzie et al., 1983; Busenberg and Plummer, 1989), came to the general conclusion that the physical and chemical heterogeneities found in biogenic Mg-calcites *a priori* exclude them from being good materials for the study of the thermochemical properties of Mg-calcite.

2.2. Mg-calcite solubility

2.2.1. The kinetic experimental method and the stoichiometric solubility product

With the exception of the precipitation experiments of Mucci and Morse (1984), Mg-calcite solubility has been measured by a rather unconventional technique. This technique is not based on obtaining a true equilibration between a given Mg-calcite and a solution, which is rarely or probably never attained in the natural environment or under laboratory conditions. It is based on an extrapolation of the concentrations of dissolved components of the dissolution to an ion activity product (IAP) calculated at infinite time at which the rate of change of the concentrations of the components approaches zero (see Garrels et al., 1960; Plummer and Mackenzie, 1974 for methodology). A particularly vexing problem for Mg-calcite solubility studies in dilute solutions is that the solution will become supersaturated with respect to a calcite phase with low Mg-content, which will start to precipitate, while the high Mg-calcite continues to dissolve (Plummer and Mackenzie, 1974; Fig. 2). To overcome this problem, data from the congruent step of the reaction is extrapolated to infinite time, making the assumption that this represents equilibrium for the solid solution. The validity of the method has been intensely debated because it considers congruent dissolution of Mg-calcite as a one-component phase or a phase of constant composition while in fact it is at least a two-component phase forming a partial solid solution series (Thorstenon and Plummer, 1977; Lafon, 1978; Garrels and Wollast, 1978; Morse and Mackenzie, 1990). The extrapolation of experimental data contains many other potential theoretical and practical pitfalls that increase with the distance between the experimental solution compositions reached and the extrapolated equilibrium solution compositions (e.g., Lafon, 1978; Garrels and Wollast, 1978; also see recent discussion of “kinetic solubility” by Gledhill and Morse, in press).

Fig. 2. The evolution of Ca²⁺ and Mg²⁺ during the dissolution of *Amphiroa rigida* in pure water. S1, congruent dissolution; S2, incongruent dissolution; S3, less Mg-rich calcite starts to precipitate while *Amphiroa rigida* continues to dissolve. (After Plummer and Mackenzie, 1974.)

Although other formulations have been proposed, the generally used convention for expressing the solubility of Mg-calcites containing a mole fraction x of Mg-carbonate ($\text{Mg}_x\text{Ca}_{1-x}\text{CO}_3$) is to use a *stoichiometric solubility product* $K_{\text{Mg-cal}}$ that is defined (Thorstenson and Plummer, 1977) as (a_i is activity of species i ; note the more common usage of the term *stoichiometric solubility product* uses concentrations not activities and unfortunately some authors compare these with the IAP values):

$$K_{\text{Mg-cal}} = a_{\text{Mg}^{2+}}^x a_{\text{Ca}^{2+}}^{1-x} a_{\text{CO}_3^{2-}} \quad (2)$$

A major problem is that although this approach fixes the cation activity product (P_x ; Eq. (3)) to a constant value that depends directly on the solubility product to carbonate ion activity ratio, the cation activity ratio (R_{cat} , Eq. (4)) is not fixed for a given value of P_x , but will vary as a function of either calcium activity (Eq. (4)) or magnesium activity.

$$P_x = a_{\text{Mg}^{2+}}^x a_{\text{Ca}^{2+}}^{1-x} = \frac{K_{\text{Mg-cal}}}{a_{\text{CO}_3^{2-}}} \quad (3)$$

$$R_{\text{cat}} = \frac{a_{\text{Mg}^{2+}}}{a_{\text{Ca}^{2+}}} \neq \text{constant} = \left(\frac{P_x}{a_{\text{Ca}^{2+}}} \right)^{1/x} \quad (4)$$

This leads to the impossible situation where a solid, with a fixed cation ratio x , can be in equilibrium with solutions with widely ranging values of R_{cat} that depend on the calcium, or magnesium, and carbonate ion activities. This clearly violates the concept of microscopic reversibility and is a fundamental problem with the use of stoichiometric solubility products to estimate the saturation state of waters with respect to Mg-calcites, which cannot be in exchange equilibrium with the solution (see Morse and Mackenzie, 1990, for discussion). To put this another way, for a given set of temperature, pressure, and solution composition conditions, only a single value of the MgCO_3 content of calcite can be in equilibrium with a solution of a given magnesium to calcium ion activity ratio. Based on numerous precipitation experiments, in seawater where the magnesium to calcium activity ratio is ~ 5 , the equilibrium mol% MgCO_3 in calcite is about 8 ± 1 (e.g., Berner, 1978; Mucci and Morse, 1984; Morse and Mucci, 1984; Mucci et al., 1985; Zhong and Mucci, 1989; Hartley and Mucci, 1996; Ohde et al., 2005). Despite the fact that seawater carbonate cements form generally in compositionally modified seawater, this clearly contrasts with the dominant Mg-calcite cement composition of ~ 12 – 13 mol% MgCO_3 (Garrels and Wollast, 1978; Videtich, 1985; Fig. 1), which raises a serious question whether or not they are formed by completely abiotic processes, as is generally presumed.

2.2.2. Observed apparent Mg-calcite solubilities

Morse and Mackenzie (1990, see their Fig. 3.7) summarized the studies of Mg-calcite solubility. They divided the results into three major categories: (1) the early results of Plummer and Mackenzie (1974), as revised by Thorstenson and Plummer (1977), for a variety of biogenic Mg-calcites which gave by far the highest values for Mg-calcite solubility

and are probably the most often quoted values in the literature; (2) the “best fit” biogenic Mg-calcite solubilities, of which here we will use the results of Bischoff et al. (1987) and Walter and Morse (1984); and (3) synthetic Mg-calcites which were based on the results of Bischoff et al. (1987) and Mucci and Morse (1984). Since the summary by Morse and Mackenzie (1990), Busenberg and Plummer (1989) reexamined the stability of a wide range of natural inorganic, biogenic, and synthetic Mg-calcite minerals. Based on their results, magnesian calcite solid-solutions were separated into two groups according to their stoichiometric solubilities. These conform to categories (2) and (3) mentioned above and confirm the previous stoichiometric solubility results of Bischoff et al. (1987), Walter and Morse (1984), and Mucci and Morse (1984). In this part of the paper dealing with Mg-calcite solubility, we will use the data for these two categories of Mg-calcite solubilities (Fig. 3), which Bischoff et al. (1987) felt were the best Mg-calcite solubility data.

The linear least squares fit for the abiotic Mg-calcite solubility as a function of mol fraction MgCO_3 (x) is given in Eq. (5). This relationship for biotic Mg-calcites is given in Eq. (6) for all data, and in Eq. (7), the data point that falls far off the linear least squares line with the arrow next to it (Fig. 3) has been excluded. Excluding this data point increases the slope from 7.1×10^{-3} to 8.9×10^{-3} , making the solubility more MgCO_3 concentration dependent. It also significantly increases r^2 from 0.31 to 0.71. The slope of the abiotic line (Fig. 3) is similar with a value of 8.6×10^{-3} and has an r^2 value of 0.87. However, the extrapolated values of $-\log \text{IAP}$ for pure calcite (0 mol% MgCO_3) are quite different for biotic and abiotic Mg-calcites at 8.35 and 8.52, respectively. The extrapolated abiotic value is very close to

Fig. 3. Solubilities of biogenic (solid symbols) and synthetic (open symbols) Mg-calcites versus mol% MgCO_3 . Lines are linear least square fits through the data sets. The data point with the arrow next to it was excluded in making the biogenic fit. Grey lines are for the solubilities of calcite and aragonite. Squares are from Bischoff et al. (1987); solid circle from Walter and Morse (1984); and open circles from Mucci and Morse (1984).

the accepted value for the solubility of pure calcite (8.48), and thus to some extent confirms the validity of the abiotic IAP versus Mg content curve. It should be noted that we did not include the solubility of [Walter and Morse \(1984\)](#) for the red algae *Goniolithon* that, as previously discussed, contains brucite. If the X-ray-based value of 18 mol% MgCO₃ were used, its solubility would plot about 0.25 – log IAP units (7.95) above the line for biogenic calcites.

$$-\log \text{IAP} = 8.52 - (8.6 \times 10^{-3})x \quad (5)$$

$$-\log \text{IAP} = 8.35 - (7.1 \times 10^{-3})x \quad (6)$$

$$-\log \text{IAP} = 8.35 - (8.9 \times 10^{-3})x \quad (7)$$

There are several noteworthy observations to be made from this treatment of Mg-calcite solubility. The first is that the results for the abiotic calcite solubility variation with mol% MgCO₃ are in excellent agreement. This is true even though the solubilities were obtained both from supersaturation and undersaturation. The observation that the hydrothermally prepared material was in good agreement with the Mg-calcite precipitates, from room temperature solutions, indicates that possible hydration of MgCO₃ and coprecipitation of ions such as sulfate and sodium did not produce measurable influences on solubility (see also [Bischoff et al., 1987](#); [Busenberg and Plummer, 1989](#)) and, as noted above, the intercept for pure calcite solubility was also in close agreement with the thermodynamic solubility of calcite. The projected change in solubility with increasing MgCO₃ content is modest, as recognized by [Bischoff et al. \(1987\)](#), and results in even a 20 mol% MgCO₃ synthetic Mg-calcite being less soluble than aragonite ([Fig. 3](#)). Consequently, if common marine high Mg-calcite cements of ~12–13 mol% MgCO₃ were indeed compositionally pure and structurally well ordered abiotic precipitates, they should be less soluble than aragonite.

The results for the biogenic Mg-calcites are considerably more perplexing. Although the change in solubility with increasing MgCO₃ content is modest and similar to that for abiotic Mg-calcites, there is a substantial offset between the solubilities that is reflected in the intercept for pure calcite being relatively close to that for aragonite solubility rather than that of calcite and about equal to the value for a 20 mol% MgCO₃ abiotic Mg-calcite. Consequently, it appears that the influences on the solubility of biogenic calcites with little-to-no MgCO₃ of carbonate anion and cation disorder and containing H₂O, OH[–], SO₄^{2–}, HCO₃[–] and perhaps other ions are similar to the influence of major concentrations of MgCO₃ on abiotic calcite solubility ([Busenberg and Plummer, 1989](#)).

A further concern is that the range of biogenic calcite solubilities, at about 12–15 mol% MgCO₃, is larger than the whole predicted influence of MgCO₃ from 0 to 20 mol% MgCO₃. The situation is even much worse if the solubility for the red algae *Goniolithon* were to be included. These results clearly illustrate that, for biogenic high and low Mg-calcites, MgCO₃ content could be a very poor predictor of solubility, which instead may be dominated by organism-

specific factors that are not readily quantified ([Busenberg and Plummer, 1989](#)). Based on the biogenic solubility data included in the current evaluation, it appears that about the best we can say for the solubility of biogenic high Mg-calcites, in the dominant composition range of about 12–16 mol% MgCO₃, is that most are only slightly (~20%) more soluble than aragonite. This is considerably different from the widely used high Mg-calcite solubility value from the early work of [Plummer and Mackenzie \(1974\)](#) who obtained a solubility of about five times (500%) that of aragonite for Mg-calcites in this compositional range. According to [Bischoff et al. \(1993\)](#), the Plummer and Mackenzie solubilities are most representative of the behavior of Mg-calcites in natural environments because the materials used in these authors' experiments received minimal treatment and preparation prior to evaluating their stabilities. In contrast, the biogenic materials used in the experiments represented by the biogenic "best fit" solubilities were cleaned and annealed before evaluating their stabilities, yielding lower solubilities relative to their untreated counterparts ([Walter and Morse, 1984](#); [Bischoff et al., 1987, 1993](#)). It is not certain which one of these solubilities most accurately conform to Mg-calcite solid solutions in the natural environment. It is likely that the solubility of biogenic Mg-calcite phases viewed only as a function of MgCO₃ content is an insufficient parameter to describe their behavior in natural aqueous solutions, as follows from our previous discussion. However, this does not preclude the use of present biogenic Mg-calcite solubility data to obtain some insights into the behavior and reaction pathways of these phases in nature. Thus in the subsequent section, the behavior of Mg-calcites under rising atmospheric CO₂ conditions and "ocean acidification" based on the solubilities of [Plummer and Mackenzie \(1974\)](#) and the biogenic "best fit" is evaluated by means of a numerical model and compared to observations from the natural environment. Using both solubility trends provides the reader with an idea of how solubility affects model output and the conclusions we draw from the modeling and field observations.

3. Response of carbonate minerals to rising pCO₂

3.1. Modeling the response of Mg-calcite minerals

Despite the uncertainties associated with Mg-calcite solubility previously described, a simple numerical model was constructed in order to predict the response of Mg-calcite minerals to rising pCO₂ based on solubility as a function of the mineral MgCO₃ content. The model environment represents the shoal-water ocean region of shelves, banks, atolls, estuaries, and reefs containing a variety of carbonate minerals, including a range of Mg-calcite compositions. Two different model scenarios were employed adopting two different solubility simulations in each model scenario. The two solubility simulations were based on the "best fit" biogenic Mg-calcite solubilities (e.g., [Bischoff et al., 1987](#);

Walter and Morse, 1984; see previous discussion in Section 2.2.2), or those solubilities corresponding to the results obtained by Plummer and Mackenzie (1974). These two solubility simulations probably reasonably bracket the behavior of the dissolution of the more abundant biogenic Mg-calcites in the natural environment. In the first model scenario, the shoal water ocean region was assumed to be a closed system and no mixing or exchange of water with the open ocean were taken into account. Simply the response of carbonate minerals to rising $p\text{CO}_2$ was investigated in this scenario. In the second model scenario, mixing with an open ocean surface seawater reservoir was considered and the combined effect of mixing and rising $p\text{CO}_2$ on carbonate mineral dissolution was investigated. It is emphasized that the objectives of the model scenarios were not to determine the inclusive effects of increasing $p\text{CO}_2$ arising from human activities on the carbonate geochemistry of the global shoal-water ocean region (e.g., Andersson et al., 2003, 2005, 2006), but simply to investigate the behavior and dissolution response, as a function of solubility and water residence time, of high Mg-calcite minerals to rising $p\text{CO}_2$ in a system constrained by the physical properties of the shoal water ocean region. Consequently, processes that are important in order to determine the integrated response of the natural system to rising $p\text{CO}_2$ including temperature, carbonate mineral precipitation, biological production and decomposition, etc., have not been included in the present model but are discussed in the aforementioned Andersson et al. papers.

3.1.1. Model methodology

A simple box model was constructed containing a seawater reservoir and 10 carbonate reservoirs representing calcite, aragonite, and individual Mg-calcite phases

containing 11–18 mol% MgCO_3 (Fig. 4). The seawater reservoir was set equal to the global shoal-water ocean volume of 3.7×10^{18} L, having an initial $p\text{CO}_2$ of 280 μatm , dissolved inorganic carbon, $\text{DIC} = 1846 \mu\text{mol kg}^{-1}$, and total alkalinity, $\text{TA} = 2200 \mu\text{mol kg}^{-1}$, corresponding to typical surface seawater conditions in the year 1700 when the model was initiated (Andersson et al., 2006). In the second model scenario, an open ocean surface seawater reservoir ($V = 9.98 \times 10^{19}$ L) with the same prescribed seawater conditions as the shoal-water reservoir was included in the model in order to allow for mixing between these two reservoirs. Sensitivity analyses on the effect of different shoal-water residence times (τ) were conducted for this model scenario. Water input via rivers and runoff were not included in any of the model scenarios. Only dissolution of carbonate minerals was investigated and no precipitation reactions were taken into account (see Andersson et al., 2005 for discussion of the precipitation issue and section 4.2). The total masses of reactive carbonate minerals were based on the estimate by Andersson (2003) of 43.1×10^{15} mol CaCO_3 . The proportions of calcite:aragonite:Mg-calcite (13%:63%:24%) were based on the relative abundance of these phases observed in neritic carbonate sediments (Land, 1967). Relative proportions of Mg-calcite minerals with different mol% MgCO_3 were obtained from the mineral distributions observed for mid-depth bank carbonate sands (Fig. 1; Agegian and Mackenzie, 1989). In both model scenarios, Mg-calcite saturation state was calculated using stoichiometric solubility products ($K_{\text{Mg-cal}(x)}$; Eq. (2)) based on the biogenic “best fit” solubilities or the Plummer and Mackenzie (1974) solubilities, according to the general equation:

$$\Omega_x = \frac{a_{\text{Mg}^{2+}}^x a_{\text{Ca}^{2+}}^{1-x} a_{\text{CO}_3^{2-}}}{K_{\text{Mg-cal}(x)}}, \quad (8)$$

Fig. 4. Model schematic of simple dissolution model representing the global shoal-water ocean environment. Arrows denote fluxes. The masses of carbonate phases are shown at the bottom of each carbonate mineral reservoir in 10^{12} mol.

where Ω_x denotes the saturation state with respect to a Mg-calcite phase with x mol% MgCO_3 and a is the total ion activity of the dissolved components in solution. Thermodynamically, net dissolution of a particular phase may occur if $\Omega < 1$. Once the saturation state with respect to a particular Mg-calcite phase was less than 1 in the model calculations, the kinetic rate of dissolution (R_d) of that phase was calculated according to the empirically derived relationship:

$$R_d = k(1 - \Omega)^n, \quad (9)$$

where k is the rate constant and n the reaction order. In either solubility scenario, the constants were based on the experimental results of Walter and Morse (1985) who investigated the dissolution kinetics of shallow marine carbonates in seawater as a function of reactive surface area, ion molal product (IMP), mineral stability, and microstructure. Because data were only available for Mg-calcite phases of 12, 15, and 18 mol% MgCO_3 , and no direct trend with Mg content was apparent, the dissolution rates for the remaining Mg-calcite phases were obtained from the mean kinetic dissolution rate observed for these phases. In reality, factors controlling dissolution kinetics are specific for each mineral grain and the rate of reaction may also be inhibited by additional factors such as dissolved phosphate and dissolved organic matter, as well as the freshness of the material (Morse and Mackenzie, 1990).

Both model scenarios were forced by observed atmospheric CO_2 concentrations between year 1700 and present followed by IPCC IS92a atmospheric CO_2 projections until year 2100 (Enting et al., 1995) and then a linear extrapolation until year 2300 assuming that equilibrium between the surface water and the atmosphere was established instantaneously i.e., the $p\text{CO}_2$ of the surface water was equal to the $p\text{CO}_2$ of the atmosphere. At this time, the global reservoirs of conventional fossil fuels will most likely be very close to exhaustion and the atmospheric CO_2 concentration is not likely to continue to rise considerably beyond the level observed at this time owing to burning of fossil fuels (Archer et al., 1998; Caldeira and Wickett, 2003; Andersson et al., 2005). However, in order to investigate the extended response of Mg-calcite minerals to elevated CO_2 concentrations, the surface water $p\text{CO}_2$ of the closed system model scenario was allowed to continue to rise linearly to a level of 20,000 μatm compared to ~ 380 μatm in the atmosphere in 2005 (at sea level) and perhaps as high as ~ 7000 – 9000 μatm in the early Phanerozoic (Bernier and Kothavala, 2001; Arvidson et al., 2006). In addition, presently, interstitial sediment pore waters may reach $p\text{CO}_2$ levels of more than several thousand μatm (e.g., Morse et al. (1985) observed $p\text{CO}_2$ s as high as $10^{-1.5}$ atm in carbonate rich sediments in Bahamas) owing to microbial decay and remineralization of organic matter deposited in the sediments, resulting in production and release of CO_2 . Consequently, the high $p\text{CO}_2$ forcing of the closed system model scenario is warranted to explore fully the behavior of Mg-

Table 1

Seawater equilibrium constants for the solubility of CO_2 (K_0), dissociation of carbonic acid (K_1^* , K_2^*), ion product of water (K_w^*), and dissociation of boric acid (K_b^* ; p denotes $-\log K$) used in the current model to calculate the dissolved inorganic carbon system at 25 °C and a salinity of 35 (Zeebe and Wolf-Gladrow, 2002)

pK_0	1.5468	Weiss (1974)
pK_1^*	5.8472	Mehrbach et al. (1973) given on pH_T by Lueker et al. (2000)
pK_2^*	8.9660	Mehrbach et al. (1973) given on pH_T by Lueker et al. (2000)
pK_w^*	13.2173	DOE (1994)
pK_b^*	8.5975	DOE (1994), based on Dickson (1990)

calcite minerals under elevated $p\text{CO}_2$. Dissolved inorganic carbon chemistry was calculated based on $p\text{CO}_2$ and TA at 25 °C and a salinity of 35 using the equilibrium constants given in Table 1 (Zeebe and Wolf-Gladrow, 2002). In order to calculate the saturation state with respect to Mg-calcite minerals, seawater concentrations of calcium, magnesium, and carbonate ions were converted to ion activities using total activity coefficients (Millero and Pierrot, 1998), so that the IAPs could be compared directly with the values of the stoichiometric solubility products. Numerical integration was conducted with Matlab (The MathWorks, Inc.) using an ordinary differential equation solver based on an explicit Runge–Kutta (4) and (5) formula.

3.1.2. Model results

As $p\text{CO}_2$ rises, the saturation state with respect to carbonate minerals rapidly decreases as carbonate ions are titrated by $\text{CO}_2(\text{aq})$ to form bicarbonate:

In the closed system model scenario adopting the biogenic “best fit” solubilities, seawater became undersaturated with respect to 18 mol% Mg-calcite once the surface seawater $p\text{CO}_2$ reached a level of 1414 μatm . Subsequently, this mineral phase became subject to dissolution (Fig. 5). The dissolution of this mineral phase was observed as a buffer effect in the seawater reservoir, i.e., the increase in alkalinity owing to carbonate dissolution strengthened the capacity of seawater to absorb CO_2 without a significant further change in pH and carbonate saturation state (Eq. (1)). By adding alkalinity to the system, a metastable equilibrium was established between the seawater and 18 mol% Mg-calcite, the most soluble carbonate phase present in the model sediments. The metastable equilibrium and the buffer effect persisted until the entire reservoir of 18 mol% Mg-calcite had dissolved and was completely exhausted. Because the 18 mol% Mg-calcite reservoir was relatively small and rapidly dissolved, the buffer effect was quite short in duration under the present CO_2 forcing. Following the exhaustion of this phase, the pH and saturation state rapidly dropped until the seawater became undersaturated with the next most soluble phase, 17 mol% Mg-calcite, which consequently started to dissolve and a new metastable equilibrium was established. The same trend then repeated itself for each

Fig. 5. Mg-calcite reservoir masses and calculated surface seawater saturation state with respect to calcite, aragonite and 11–18 mol% Mg-calcite based on the biogenic “best fit” solubility data (A, C, E) and the Plummer and Mackenzie (1974) solubility data (B, D, F) as a function of $p\text{CO}_2$ in the closed system model scenario. Seawater total alkalinity is also shown. The same saturation state data are shown in panel A and C, B and D, but on different scales in order to highlight the sequential dissolution of the most soluble carbonate phase present in the model simulation as well as the establishment of a metastable equilibrium between the seawater and this phase.

consecutive mineral phase following this sequence of events:

1. Seawater pH and carbonate saturation state decrease owing to increasing CO_2 .
2. Seawater becomes undersaturated with respect to the most soluble carbonate phase present in the sediments, and undergoes dissolution.
3. The dissolving phase maintains a metastable equilibrium with seawater and produces a buffer effect that maintains pH and saturation state relatively constant. The metastable equilibrium persists until the dissolving phase has completely dissolved. The stage at which the phase completely dissolves depends on the CO_2 forcing, the rate of dissolution, and the total mass of the dissolving mineral phase.

4. Once the dissolving phase has completely dissolved, seawater pH and carbonate saturation state will decline until a new metastable equilibrium has been established with the next most soluble carbonate phase present in the sediments, and so on.

In the closed system model scenario adopting those solubilities determined by Plummer and Mackenzie (1974), the seawater was initially significantly undersaturated with both 17 and 18 mol% Mg-calcite. Consequently, these reservoirs rapidly dissolved and immediately raised the total alkalinity, pH, and carbonate saturation state of the seawater in the first year of the simulation (Fig. 5). Eventually, the seawater became undersaturated with respect to 16 mol% Mg-calcite, which then became subject to dissolution. A metastable equilibrium was established between the

seawater and the 16 mol% Mg-calcite, which persisted until this phase had completely dissolved. From then on, not unexpectedly, the same sequential dissolution trend observed in the first solubility simulation was also observed in the second solubility simulation. It should be noted that although the two solubility simulations predict sequential dissolution of distinct Mg-calcite phases, in reality the dissolution pathway would more likely follow a continuum since the distribution of Mg-calcite compositions in nature may be more of a continuum.

In the open system model scenario, the initial responses and the overall trends of the two solubility simulations were similar to the results observed for the closed system solubility simulations. However, any buffer effect produced from carbonate dissolution and resulting accumulation of alkalinity in the surface seawater was rapidly diluted by mixing with the much larger open ocean reservoir. In the

biogenic “best fit” solubility simulation, the effect of mixing on the surface seawater carbonate chemistry was negligible independent of the residence time because the surface water remained supersaturated with respect to the most soluble carbonate mineral phase present in the model until year 2236. No dissolution took place prior to this year. Consequently, the surface seawater pH decreased almost as much in a scenario of infinite residence time and taking carbonate dissolution into account, as the pH decreased in a scenario assuming CO_2 solution in seawater to be a simple homogenous reaction (Fig. 6). The latter represents the maximum change in pH projected from the present CO_2 forcing. Adopting the Plummer and Mackenzie solubilities, the results were significantly different (Fig. 6). Because dissolution of carbonate minerals was ongoing at the onset of this solubility scenario, an infinite residence time and subsequent accumulation of alkalinity within the shoal-water

Fig. 6. Open system model results between years 1700 and 2300 for the biogenic “best fit” solubility (A, C, E) and the Plummer and Mackenzie (B, D, F) solubility simulations. (A, B) $p\text{CO}_2$ forcing and resulting surface seawater pH in multiple scenarios adopting different shoal-water residence times (τ). The results of panels C–F are based on the scenario of a 3 year residence time showing, (C, D) surface seawater carbonate saturation state (Ω), and (E, F), Mg-calcite reservoir masses.

ocean reservoir produced a strong buffer effect and a significantly higher surface seawater pH than if solution of CO_2 in seawater were simply homogeneous (Fig. 6). However, the buffer effect was rapidly diluted if the shoal-water ocean residence times were considered to be a few years or even several decades. In this model scenario, the entire Mg-calcite reservoir was exhausted by the year 2200 adopting a water residence time of 3 years (Chavez and Toggweiler, 1995).

3.1.3. Model discussion

Although the results of the different modeling scenarios show differences in trends and timing of events, they indicate that once dissolution is initiated, a metastable equilibrium could be established between the seawater and the dissolving mineral phase, provided that the rate of carbonate dissolution is fast enough relative to the rate of increase in $p\text{CO}_2$ and the rate of water mixing. The establishment of a metastable equilibrium was suggested decades ago by Chave (1962; Schmalz and Chave, 1963) based on observational data from Bermuda. If an existing metastable equilibrium between seawater and the most soluble carbonate phase present in the sediments were able to keep up with the current rise in $p\text{CO}_2$, surface seawater pH and carbonate saturation state would remain relatively constant and the seawater would be buffered owing to carbonate mineral dissolution. Consequently, the rate at which marine calcifying organisms produce their shells, tests, and skeletons would probably not be negatively affected owing to a decrease in surface water carbonate saturation state arising from increasing $p\text{CO}_2$ (Halley and Yates, 2000; Barnes and Cuff, 2000; Andersson et al., 2003).

The results of the biogenic “best fit” solubility simulations of the current model scenarios suggest that a buffer effect owing to carbonate dissolution will not be in effect until year 2236 or when the $p\text{CO}_2$ is equal to 1414 μatm . At this time, the saturation state with respect to aragonite and calcite will already be low enough to decrease the rate of calcification of marine calcareous organisms based on current experimental results (e.g., Gattuso et al., 1999; Langdon et al., 2000; Orr et al., 2005). In contrast, the results of the Plummer and Mackenzie solubility simulations indicate that the shoal-water surface seawater reservoir is currently close to or in metastable equilibrium with a Mg-calcite phase of 15 mol% MgCO_3 that consequently is subject to dissolution and acts to buffer the carbonate chemistry of the seawater reservoir. However, under the present CO_2 forcing, the apparent buffer effect is only significant if one assumes an infinite residence time and allows alkalinity to accumulate within the shoal-water reservoir (Fig. 6). The buffer effect becomes rapidly insignificant if water exchange with the open ocean is taken into account. Even at unrealistic long residence times, the buffer effect is insignificant despite substantial carbonate dissolution. As a result, it is not likely that marine calcifying organisms will be significantly protected from rising atmospheric $p\text{CO}_2$ owing to dissolution of high Mg-calcite minerals. This con-

firms the results of Andersson et al. (2003, 2005, 2006); they investigated the integrated effect of both rising $p\text{CO}_2$ and temperature on the global coastal ocean and concluded that metastable carbonate minerals will not dissolve rapidly enough to provide sufficient alkalinity to buffer the global coastal surface ocean against changes in seawater chemistry arising from increasing atmospheric CO_2 on the time scale of hundreds of years. A minor buffer effect could be observed in certain regions of restricted circulation such as atolls and lagoons once dissolution of carbonate minerals exceeds precipitation (Andersson et al., 2003, 2005, 2006). However, it is important to realize that even if the entire reactive Mg-calcite reservoir dissolved, and the rate of dissolution were equal to the rate of CO_2 invasion into the surface ocean, the buffer effect would only last for a few decades. Assuming an oceanic uptake of anthropogenic CO_2 of about 2 Gt C yr^{-1} (167×10^{12} mol C yr^{-1} ; e.g., Sarmiento and Gruber, 2002) and a rate of dissolution of high Mg-calcite minerals equal to the uptake rate, our estimate of 10.3×10^{15} mol of readily accessible reactive high Mg-calcite (24% of 43.1×10^{15}) present in the sediments of the global coastal ocean would be exhausted in only 62 years.

Even though no significant buffer effect may be observed from carbonate dissolution induced by rising $p\text{CO}_2$, the results of the open system model scenario adopting the Plummer and Mackenzie solubilities, and a shoal-water ocean residence time of 3 years, suggest that the average shoal water carbonate content and composition could change dramatically. By year 2200, the entire reservoir of readily available reactive Mg-calcite had dissolved and the sediments were solely comprised of calcite and aragonite in this model simulation. In contrast, the sediment Mg-calcite content and composition were little affected in the biogenic “best fit” solubility simulation. As previously discussed, it is far from certain what solubility scenario most accurately reflects the behavior of Mg-calcite minerals in the natural environment. Observations from tropical and subtropical surface seawater suggest that these waters are in metastable equilibrium with a Mg-calcite phase of 13–16 mol% MgCO_3 based on the solubilities of Plummer and Mackenzie. This is very close to the average composition of Mg-calcite phases (13–15 mol%; Fig. 1) found in neritic sediments of these ocean regions. In comparison, the same waters are supersaturated by 200–360% with respect to 20 mol% Mg-calcite based on the biogenic “best fit” solubilities. Furthermore, the modal magnesium content in skeletons and shells of calcareous organisms producing Mg-calcite (Chave, 1954; Mackenzie et al., 1983) appears to correlate well with the Mg-calcite phase in metastable equilibrium with surface seawater according to the Plummer and Mackenzie solubilities based on ion activity products calculated as a function of latitude using the WOCE P15 leg surface water dissolved inorganic carbon hydrographic data for the Pacific Ocean (<http://whpo.ucsd.edu/index.htm/>; Fig. 7). However, the range of Mg content in biogenic hard parts is large (Fig. 7), and factors other than

Fig. 7. Latitudinal distribution of the MgCO_3 content of skeletal Mg-calcite (Chave, 1954; Mackenzie et al., 1983) and the Mg-calcite phase in metastable equilibrium with surface seawater based on the Plummer and Mackenzie (1974) solubility curve and ion activity products (IAPs) in the Pacific Ocean calculated from WOCE section P15 (CLIVAR and Carbon Hydrographic Data Office; <http://whpo.ucsd.edu/index.htm>). In calculating surface seawater ion activities of Mg^{2+} , Ca^{2+} , and CO_3^{2-} from ion concentrations, a range of total ion activity coefficients given in the literature (Millero and Pierrot, 1998), was used in order to calculate the full range of Mg-calcite phases potentially in metastable equilibrium with the surface seawater.

seawater saturation state, such as temperature and growth rate, could be more important in controlling the Mg content of these calcareous hard parts (Chave, 1954; Mackenzie et al., 1983). In addition, if one were to apply the solubilities of Plummer and Mackenzie to interstitial pore waters, which have significantly different dissolved inorganic carbon chemistry than surface seawater owing to microbial decomposition of organic matter in the sediments, these waters would be significantly undersaturated with respect to the average Mg-calcite composition found in shoal water sediments. In contrast, the biogenic “best fit” solubilities projects that these porewaters are close to a metastable equilibrium with the average Mg-calcite sediment composition. Thus, observations from the natural environment do not unequivocally agree on which one of the evaluated solubilities is most realistic. Furthermore, they raise the question: is it the surface seawater chemistry or the interstitial porewater chemistry that controls the bulk carbonate composition in sediments?

Porewater chemistry is strongly controlled by the various microbial processes taking place in the sediments, the delivery rate and amount and reactivity of organic matter deposited, and the rate of water exchange with the overlying seawater. The extensive decay of organic matter that takes place within sediments produces CO_2 and consequently consumes carbonate ions according to Eq. (10), resulting in a lower saturation state with respect to carbonate minerals and dissolution of mineral phases with which the water is undersaturated. In fact, the extent of carbonate

dissolution could be controlled by the amount and the rate at which organic matter is being remineralized (Moulin et al., 1985; Morse and Mackenzie, 1990; Andersson et al., 2005). However, it should be pointed out that as the interstitial waters of sediments become anoxic with sediment depth and microbial sulfate reduction becomes important, alkalinity is produced from this process, increasing the saturation state with respect to carbonate minerals and potentially leading to carbonate precipitation rather than dissolution (Ben-Yaakov, 1973; Morse and Mackenzie, 1990). If 28 mmol kg^{-1} of SO_4^{2-} in sediment pore waters are reduced, this can potentially lead to production of 56 meq kg^{-1} of total alkalinity and oversaturation of the pore waters with respect to carbonate mineral phases.

3.2. Laboratory experiments

We recognize that the modeling scenarios presented previously are purely hypothetical and unrealistic in several different ways, but they still represent important results regarding the responses of Mg-calcite minerals to increasing $p\text{CO}_2$ because they conform to laboratory experiments and observations from the natural environment, as well as to theoretical considerations, and provide boundaries on the pathways of dissolution of the Mg-calcites under rising atmospheric CO_2 conditions and “ocean acidification”.

Fig. 8 illustrates the results from satumetry experiments with seawater containing equal amounts of high Mg-calcite (15–18 mol% MgCO_3) derived from the coralline algae *Porolithon gardineri* or Iceland spar calcite of similar grain size. An instant addition of a constant volume of acid (0.1 N HCl) was added to solutions of pure seawater, seawater containing calcite, and seawater containing Mg-calcite, and the changes in pH were recorded. A decrease in pH owing to a small acid addition shifts the equilibrium of the dissolved inorganic carbon species resulting in an increase in CO_2 and HCO_3^- and a decrease in CO_3^{2-} concentration, and consequently, the saturation state with respect to carbonate minerals. As was expected, a significantly larger buffer effect owing to carbonate dissolution was observed in the experiment containing the high Mg-calcite phase compared to the experiment with Iceland spar calcite because of the former mineral’s higher solubility (Fig. 8A). In a second experiment, a constant volume of acid was added at regular intervals to a solution containing equal amounts of either seawater and calcite or seawater and Mg-calcite while the pH was continuously monitored. In both experiments, after each acid addition and an initial decrease in pH, the pH slowly increased owing to mineral dissolution until the pH approached a steady state value (Fig. 8B). After each acid addition, the pH returned close to this steady state value, probably reflecting a metastable equilibrium between the solution and the most soluble carbonate phase present in the solution, analogous to the trend previously shown in the numerical simulations.

Fig. 8. (A) Responses of seawater, seawater containing Iceland spar calcite, and seawater containing Mg-calcite from the coralline red algae *Porolithon gardineri* to a single addition of an equal volume of HCl. Adding HCl to seawater changes the carbonate equilibrium resulting in an increase in CO_2 , HCO_3^- and a decrease in CO_3^{2-} and consequently the saturation state with respect to carbonate minerals. Note the difference between Mg-calcite and calcite in their ability to restore the pH after the acid addition, reflecting the higher solubility of Mg-calcite. This difference is also clearly demonstrated in (B), illustrating the response of seawater containing an equal amount of Mg-calcite or calcite to multiple additions of a constant volume of HCl. For each acid addition, the pH decreases until it approaches an equilibrium value (dashed lines). If the two scenarios were combined, one would expect the pH to decrease until a metastable equilibrium was established between the seawater and the Mg-calcite phase. This metastable equilibrium would persist until the Mg-calcite has completely dissolved, followed by a drop in pH until a new equilibrium was established with the calcite phase.

In a different experiment, reagent-grade calcite seeds were submerged in seawater collected from the Sargasso Sea offshore of Bermuda. The seawater was initially equilibrated with an air mixture of 330 ppm CO_2 and nitrogen gas, and then followed by equilibration of the seawater with 605 ppm CO_2 in N_2 (Tribble and Mackenzie, 1998). Initially during the first stage of the experiment, a drop in pH and total alkalinity was interpreted by the authors to represent precipitation of carbonate coatings on the pure calcite seeds. The initial pH drop was then followed by an additional drop in pH, but an increase in total alkalinity during the second stage of the experiment, indicating

Fig. 9. Trends of Sargasso seawater pH and total alkalinity during reaction of calcite seeds in an open system equilibrated first with 330 ppm CO_2 , then with 605 ppm CO_2 , adopted from Tribble and Mackenzie (1998). The initial decrease in pH and total alkalinity reflects precipitation and coatings on the calcite seeds. The observed decrease in pH and increase in total alkalinity after equilibration with 605 ppm CO_2 reflects dissolution of a carbonate phase. Because the seawater was still supersaturated with respect to calcite and aragonite the dissolving phase was concluded to be Mg-calcite.

dissolution as the system equilibrated with the gas containing 605 ppm CO_2 (Fig. 9). Because the seawater was supersaturated with respect to aragonite and calcite, the dissolving material was thought to be a Mg-calcite phase that probably was precipitated on the calcite seeds during the first stage of the experiment.

The results of the numerical model and the laboratory experiments all agree, and suggest that Mg-calcite minerals will respond to increasing $p\text{CO}_2$ and subsequent decreasing saturation state by sequential dissolution based on mineral stability, progressively leading to removal of the more soluble phases until the least soluble phases remain. Such selective dissolution of metastable carbonate minerals has been observed in both experiments and natural environments (Chave, 1962; Schmalz and Chave, 1963; Neumann, 1965; Wollast et al., 1980; Balzer and Wefer, 1981; Morse and Mackenzie, 1990). Observations from carbonate sediments in Bermuda follow a trend of increasing carbonate mineral stability with decreasing grain size, which most likely indicates selective dissolution of highly soluble Mg-calcite phases (Chave, 1962; Schmalz and Chave, 1963; Neumann, 1965).

4. Observations from carbonate-dominated regions

4.1. Bermuda

During spring and summer, a strong thermocline is developed in the water column in Devil's Hole, located within Harrington Sound, Bermuda. As organic matter produced in the surface waters sinks, it is remineralized by microbial activity below the thermocline, releasing CO_2 and driving the $p\text{CO}_2$ to very high levels and the

Fig. 10. (A) Vertical profiles from Devil's Hole, Harrington Sound, Bermuda, during summer showing saturation state with respect to calcite (circles), aragonite (squares) 15 mol% Mg-calcite (triangles) and $p\text{CO}_2$ (no symbol). Due to the development of a seasonal thermocline during summer, decay of organic matter below this boundary produces very high $p\text{CO}_2$ and consequently low saturation state with respect to carbonate minerals, which may become subject to dissolution. Solid lines indicate present summer conditions observed in August 2004 and dashed lines the conditions projected for the year 2100. The saturation state with respect to 15 mol% Mg-calcite was calculated from the solubility of the "biogenic best fit" data (see discussion in Section 2.2.2). (B) Changes in total alkalinity and calcium concentration with depth confirming dissolution of calcium carbonate minerals.

saturation state with respect to carbonate minerals down (Fig. 10). As summer progresses and the stratification of the water column usually becomes stronger, DIC builds up owing to organic matter decay and dissolution of carbonate minerals, and the $p\text{CO}_2$ may reach levels of several thousand μatm . The bottom water overlying the sediments is significantly undersaturated with respect to high Mg-calcite minerals and sometimes even aragonite, leading to dissolution of these phases. This is clearly demonstrated by a change in total alkalinity and calcium concentrations with depth (Fig. 10). Investigations of the mineral composition of subthermocline sediments in Harrington Sound have shown that these sediments are depleted in high Mg-calcite minerals despite significant biogenic production of these

phases by coralline algae, echinoids, and other Mg-calcite calcifiers in the shallow waters of the sound (Neumann, 1965). This confirms that the chemical changes observed in the water column most likely arise from mineral dissolution and consequently confirm what is predicted from thermodynamic and laboratory considerations.

As the atmospheric CO_2 concentration continues to rise, the surface water carbonate saturation state within Harrington Sound will decrease. Consequently, in future years from today, the initial carbonate saturation state likely will be lower during the onset of the development of the thermocline in the spring or early summer. Assuming that the transport of organic matter to the sediments and the extent of remineralization remain constant, the carbonate saturation state of the bottom water in Devil's Hole will be even lower than what is observed today, shifting the saturation state trend throughout the water column towards the left as shown in Fig. 10a. Consequently, dissolution will follow the sequence of events previously described and supported by modeling and laboratory experiments. A similar effect to that taking place in the water column of Devil's Hole owing to increasing atmospheric CO_2 will also apply to sediment interstitial waters, because the surface seawater will have an initial higher $p\text{CO}_2$ and lower carbonate saturation state upon entry into the porewater-sediment system in the future relative to today. However, the projected changes in surface seawater $p\text{CO}_2$ are relatively small compared to the CO_2 levels observed in porewaters owing to remineralization of organic material. Consequently, changes in organic matter deposition and remineralization may have a much larger effect on the interstitial porewater chemistry, carbonate composition, and dissolution than the projected changes in atmospheric CO_2 (Andersson et al., 2005).

4.2. The Great Bahama Bank

The waters and sediments of the Great Bahama Bank have been intensely studied for more than 40 years (see for example Morse et al., 2003, and the many references given therein). This is in large part because of the carbonate "whittings" that occur on the northern part of the bank, whose abiotic versus biotic origins have been widely disputed, and the long residence time (~ 240 days) of the shallow inner bank waters where about a third of the specific alkalinity has been lost. These conditions make this area a "natural laboratory" where, although the decreased saturation state of the waters is largely due to a loss of alkalinity rather than an increase in $p\text{CO}_2$, potential insights on the behavior of shallow water carbonate sediments under reduced saturation conditions may be obtained.

Fig. 11 presents the change in the CaCO_3 ion concentration product (ICP) for seawater at constant salinity, temperature, and TA as a function of $p\text{CO}_2$. The current ICP and that calculated for inner Bank waters also appear on the curve. The ICP of the inner bank waters is the ICP that would be obtained for a $p\text{CO}_2$ of $\sim 880 \mu\text{atm}$ when the

Fig. 11. The CaCO_3 ion concentration product (ICP) versus $p\text{CO}_2$ for seawater of $S = 35$, $t = 25^\circ\text{C}$, $TA = 2300 \mu\text{mol kg}^{-1}$ (solid curve where X marks current $p\text{CO}_2$). Shown in grey are the equilibrium ICP values for calcite, aragonite, and 15 mol% Mg-CO_3 Mg-calcite from synthetic, best biogenic, and Plummer and Mackenzie (1974). The dashed line is the ICP of inner Great Bahama Bank waters.

alkalinity change is converted to a change in $p\text{CO}_2$. For 15 mol% Mg-calcite , this ICP value is intermediate between that for our “best biogenic” and Plummer and Mackenzie (1974) values, and not surprisingly well above that for synthetic Mg-calcite of this composition.

Morse et al. (2003) determined the “kinetic solubility” of suspended whiting material to be about 1.9 times that of aragonite. These experiments were conducted in a manner similar to the experiments of Mucci and Morse (1984) on calcite where a much lower equilibrium ICP value (about 1/3) was obtained using synthetic calcite as a substrate in seawater. Morse et al. (2003) compared their kinetic solubility value with ICPs of Great Bahama Bank waters (Fig. 12), where it can be seen that the inner Bank waters are close to metastable equilibrium with the phase that gives this kinetic solubility. Consequently, if this equilibrium ICP value were to be maintained in the future, a smaller decline in TA will occur as $p\text{CO}_2$ rises. This means that the amount of abiotic carbonate production on the Great Bahama Bank will decline as $p\text{CO}_2$ rises adding to the impact of declining biotic calcification rates.

Although there is some scatter, it is interesting that similar values of ICP were observed for many porewaters from many carbonate-rich sediments in this region (Fig. 13; Morse et al., 1985) to the kinetically measured value. Bernstein and Morse (1985) conducted closed system solubility experiments on carbonate-rich sediments from the Bahamas. Measurements from initially under- and super-saturated seawater, with and without biocide and destruction of organic matter, and ranging from 8 to 50 days of reaction, gave similar results. Fine-grained aragonitic muds yielded steady-state IAP values close to that for the solubility of aragonite, whereas coarser sediments yielded steady-

Fig. 12. Contours of the saturation state of Great Bahama Bank waters with respect to the experimentally determined “kinetic” solubility of suspended whiting carbonates of Morse et al. (2003). Note that the inner Bank waters are very close to being in equilibrium with this solubility which is ~ 1.9 times that of aragonite. Solid triangles are sampling stations (Figure published with the kind permission of Elsevier.)

Fig. 13. Data for aragonitic muds in the Bahamas derived from Morse et al. (1985). Sixty percent of the data fall within the uncertainty of about ± 0.1 pH units for “punch-in” electrode measurements of the line for the “kinetic solubility product”. Five points fall above the uncertainty and six below. Three points were excluded from the plot at extremely high and low pH, and high alkalinity, respectively. The dashed line is for the stoichiometric solubility product of aragonite. Note that in this figure only the pH values are on the NBS scale as reported by Morse et al. (1985).

state IAP values up to about 2.8 times that of aragonite solubility. It is also interesting to note that the kinetic solubility value obtained for the dominantly aragonitic suspended sediment from the Bahamas is very similar to that obtained by Tribble and Mackenzie (1998) for thin overgrowths on calcite (see Morse et al., 2003, for discussion).

The studies from the Bahamas yield a considerable body of evidence that some carbonate phase with a solubility on the order of two times that of aragonite is what current Bahamas Bank seawater will come to equilibrium with given either enough time or a high enough solid to seawater ratio. The presumption of most investigators in these studies has been that this is a high Mg-calcite , the composition

of which depends on whose solubility values are chosen. However, as discussed previously in this paper, the Mg content is not necessarily the only component controlling the solubility of the Mg-calcites. It is possible, and even likely, that a surface phase is formed that may be highly hydrated, disordered, or compositionally impure. The practical consequence of this is that for seawater with a TA typical of that found today, this solubility-controlling phase will probably not be able to form from seawater with a $p\text{CO}_2$ greater than about 900 μatm .

5. Summary

Shallow water Mg-calcite minerals represent a major reservoir that could rapidly react to increasing $p\text{CO}_2$ and “ocean acidification”, being the “first responder” to decreasing carbonate saturation state because of their higher solubility than aragonite, and acting as a potential sink for anthropogenic CO_2 . If the total reservoir of reactive high Mg-calcite were completely dissolved in proportional amounts to the present annual oceanic uptake of anthropogenic CO_2 , surface ocean pH and aragonite saturation state would remain unchanged for about 60 years. In order to predict the response of Mg-calcite minerals to increasing $p\text{CO}_2$, it is critical to understand their solubilities as a function of seawater chemistry. At present, it is only the solubilities of the synthetic Mg-calcite minerals that can be considered valid as a function of mol% MgCO_3 because these solubilities have been achieved from both over- and under-saturation. Current solubility estimates of biogenic Mg-calcites show a wide degree of scatter between different studies and even between Mg-calcite phases of similar MgCO_3 content making it difficult to predict the behavior of these mineral phases in the *natural environment*. The wide scatter also indicates that factors other than Mg content such as structural disorder and impurities can significantly influence solubility. Nevertheless, because the Mg content of skeletal Mg-calcite appears to correlate with the trend of Mg-calcite phases in metastable equilibrium with surface seawater ion activity products (IAPs) as a function of latitude (Fig. 7), solubilities as a function of MgCO_3 content may have merit to some extent.

Numerical simulations show that once the surface seawater is undersaturated with respect to a particular Mg-calcite phase, this phase may undergo dissolution. Depending on the solid to solution ratio, rate of dissolution, and the rate of physical mixing of the water mass, a metastable equilibrium may be established between the dissolving phase and the seawater. This metastable equilibrium will persist until the dissolving phase has completely dissolved and a new metastable equilibrium can be established with the next most soluble solid carbonate present in the sediments. The trend of sequential dissolution based on mineral stability, progressively leading to removal of the more soluble phases until the least soluble phases remain, is confirmed by laboratory experiments and by observations from Bermuda. As the atmospheric CO_2 concentration continues to increase

owing to burning of fossil fuels, the average composition of contemporary carbonate sediments may change in favor of minerals with lower magnesium content and consequently higher stability. Furthermore, considerable evidence from the Bahamas suggests that the amount of abiotic carbonate production on the Great Bahama Bank will decline as $p\text{CO}_2$ rises, in accord with model predictions for the global coastal ocean in the future (Andersson et al., 2005).

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