DESIGN AND EXPERIMENTAL TESTING OF A HIGH PRESSURE, HIGH TEMPERATURE FLOW-THROUGH ROCK CORE REACTOR USING SUPERCritical CARBON DIOXIDE

by

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October, 2009
APPROVAL

of a thesis submitted by

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Logan Carl Hansen

October, 2009
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## Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>analyte</td>
<td>substance or value assessed by analytical procedure</td>
</tr>
<tr>
<td>anthropogenic</td>
<td>produced by human activity</td>
</tr>
<tr>
<td>aquifer</td>
<td>water bearing rock unit</td>
</tr>
<tr>
<td>brine-bearing</td>
<td>salt water bearing</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon Capture and Storage; injecting CO₂ underground to prevent release to the atmosphere</td>
</tr>
<tr>
<td>EC</td>
<td>Electrical Conductivity; a measure of the ability of a liquid to conduct electricity</td>
</tr>
<tr>
<td>pH</td>
<td>measure of fluid acidity</td>
</tr>
<tr>
<td>Gt</td>
<td>gigaton; one billion tons</td>
</tr>
<tr>
<td>labile</td>
<td>free to react, as in a chemical species</td>
</tr>
<tr>
<td>lithified</td>
<td>minerals consolidated as rock</td>
</tr>
<tr>
<td>mg L⁻¹</td>
<td>milligrams per liter; unit of concentration measurement</td>
</tr>
<tr>
<td>MPa</td>
<td>MegaPascal; unit of pressure measurement; 1MPa=145 psi=10 bar</td>
</tr>
<tr>
<td>ppmv</td>
<td>parts per million by volume; unit of concentration measurement</td>
</tr>
<tr>
<td>sequestration</td>
<td>interchangeable with CCS</td>
</tr>
<tr>
<td>supercritical</td>
<td>physical fluid state at pressure and temperature above critical point</td>
</tr>
<tr>
<td>TDS</td>
<td>total dissolved solids in a liquid</td>
</tr>
<tr>
<td>weathered</td>
<td>physically, chemically and/or biologically altered by near-surface processes</td>
</tr>
</tbody>
</table>
Anthropogenic CO$_2$ emission is of concern due to its likely contribution to global climate change. Geologic storage of CO$_2$ in deep brine-bearing aquifers is currently viewed as an alternative to its release to the atmosphere. The effects of injecting CO$_2$ into these aquifers are poorly understood. An experimental apparatus was developed to reproduce subsurface conditions relevant to geologic sequestration to simulate CO$_2$ injection and assess CO$_2$-brine-rock interactions. Technology available for this type of experimental apparatus was advanced by enhancing monitoring capabilities to include in situ pH, EC, pressure, and temperature measurement and continuous logging of these variables. This thesis describes the experimental apparatus and its novel capabilities, demonstrates its accuracy and precision, and presents and discusses a suite of CO$_2$-brine and CO$_2$-brine-rock interaction studies relevant to geologic sequestration.

Experiments were conducted by flowing brine and/or supercritical CO$_2$ through the apparatus, with and without rock cores in line. Rock samples were limestones/dolostones from the Madison Formation in the western Black Hills, South Dakota, which was selected based on its applicability as a primary large-scale geological CO$_2$ storage target. Outcrop blocks were machined to produce cores with minimal evidence of weathering to best simulate subsurface Madison Formation rock. Brines were prepared in the laboratory of a similar composition to reported literature values for in situ Madison formation fluids.

Results from the experimental system show good agreement with bench pH and EC measurements when utilizing standardized fluids. Experimental data indicate that adding CO$_2$ to brine under all tested conditions significantly reduces brine pH, an important control on subsurface geochemistry. This effect is partially buffered by flowing the fluids through Madison rock cores, due to dissolution of carbonate minerals, predominantly dolomite. The experiments indicate that samples of the Madison Formation with in situ brines can be partially dissolved via exposure to supercritical CO$_2$. Similar processes would likely occur in the subsurface Madison Formation in response to addition of supercritical CO$_2$. The novel experimental system provided new data that could be utilized in refining geochemical models; however, further improvements can be made to the system to improve its capabilities in this regard.
INTRODUCTION

Scientific Problem

Concern over Increasing CO₂ Emissions

Rising atmospheric carbon dioxide (CO₂) concentrations are of concern due to its likely contribution to global climate change (IPCC, 2007). Much of the increase in atmospheric CO₂ observed in the past 200 years (from a maximum ~ 260 parts per million by volume [ppmv] over the last 650,000 years to ~385 ppmv currently) is attributed to anthropogenic release via fossil fuel combustion (IPCC, 2007). An upper limit of 550±50 ppmv has been suggested to limit major negative long-term climatic effects; maintaining concentrations below the suggested limit would require avoiding more than 175 billion tons (Gt) C predicted to be released by 2050 if current emissions trends are followed (IPCC, 2007).

There is currently no single technology available that can provide this level of emissions reduction while meeting the energy demands of a growing global population with increasing energy consumption (IPCC, 2007). Smaller additive solutions include increasing vehicle, building, and power generation efficiency; switching to less carbon-intensive fossil fuels than coal, e.g. oil or natural gas; increasing nuclear power capabilities; increasing renewable power capabilities; reducing power consumption; and carbon capture and storage (CCS) (Pacala and Socolow, 2004). CCS alone has been projected to potentially prevent release of 25 Gt C by 2050 if used on 800 GW coal or
1600 GW gas power generation plants and is thus viewed as an important part of any realistic emissions mitigation portfolio (Pacala and Socolow, 2004).

Carbon Capture and Storage (CCS)

CCS is the process by which CO₂ is isolated from effluent waste streams at major point sources (e.g. power plants, oil processing facilities, concrete production facilities) and injected underground to prevent its release to the atmosphere (White et al., 2003). Several possible injection target types are being evaluated for storage potential and include depleted oil and gas reservoirs, deep unmineable coal seams, and deep brine-bearing, or saline, aquifers (White et al, 2003). Each target type has distinct characteristics that are expected to influence CO₂ storage efficacy; these include physical (porosity, permeability, pressure, temperature, fracture networks), chemical (mineralogy, \textit{in situ} water and gas chemistry), and logistical (infrastructure for injection and monitoring, potential leakage pathways, accessibility of surface above injection target) attributes that must be evaluated before wide-spread adoption of CCS as a large-scale emissions mitigation strategy (Hitchon et al., 1999; White et al., 2003). This study focused on advancing experimental technology to improve assessment of the potential physical and chemical affects of carbon storage in subsurface rock formations. Rock samples used for testing the apparatus were collected from a potential sequestration target formation that is a brine-bearing aquifer in the Powder River Basin (at top depths up to 18,000 ft) (Fischer et al., 2005).
**Supercritical CO\textsubscript{2} Overview**

This study utilized supercritical CO\textsubscript{2} since the supercritical phase is widely considered the relevant fluid phase for subsurface storage (Holloway, 1997). Certain fluids (e.g. H\textsubscript{2}O, CO\textsubscript{2}, and several hydrocarbon compounds) exist in a supercritical state when pressure and temperature conditions exceed a thermodynamic critical point specific to that fluid (Sengers, 1994). The fluid exists in a gaseous state if below the critical point in pressure but above in temperature and in a liquid state if below the critical point in temperature but above in pressure. The supercritical state can be thought of as a mixed gas/liquid phase, for which viscosity is similar to that of the gaseous phase, density is similar to that of the liquid phase, and reactivity shares features with the liquid and gas phases (Sengers, 1994). The supercritical fluid can dissolve or be dissolved into other fluids and is generally more reactive than the gas phase (Sengers, 1994).

These characteristics indicate that supercritical CO\textsubscript{2} can be injected into a pressurized and fluid-saturated formation with less work than as a more viscous liquid and maximizes CO\textsubscript{2} mass per unit volume of rock porosity (Span and Wagner, 1996; Holloway, 1997). Conditions for CO\textsubscript{2} supercriticality occur deeper than approximately 800m in the subsurface (conditions exceeding 31.2°C [\sim 305 K] and 7.38 MPa [1070 psi, 73.8 atm]); much greater injections depths are preferred, however, to reduce risk of leakage to the surface and maintain the CO\textsubscript{2} in its supercritical phase (Span and Wagner, 1996). Thus, we utilized the supercritical CO\textsubscript{2} phase in our experiments since it is the relevant physical state for simulating CCS environments.
Previous Research on Supercritical CO\textsubscript{2}-Brine-Rock Interaction

Previous laboratory studies have assessed some physical and chemical effects of supercritical CO\textsubscript{2}-rock interaction (e.g. Shiraki and Dunn, 2000; O’Connor and Rush, 2005; Kaszuba et al., 2003). However, these studies utilized a variety of lithologies and test conditions, thus the results from these studies are not directly comparable to one another. The three common types of CO\textsubscript{2}-brine-rock laboratory reactor designs are flow-through, flow-loop, and batch type reactors. Flow-through reactors only inject fresh fluids into cores; effluent fluid is collected but not re-injected, thus only initial fluid chemistry and core mineralogy can influence the resulting reactions (Shiraki and Dunn, 2000). Flow-loop reactors re-inject fluids previously reacted with the core (O’Connor and Rush, 2005). Batch reactors allow an initial quantity of fluid and solids to react with no fluid flow which is useful for determining reaction rates for specific mineral-brine compositions and proportions (Kaszuba et al., 2003).

Shiraki and Dunn (2000) flooded 1.5” diameter by 3” length core plugs from Tensleep sandstone, a quartzarenite with calcite and anhydrite cement from the Bighorn Basin, WY, with supercritical CO\textsubscript{2} and artificial brines based on formation water chemistry at 80\textdegree}C and 16.5 MPa. Cores were flooded for one week with a mixed solution of brine and CO\textsubscript{2}. Permeability generally decreased in each run, due to alteration of potassium feldspar to kaolinite, which tended to clog pore throats. O’Connor and Rush (2005) conducted CO\textsubscript{2} challenges to Mt. Simon sandstone cores with reproduced formation water. Increases in core permeability and porosity were observed in the initial ~500 hours of flooding followed by decreases thereafter. A 60% decrease in core fracture
strength after CO₂ challenge was also observed. Kaszuba et al. (2003) reacted a synthetic arkose and shale with CO₂ and brine at 200°C and 17.2 MPa for 80 days in a batch reactor. Reactions in the batch experiment damaged quartz surfaces and precipitated magnesite.

None of these previous studies utilized real time *in situ* pH or EC measurements or established baseline experimental data with CO₂ and brine prior to its reaction with the mineral or rock. This research focused on 1) establishing baseline brine-CO₂ reaction data to aid in interpreting data from the more complex CO₂-rock-brine interactions and 2) including real time *in situ* pH or EC measurements to better understand geochemical changes occurring in the system.

**Experimental Rationale and Hypotheses**

This research aimed to advance understanding of potential physicochemical effects of CCS by evaluating pore- and core-scale geochemical and physical effects of exposing carbonate rock and brine analogous to natural saline aquifer systems to CO₂ under experimental conditions relevant to carbon sequestration (i.e. elevated pressure and temperature with flowing interstitial fluid). Experimental analogs for saline aquifers were targeted since saline aquifers offer several advantages to other geologic storage options: they are widespread across the U.S. and thus close to many major point sources of CO₂; they typically have porosities and permeabilities amenable to fluid injection; and they offer large potential storage volume (White et al, 2003).
The physicochemical environments expected to occur as a result of injecting supercritical CO₂ into deep saline aquifers are complex. For example, industry-standard aqueous geochemical models such as PHREEQC (Parkhurst, 1995), Geochemist’s Workbench (Bethke, 2002) are not capable of appropriately simulating these environments because they cannot accurately parameterize the properties of supercritical fluids. Experimentation offers control over system parameters and the ability to alter individual primary variables in the system such as temperature, pressure and brine concentration. Potential interactions between supercritical CO₂, brine and rock are not fully understood for the supercritical CO₂ chemical system, but interactions between variables at subcritical CO₂ conditions are reasonably well constrained and can be used to develop hypotheses for likely interactions in the supercritical system.

Experiments were conducted in this thesis to test the following hypotheses:

1) Mixing brine and supercritical CO₂ at supercritical conditions will reduce brine pH and increase brine electrical conductivity

2) Increased brine total dissolved solids (TDS) will decrease CO₂ solubility

3) Increased temperature will decrease CO₂ solubility

4) Reduced brine pH resulting from addition of CO₂ will promote solid-phase dissolution of carbonate rock cores. Increasing brine TDS and temperature will decrease this effect via Hypotheses 2 and 3.

That exposing water to increased ambient gaseous concentrations of CO₂, all else held constant, reduces water pH is well established (Stumm and Morgan, 1996). Much research has been conducted on the effects of atmospheric concentration of CO₂ on
surface and ground water pH in the context of drinking water quality, industrial water quality, subsurface aquifer connectivity, and understanding atmospheric chemistry in deep geologic time, among other applications (Deutsch, 1997). The general reaction pathway is commonly illustrated as follows (Morse and Mackenzie, 1990):

$$\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \quad (1)$$

$$\text{CO}_2(aq) + \text{H}_2\text{O}(aq) \leftrightarrow \text{H}_2\text{CO}_3(aq) \quad (2)$$

$$\text{H}_2\text{CO}_3(aq) \leftrightarrow \text{H}^+(aq) + \text{HCO}_3^-(aq) \quad (3)$$

$$\text{HCO}_3^-(aq) \leftrightarrow \text{H}^+(aq) + \text{CO}_3^{2-}(aq) \quad (4)$$

Ambient gaseous CO2 concentration, pressure, and temperature control aqueous concentrations of dissolved CO2 (1). Dissolved CO2 reacts with water to yield carbonic acid (\(\text{H}_2\text{CO}_3(aq)\)) (2). Carbonic acid, in waters of near-neutral pH, dissociates to yield a labile proton and a bicarbonate molecule (3). Bicarbonate may further dissociate to yield another proton and a carbonate molecule (4). These reactions are pH dependent (Figure 1.1). The second version of the experimental apparatus incorporated in situ pH monitoring to address the pH effects of mixing supercritical CO2 and brine (Hypothesis 1).

These reactions illustrate the potential control of gaseous CO2 concentration on water pH. CO2 can readily react with water to liberate a proton at pH < 10 which increases \(\text{H}^+(aq)\) concentration and thus reduces solution pH (Stumm and Morgan, 1996). Increased aqueous CO2 concentration will increase aqueous electrical conductivity (EC). Aqueous EC is a proxy for total ionic strength of a solution, as increased concentration of dissolved ions generally allows for more efficient conduction of electricity. Since CO2
Figure 1.1: Concentration of carbonate species as a function of pH. HCO$_3^-$ is the most abundant species in most natural waters (6 < pH < 9) but H$_2$CO$_3$ is the most abundant below pH ~6 (after Lagneau et al., 2005).

dissolution into water increases carbonic acid, bicarbonate, carbonate, and proton concentrations, we expect that dissolution of CO$_2$ into water, all else constant, will increase aqueous EC. The second version of the experimental apparatus incorporated in situ EC measurements to assess the effects of mixing brine and supercritical CO$_2$ (Hypothesis 1).

Increasing concentration of NaCl(aq) in water decreases solubility of supercritical CO$_2$ into the aqueous phase over a range of pressures (ambient to 50 MPa) (Duan and Sun, 2002; Lagneau et al., 2005, Figure 1.2). This is generally referred to as a “salting-out” effect (also known as the common ion effect) by which concentration of dissolved ionic species influences solubility of other species. The salting-out effect is not well constrained for species other than NaCl and supercritical CO$_2$. Two brine concentrations were tested to assess potential salting-out effects (Hypothesis 2).
Figure 1.2: Increasing NaCl concentration reduces CO₂ solubility over a range of pressures (after Lagneau et al., 2005; data from Duan and Sun, 2003).

CO₂ solubility in water decreases with increasing temperature in the range to be simulated with the experimental apparatus (Ellis, 1959a). This follows Henry’s Law which indicates that at higher kinetic energy (i.e. temperature) fluids prefer the more chaotic fluid state. This means that CO₂ will prefer a gaseous or supercritical state to the aqueous state more strongly with increasing temperature. Because of the inverse relationship between CO₂ solubility in water and temperature within the relevant range, we expected CO₂ solubility to decrease at higher temperatures (Hypothesis 3) as would be indicated by a smaller pH and EC change at higher temperatures relative to lower temperatures. Increasing temperature generally increases reactivity rates but this effect is expected to be minor compared to the effects of reduced supercritical phase CO₂ solubility into brine at higher temperatures (Stumm and Morgan, 1996).
Interactions between dissolved supercritical CO₂ and the solid mineral phase are dominated by the effect of a reduced brine pH. Low pH (< 7) has been correlated with enhanced dissolution of solids, mobilization of ions, and a general destabilization of solid phases (Thomas and Hargrove, 1984). Carbonate minerals are especially sensitive to pH changes; solubility of carbonate minerals increases with decreasing solution pH in the range that we expected to produce experimentally (i.e. pH < 6.5 as this was the initial brine value and adding CO₂ was expected to decrease pH). Therefore, we expected our experiments to promote dissolution of carbonate mineral phases as a function of reduced brine pH (Hypothesis 4). Pressure conditions have been demonstrated to strongly influence aqueous system chemistry (Hamann, 1957; Stumm and Morgan, 1996). Increasing pressure was expected to increase CO₂ solubility into the aqueous phase, which should further reduce pH and increase solid phase reactivity compared to reactivity at ambient pressure.

Experimental Approach

This study utilized rock cores machined from surface outcrop blocks of Madison Formation, Powder River Basin, South Dakota, and brine prepared in the laboratory to represent in situ formation water in the subsurface basin (Busby et al., 1995; See Appendix A.1 for brine details). The Madison Formation is a Mississippian (330-430 Ma) carbonate comprised of mixed limestone/dolostone commonly ~600 ft. thick in the Powder River Basin and lies at depths of up to 25,000 ft (Sonnenfeld, 1996). The Madison Formation is a saline aquifer system at top depths of up to 18,000 ft, where it is capped by the Amsden formation as an aquitard (Sonnenfeld, 1996; Melick et al., 2009).
The Powder River Basin is a Laramide (~70 Ma) age asymmetric structural basin formed by uplift of the Bighorn Mountains, WY, and Black Hills, SD, and is ringed by the Hartville Uplift, Casper Arch, and Wind River Mountains.

![Figure 1.3: Cross-section depiction of the Powder River Basin illustrating basin asymmetry. The Madison Formation is depicted as the blue layer (modified from Melick et al., 2009).]

The Madison Formation has been suggested as a potential large-scale sequestration target because it is thought to be capable of storing up to 60 Gt CO₂, is deep in the basin, is penetrated by relatively few wells (i.e. few man-made potential leakage pathways), and is proximal to several of large CO₂ point sources (Fischer et al., 2005).

Blocks of outcrop rock near Sturgis, SD, in the Black Hills were collected for the experiments, trimmed to remove weathered surfaces, and multiple 1” diameter by 9” long cores were cut from the same block to minimize heterogeneity among the cores in terms of mineralogy, porosity, and permeability. Cores were then trimmed to the desired lengths for the experiments: 6” for initial experiments and, 4” for the experiments with the second version of the apparatus (a functional choice based on availability of rock material). Brines were prepared in the laboratory using the salts MgCO₃, CaSO₄, NaCl,
and CaCl₂ to approximate *in situ* fluid chemistry of Madison Formation waters (Busby et al., 1995; Table 1.1; Appendix A.1). Three brine concentrations were prepared for the experiments: one for the system proof-of-concept and two for more complex core tests. The concept proof brine had a final concentration of 0.9 g L⁻¹ as measured by ion chromatography. Two brine concentrations, 1 g L⁻¹ and 10 g L⁻¹, with the same relative cation and anion composition were proposed to bracket the concentration gradient.
reported across the basin from near the Black Hills (1.32 g L\(^{-1}\)) to the basin axis (7.1 g L\(^{-1}\)) (Busby et al., 1995). Due to an omission during preparation, the final brine did not include MgSO\(_4\) thus final brine concentrations were 0.5 g L\(^{-1}\) and 5 g L\(^{-1}\) as measured by inductively-coupled plasma mass spectrometry (ICP-MS). Reported formation water pH ranges from near the Black Hills (6.5) to the axis (7.8). The pH of the prepared brines was adjusted to 6.5 to provide comparable initial pH conditions, a key variable in the experiments. Brine and/or rock cores were reacted with 99.5% pure CO\(_2\) in all experiments.

Table 1.1: Initial chemistry of experimental brines, simulating components of Madison Formation waters

<table>
<thead>
<tr>
<th>Brine Solution</th>
<th>pH</th>
<th>Na(^+) (mmol)</th>
<th>Cl(^-) (mmol)</th>
<th>SO(_4^{2-}) (mmol)</th>
<th>Mg(^{2+}) (mmol)</th>
<th>Ca(^{2+}) (mmol)</th>
<th>HCO(_3^{-}) (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9 g L(^{-1})</td>
<td>6.5</td>
<td>1.0</td>
<td>0.7</td>
<td>6.4</td>
<td>1.6</td>
<td>4.1</td>
<td>0.05</td>
</tr>
<tr>
<td>0.5 g L(^{-1})</td>
<td>6.5</td>
<td>3.2</td>
<td>9.1</td>
<td>0</td>
<td>0.06</td>
<td>2.9</td>
<td>0.06</td>
</tr>
<tr>
<td>5 g L(^{-1})</td>
<td>6.5</td>
<td>32.0</td>
<td>90.7</td>
<td>0</td>
<td>0.6</td>
<td>29.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>
This chapter discusses designing and testing the first version of the reactor system. Two experiments were conducted for proof-of-concept and to assess the effects of injecting CO₂ alone and the effects of injecting CO₂ and brine into a Madison Formation rock core. The purpose of the initial experiments was to demonstrate the experimental apparatus design efficacy and to identify areas of potential technological improvement for further studies. Thus the data set generated using the first system version is not as extensive as for the second; this is by design.

The experimental apparatus was designed to flow fluids through rock cores under elevated pressure and temperature and to allow for extraction and analysis of the core and discrete fluid samples. The system is capable of applying pressures from ambient to 17.2 MPa and temperatures from ambient to 95°C. These ranges are comparable to conditions observed in CO₂ sequestration field studies in the Rangely and Weyburn fields that are currently being used as test sites for CO₂ sequestration (Kaszuba and Janecky, in press) and are thus considered relevant for subsurface sequestration studies.

**System Design**

The apparatus was designed as two pressurized fluid reservoirs with a rock core holder in between. The core holder, from Temco, Inc., is a flow-cell that houses a rock core of 1” diameter by up to 6” length (Figure 2.1). It can contain lithified geologic materials; other available designs can house unconsolidated material (weathered rock, powdered minerals or soil). The core holder consists of a set of flow plugs that spread
fluid flow over the entire core face, a rubber sleeve that holds the flow plugs and rock core in series, locking and sealing caps that secure an outer stainless steel shell to the flow plugs and sleeve, and a pressurizing fluid cavity used to collapse the rubber sleeve onto the core through overburden pressure, usually applied through a mineral oil medium, that exceeds system flowing pressure to ensure fluid flows through the core rather than between core and sleeve.

Figure 2.1: a) Core holder exterior b) cutaway diagram of core holder (images supplied by Temco, Inc.).
Two piston accumulators (1 L cylinders) from Calkins Fluid, Inc. comprise the fluid containment, pressure application, and fluid flow control systems. The accumulators, one influent that contains “fresh” or unreacted fluids and one effluent that contains “used” or reacted fluids, are steel-lined cylinders with gas-tight pistons that move in response to differential pressure across a piston head. Pistons separate a pressurizing fluid, N₂ for this study, from the reacting fluids, brine and/or CO₂. System pressure is applied to the accumulator N₂ side, pressure supply is then isolated to each accumulator, and effluent pressure is reduced to establish a differential pressure and thus system flow from influent to effluent. Reacted fluids collect in the effluent accumulator and remain at elevated pressure and temperature until extraction for analysis. Discrete fluid samples are extracted from multiple ports to allow analysis of fluids before injection into the rock core and during collection in the effluent accumulator (see Figure 2.2).

**Experimental Methods**

Two experiments were conducted to assess 1) the effects of flowing supercritical CO₂ alone (“dry” experiment) and 2) of alternately flowing reproduced formation water and supercritical CO₂ (“wet” experiment). Reacting fluids were flowed through Madison Formation rock cores at 55°C, 10.34 MPa (1500 psi) flowing pressure for five days. The core was held at an overburden pressure of 13.79 MPa (2000 psi) for the duration of the experiments. Supercritical CO₂ was flowed through the core for 120 hours in the “dry” experiment. No metric was established to accurately measure CO₂ flowrate for the “dry” experiment but it was less than 0.7 mL min⁻¹ as CO₂ was still present in the influent
Figure 2.2: Version one of the high pressure system a) Schematic diagram. N₂ gas controls a pressure imbalance between the piston accumulators, driving CO₂ through the system. b) Photograph. All components with the exception of the effluent accumulator were housed inside an incubator to maintain elevated system temperature.
accumulator at each CO₂ recharge every 24 hours. Each 24 hours, the influent accumulator was filled with 1 L liquid CO₂ (volume was measured in liquid form but injected in the supercritical phase) with a high-pressure liquid pump during which time system flow was stopped. Reproduced 0.9 g L⁻¹ formation water and supercritical CO₂ were flowed through the core per 120 hours for the “wet” experiment, with injection of each fluid alternated every 12 hours. Each 12 hours, the influent accumulator was recharged either with 1 L brine or 1 L liquid CO₂ during which time system flow was halted. The influent accumulator was recharged with CO₂ via a high-pressure liquid pump and with brine by filling the accumulator at ambient conditions. Flowrate was ~1 mL min⁻¹ estimated manually by sample extraction rate from the effluent sampling port. Some CO₂ or brine remained in the influent accumulator prior to each recharge. The overall system volume for the apparatus first design was about 125 mL not including the two 1 L accumulators. Discrete fluid samples (~15 mL) were taken directly into 50 mL BD Falcon™ polycarbonate sampling tubes every 24 hours prior to accumulator recharge during the “wet” experiment. Samples were allowed to degas, sealed, and stored at -20°C prior to analysis.

One inch subsamples of an untested core and both tested cores were analyzed for porosity, permeability, and unconfined crush strength (see Figure 2.3 for core sampling scheme). Porosity and permeability were evaluated by Core Lab Petroleum Services, Denver, CO, via mercury injection and compressed air injection using a Core Laboratories patented CMS-300 core analyzer. Crush strength was evaluated via hydraulic anvil press in the Civil Engineering Department, MSU Bozeman. Major cation
and anion concentrations of the discrete samples were measured via ion chromatography (IC) for the “wet” experiment in the Skidmore Laboratory, MSU Bozeman (following the methods of Montross, 2007). IC analyses were performed on a Metrohm-Peak IC unit operated per manufacturer’s instructions with a 250 µL sample loop and eluent flowrates of 0.7 mL min\(^{-1}\) for anions and 1.0 mL min\(^{-1}\) for cations. Cation concentration was measured with a Metrosep C-2-250 analytical column and utilized a 4 mmol L\(^{-1}\) tartaric acid/0.75 mmol L\(^{-1}\) dipicolinic acid eluent. Anion concentration was measured with a Metrosep A-2-250 analytical column and utilized a 3.2 mmol L\(^{-1}\) sodium carbonate/1.0 mmol L\(^{-1}\) sodium hydrogen carbonate solution and 100 mM H\(_2\)SO\(_4\) chemical suppression medium. Laboratory prepared standards, certified standards, and procedural blanks were analyzed before and after each run for quality control.

**Results and Discussion**

Evolution of the geochemistry of the brine during the “wet” experiment is shown in Figure 2.3. The measurements are normalized such that the ionic concentration at time \(t = 0\) represents the starting brine chemistry of 0.9 g L\(^{-1}\). A significant increase in \(\text{Mg}^{2+}\) was observed in the first 96 hours with minimal subsequent change. Changes in other analytes were recorded during the experiments however their concentrations after 120 hours were similar to initial concentrations at \(t = 0\). \(\text{HCO}_3^-\) was not measured via IC but is the complementary anion to \(\text{Mg}^{2+}\) as determined via charge balance, given no significant changes in \(\text{Cl}^-\) and \(\text{SO}_4^{2-}\).
Figure 2.3: Core sampling scheme for porosity, permeability, and crush strength analyses. Samples were 1” lengths cut from 6” long cores.

Figure 2.4: Cation and anion concentrations through time in the “wet” experiment. See Appendix A.3 for data. Precision was <17%, 13%, and 9% for Ca$^{2+}$, Na$^+$, and Mg$^{2+}$ and <14% and 7% for Cl$^-$ and SO$_4^{2-}$. 
Porosity, permeability, and crush strength data are shown in Table 2.1. The core plug from the “dry” experiment had a 2.6 % higher porosity and similar permeability and crush strength compared to the control (not exposed to CO$_2$ or CO$_2$/brine mix) core plug. The “wet” core plug had a 87% higher permeability, 13% lower crush strength, and similar porosity to the untested core plug.

Table 2.1: Core analysis: Porosity, permeability and fracture strength

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
<th>Liquid Permeability (mD)</th>
<th>Air Permeability (mD)</th>
<th>Unconfined Fracture Strength (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>13.0</td>
<td>23</td>
<td>29</td>
<td>5460</td>
</tr>
<tr>
<td>Dry</td>
<td>15.6</td>
<td>24</td>
<td>30</td>
<td>5535</td>
</tr>
<tr>
<td>Wet</td>
<td>14.1</td>
<td>43</td>
<td>52</td>
<td>4780</td>
</tr>
</tbody>
</table>

The only significant difference between the control core plug and that following the “dry” experiment was a higher core porosity. This difference in porosity may be due to natural variability in the Madison Formation samples (Henriette et al., 1989) and is difficult to ascribe to the effects of the CO$_2$ flood without a more extensive data set on both flooded and unflooded cores. The increase in Mg$^{2+}_{(aq)}$ for the “wet” experiment without significant changes in Ca$^{2+}_{(aq)}$ indicates preferential dissolution of Mg$^{2+}$ from the dolomite within the core. The large difference in core permeability between the control and “wet” core plugs without a large change in porosity may indicate expansion of preferred permeability pathways, which may not require a proportional porosity change. However, without evaluating more core plugs, it is difficult to definitively attribute differences in core properties to the experiment rather than it being natural variability in the rock sample.
Version one of the core reactor system was considered a success since two experiments with multiple fluid types were conducted with no evidence of system failure (e.g. leakage or loss of pressure). Further, the CO$_2$ / brine mixture produced significant dissolution effects within the experimental time frame of 5 days. The data set was limited for these experiments, which was by design, and several areas for improving data density and quality were identified and incorporated into the second system design and experimental testing, described in Chapter 3.
EXPERIMENTAL SYSTEM VERSION TWO

System Design

This chapter describes the redesign and testing of the reactor system to include novel capabilities for real time in situ measurement of system pressure and temperature and brine EC and pH (Figures 3.1). The altered apparatus retains the ability to discretely sample reacted fluids. The system has two configurations: 1) brine and supercritical CO₂ are mixed and allowed to flow through the system with no rock core; and 2) brine and supercritical CO₂ mixture flows through and reacts with a rock core (Figure 3.1). The alternate flow paths allow baseline CO₂-brine reactivity to be analyzed prior to introducing a solid phase to the experiments.

This apparatus design advances flow-through reactor technology by incorporating novel in situ monitoring capabilities which allow for real-time 24 hour monitoring and data logging of influent and effluent pressure, core confining pressure, multiple temperature readings, pH, and EC. Temperature and pressure data is collected using probes from Omega Engineering, Inc. and pH and EC data using probes from Barben Analyzer Technology. All data are logged using a Campbell Scientific CR1000 data logger. Multiple automated data backups, redundant power supply, and voice and data alarm systems minimize risk of data loss in the event of hardware or software failure. The total system volume was increased to ~385 mL to incorporate the new monitoring probes.
Figure 3.1: a) Schematic diagram of high pressure system with alternate design. Flow path 1 bypassing the core holder was used in the experiments with no inline rock core and flow path 2 was used in the experiments with an inline rock core. b) Photograph of redesigned system including new monitoring probes (right), and data collection and logging system, and alarm system (left).
Proof of Concept Tests without Core

Multiple pH and EC National Institute of Standards and Technology (NIST) traceable standards were flowed through the system at elevated temperature and pressure (45°C and 10.3 MPa) with no CO₂. Each standard was flowed through the system for one hour. pH standards included 2.24, 4.12, and 7.01 (values at 25°C). EC standards included 1.42, 10.01, and 20.01 mS cm⁻¹ (values at 25°C). Standards were also measured with an Orion 4-Star Plus benchtop pH and EC meter at ambient laboratory conditions (23°C and 0.1 MPa). All data were corrected to 25°C. Scatterplots of the bench top measurements and those at elevated temperature and pressure using the inline probes showed correlations with R² values of 0.994 and 0.991 for pH and EC respectively demonstrating the accuracy of the probe measurements (Figure 3.2).

![Figure 3.2](image-url)  
**Figure 3.2:** Comparison of in situ and ex situ measurements of pH and EC standards illustrating good agreement between the novel in situ probes and bench measurements.

A suite of experiments were conducted to measure various aqueous phase properties (in situ pH, EC, pressure, and temperature, and ex situ pH and EC) of the
brine-CO₂ system under a range of system pressures and temperatures, testing hypotheses 1-3.

1) Mixing brine and supercritical CO₂ at supercritical conditions will reduce brine pH and increase brine electrical conductivity

2) Increased brine TDS will decrease CO₂ solubility

3) Increased temperature will decrease CO₂ solubility

All experiments were conducted in triplicate for 8-10 hour test duration.

Experiments to assess the effects of CO₂ on brine pH and composition were conducted with brine only and repeated with a mixture of 0.8 L brine and 1 L CO₂ (measured at 25ºC and 0.1 MPa) with each of two brine concentrations, 0.5 and 5 g L⁻¹ TDS. These types of real-time, *in situ* data are novel for this type of experiment and provide significant insight into CO₂-brine interactions. See Table 3.1 for brine chemistry and Table 3.2 for experimental matrix.

### Table 3.1: Initial conditions for experimental and modeled brines

<table>
<thead>
<tr>
<th>Brine Solution</th>
<th>T (°C)</th>
<th>pH</th>
<th>Na⁺ (mmol)</th>
<th>Cl⁻ (mmol)</th>
<th>SO₄²⁻ (mmol)</th>
<th>Mg²⁺ (mmol)</th>
<th>Ca²⁺ (mmol)</th>
<th>HCO₃⁻ (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 g L⁻¹</td>
<td>25</td>
<td>6.5</td>
<td>3.2</td>
<td>9.1</td>
<td>0</td>
<td>0.06</td>
<td>2.9</td>
<td>0.06</td>
</tr>
<tr>
<td>5 g L⁻¹</td>
<td>25</td>
<td>6.5</td>
<td>32.0</td>
<td>90.7</td>
<td>0</td>
<td>0.6</td>
<td>29.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Table 3.2: Boundary conditions for eight experiments

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>T (°C)</th>
<th>Pressure (MPa)</th>
<th>Brine volume (L)</th>
<th>Brine TDS (g L⁻¹)</th>
<th>CO₂ (L at STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45-95</td>
<td>10.3</td>
<td>1</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>45-95</td>
<td>10.3</td>
<td>0.8</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>45-95</td>
<td>10.3</td>
<td>1</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>45-95</td>
<td>10.3</td>
<td>0.8</td>
<td>5.0</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>8.3-13.8</td>
<td>1</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>45</td>
<td>8.3-13.8</td>
<td>0.8</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>45</td>
<td>8.3-13.8</td>
<td>1</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>45</td>
<td>8.3-13.8</td>
<td>0.8</td>
<td>5.0</td>
<td>1</td>
</tr>
</tbody>
</table>

Experiments were conducted by initially introducing brine to the system influent accumulator. The brine, and all system hardware, was heated to the experimental temperature (45°C) and allowed to equilibrate for one hour. CO₂ was added for experiments 2, 4, 6, and 8. The system was then pressurized to the initial experimental pressure (10.3 MPa [1500 psi] for experiments 1-4 and 8.3 MPa [1200 psi] for experiments 5-8) and allowed to equilibrate for one hour. System flow rate, approximately 1 mL min⁻¹, was established and maintained throughout each experiment via an imposed pressure differential between the influent and effluent accumulator.

Bench pH and EC measurements were taken every hour within one minute of extraction from the system. *In situ* pH and EC were measured and logged each 30 seconds. System and bench EC probes utilize a temperature compensation of 2% °C⁻¹.

**Variable Temperature Tests**

Experiments 1-4 were conducted to assess affects of a range of temperatures on the brine-CO₂ system with brine only and repeated with 1 L CO₂ (Table 3.2) added to the
influent accumulator prior to pressurizing the system. With constant system pressure, temperature was varied from 45°-95°C allowing the system to equilibrate for one hour each 10°C temperature increase.

**Variable Pressure Tests**

The same methods as for the variable temperature tests were applied in experiments 5-8, in terms of system operation except pressure was varied (8.3-13.8 MPa) with constant system temperature (45°C) (Table 3.2). The system was allowed to equilibrate for 1 hour each 0.7 MPa (100 psi) system pressure increase.

**Modeled pH Values**

Equilibrium pH was modeled using PHREEQC for CO₂-brine reactions over the temperature range 45 – 95°C at 10°C intervals. The brine compositions are detailed in Table 3.1. Modeled pH values were calculated by equilibrating brines with CO₂ at atmospheric pressure (0.1MPa).

**Flow-through Experimental Results**

Results of the variable temperature and pressure brine-CO₂ experiments are shown in Figure 3.3.
Addition of CO₂ to brine at all tested conditions significantly reduced brine pH. Dilute brine (0.5 g L⁻¹) pH was reduced to a greater degree, a reduction of ~3.5 pH units, than the concentrated brine (5 g L⁻¹), a reduction of ~2.5 pH units. A minor increase in pH of ~0.1 units was observed with increasing temperature from 45 to 95°C for the 0.5 g L⁻¹ brine. However, this falls within the error envelope of the measurements and thus is not considered statistically significant. A minor decrease in pH of ~0.1-0.2 units was observed with increasing pressure from 1200 – 1600 psi, however the further increases in
pressure to 2000 psi did not result in any further change in pH. No statistically significant change in EC was observed for any experiment.

Comparison of *In Situ* and *Ex Situ* Data

System pH as measured by the *in situ* pH probes was compared to bench measurements taken within one minute of sample extraction from the system approximately every hour during each experiment (Figure 3.4). All data are from triplicate experiments.

Discrete bench EC measurements agree well with *in situ* EC probe data over all temperature and pressure conditions measured and with both the 0.5 and 5 g L\(^{-1}\) brines. Discrete bench pH measurements agree well with *in situ* pH probe data for experiments conducted with brine only, i.e. no added CO\(_2\). A reproducible difference of ~ 0.5-1.25 pH units is observed between discrete bench measurements and the *in situ* pH probe data in experiments conducted with CO\(_2\) for 5 g L\(^{-1}\) brine and 0.5 g L\(^{-1}\) brine respectively. In all cases the discrete pH measurements are higher than the measured *in situ* pH values.

Results of geochemical modeling at ambient pressure of 1 atm (0.1MPa) (Table 3.3) were compared to *in situ* (continuous) at elevated pressure and *ex situ* (discrete) pH measurements also at ambient pressure (see Figure 3.5).
Figure 3.4: Comparison of continuous in situ pH and EC (solid and dashed lines) and discrete bench top measurements taken within one minute of sample extraction versus time as a function of varying system temperature and pressure. Error envelopes for pH and EC data have been excluded for plotting simplicity.

Table 3.3: Modeled pH for CO$_2$-brine reactions from 45 – 95°C using PHREEQC

<table>
<thead>
<tr>
<th>Brine</th>
<th>45°C</th>
<th>55°C</th>
<th>65°C</th>
<th>75°C</th>
<th>85°C</th>
<th>95°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 g L$^{-1}$</td>
<td>3.85</td>
<td>3.89</td>
<td>3.93</td>
<td>3.98</td>
<td>4.03</td>
<td>4.07</td>
</tr>
<tr>
<td>5 g L$^{-1}$</td>
<td>4.11</td>
<td>4.17</td>
<td>4.24</td>
<td>4.30</td>
<td>4.37</td>
<td>4.43</td>
</tr>
</tbody>
</table>
PHREEQC predicted reduced pH values for the brine-CO₂ mixture for both brines at ambient pressure under the range of modeled temperature conditions. The 0.5 g L⁻¹ brine pH was reduced to 3.85 at 45°C rising to 4.07 at 95°C and the 5 g L⁻¹ brine pH was reduced to 4.11 at 45°C rising to 4.43 at 95°C (Table 3.3, Figure 3.5). The modeled rise in pH in response to elevated temperatures was not observed in either the in situ or bench pH data and the modeled data agreed most closely with the empirical bench pH data at higher temperatures (>75°C). A closer correlation between the modeled pH data and bench top measurements was evident with the 5 g L⁻¹ brine relative to the 0.5 g L⁻¹ brine.

PHREEQC predicted higher pH values, up to 1.2 pH unit difference in all modeled scenarios than the in situ pH data. The discrepancy was ∼ 0.3 to 0.5 pH units for the 5 g L⁻¹ brine and 0.7 – 1.2 pH units for the 0.5 g L⁻¹ brine with the difference increasing at

Figure 3.5: Comparison of continuous in situ pH and EC (solid and dashed lines), discrete bench measurements, and modeled results using PHREEQC versus time as a function of varying system temperature. Error envelopes have been excluded for simplicity.
higher temperatures. This highlights the limitation of current geochemical models e.g. PHREEQC in representing scenarios that include supercritical fluids.

The significant pH reduction observed across all experiments for the brine-CO$_2$ system is due to dissolution of CO$_2$ into the brine forming carbonic acid H$_2$CO$_3$(aq). CO$_2$ solubility as reflected by pH reduction decreased with increasing brine concentration as indicated by higher pH values for the more concentrated brine. Increased pressure over ambient atmospheric increased CO$_2$ solubility, producing H$_2$CO$_3$(aq) as indicated by reduced pH at elevated system pressure. The significant increase in pH by up to ~ 1 pH unit in the bench top measurements of pH reflects rapid CO$_2$ degassing on removal from the system. The bench top measurements at ambient pressure show much closer agreement with the modeled results from PHREEQC, also at ambient pressure.

No statistically significant difference in EC was observed in the experiments that used only brine and those with CO$_2$ added to the brine. All measured EC values fell within the error envelopes of baseline experimental data. However the pH data indicates there is dissolution of CO$_2$ into the brine and thus this should result in an increase in EC.

The minimum amount of dissolved CO$_2$ to produce carbonic acid H$_2$CO$_3$(aq) necessary to reduce pH as observed is calculated as 44 mg L$^{-1}$ for 1 L of brine. This represents a 9 and 0.9 % change in total dissolved solids for the 0.5 g L$^{-1}$ and 5 g L$^{-1}$ brine respectively and these values appear to be below the detection threshold of the EC probe. To calculate the minimum amount of H$_2$CO$_3$(aq) needed to change 1 L brine pH from 6.5 to a minimum of ~3 as observed in the brine-CO$_2$ reaction studies, first the amount of H$^+(aq)$ required was calculated as:
\[ \Delta pH = -\log_{10} \Delta [H^+] = 3.5 \]

\[ 10^{-6.5} = 3.2 \times 10^{-7} \text{ moles and } 10^{-3} = 1 \times 10^{-3} \text{ moles. Difference is } \sim 1 \times 10^{-3} \text{ moles} \]

Since one proton is supplied by the dissociation of one molecule of H\textsubscript{2}CO\textsubscript{3}\textsubscript{(aq)} to HCO\textsubscript{3}\textsuperscript{-} (aq) below pH 6.5, the minimum amount of CO\textsubscript{2}\textsubscript{(aq)} needed to change the pH as observed is equal to the number of moles of H\textsuperscript{+} (aq), or 1 x 10\textsuperscript{-3} moles. The molecular mass of CO\textsubscript{2} is 44 grams mol\textsuperscript{-1}, so the minimum concentration required is 44 mg L\textsuperscript{-1} or 44 ppm.

The experiments demonstrated that mixing supercritical CO\textsubscript{2} with brine decreases brine pH significantly (first posit of Hypothesis 1) but did not change EC significantly (second posit of Hypothesis 1). The latter posit of Hypothesis 1 was not refuted as the in situ EC probe may not have been able to detect the relatively small increases in EC as discussed above. The experimental data further indicate that increasing brine TDS decreases CO\textsubscript{2} solubility (Hypothesis 2) as indicated by smaller decrease in brine pH resulting from mixing with supercritical CO\textsubscript{2}. Finally, the data indicate that increasing temperature did not significantly decrease CO\textsubscript{2} solubility for either the 0.5 or 5 g L\textsuperscript{-1} brine (Hypothesis 3).

**Proof of Concept Tests with Core**

Four core-flood experiments were conducted to assess the effects of injecting supercritical CO\textsubscript{2} into brine-bearing Madison Formation rock cores. Each experiment was conducted once utilizing Madison Formation rock cores and reproduced Madison formation water for 120 hour test duration. Experiments were conducted with a mixture
of 0.8 L brine and 1 L CO₂ (measured at 25°C and 0.1 MPa) with each of two brine concentrations, 0.5 g L⁻¹ and 5 g L⁻¹ (Table 3.1), and each of two temperatures, 50° C and 90° C. These experiments address Hypothesis 4: Reduced brine pH resulting from addition of CO₂ will promote solid-phase dissolution of rock cores. Increasing brine TDS and temperature will reduce this effect via Hypotheses 2 and 3 ([2] increased brine TDS will decrease CO₂ solubility and [3] increased temperature will decrease CO₂ solubility).

Experiments were conducted by initially introducing 0.8 L brine to the system influent accumulator. The brine, and all system hardware, was heated to the experimental temperature (either 50°C or 90°C) and allowed to equilibrate for twelve hours. CO₂ was added and the system was then pressurized to the experimental pressure (13.8 MPa [2000 psi]) and allowed to equilibrate for one hour. System flow rate, less than 1 mL min⁻¹ (this was the minimum measureable flowrate with the current system), was established via an imposed pressure differential between the influent and effluent accumulator and maintained throughout each experiment.

*In situ* pH, EC, pressure, and temperature were measured and logged each 30 seconds. Discrete fluid samples, collected into 50 mL BD Falcon™ polycarbonate sampling tubes at hours 0, 3, 6, 9, 12, 18, 24, 48, 72, 96, and 120 after the start of the experiment, were analyzed for major cation concentration via inductively-coupled plasma mass spectrometry (ICP-MS) at the Chemical and Biological Engineering Department, MSU-Bozeman, with an Agilent 7500ce unit. Liquid samples were allowed to degas, then sealed and stored at 25°C until analysis. Samples were acidified to a concentration of 6 M HNO₃ to dissolve any precipitates, then diluted 1:10 (0.5 g L⁻¹ brine) or 1:100 (5 g L⁻¹ brine)
brine), with deionized water and acidified to a final concentration of 1 M HNO₃. Optima standards and procedural blanks were analyzed before, during, and after sample analyses to maintain quality assurance and quality control. One inch plugs from each end of the tested rock cores were analyzed for porosity and permeability. Four additional core plugs not subjected to CO₂ flood were analyzed for porosity and permeability to help assess the degree of natural heterogeneity of these parameters in the rock.

**Results**

Injection of the CO₂/brine mixture into Madison Formation rock cores decreased brine pH in all four experiments (Figure 3.6). There was a sharp initial reduction of 1 pH unit in the 90°C experiments with both the 0.5 and 5 g L⁻¹ brine. At 50°C the initial pH reduction was 1.5-1.8 pH units with the lowest value recorded with the 0.5 g L⁻¹ brines. A gradual increase in pH occurred in all experiments over the following hours with a plateau in pH being measured at 40 hours for the 50°C 0.5 g L⁻¹, 80 hours for the 90°C 0.5 g L⁻¹ and 100 hours for the 90°C 5 g L⁻¹. Only in the 50°C, 5 g L⁻¹ experiment did the pH continue to rise gradually over the 120 hour experiment. Brine pH only returned to its original value of 6.5 in the 90°C experiment with 5 g L⁻¹ brine after ~100 hours, however, the marked increase to ~6.3 at 78 hours may be an experimental artifact. Whereas, in the 90°C 0.5 g L⁻¹, 50°C 0.5 g L⁻¹ and 50°C 5 g L⁻¹ experiments final pH values were 6.1, 5.35 and 5.47 respectively. After ~30 hours the pH profile for the 50°C experiments was largely similar, to within ~0.1 pH units with both brine concentrations. The pH profiles in the 90°C experiments were also somewhat similar with the 5 g L⁻¹ solution consistently higher than the 0.5 g L⁻¹ solution by ~0.1 pH units from 4-78 hours.
EC increased slightly overall for each experiment (Figure 3.6) and showed some intermittent erratic measurements, especially for the high temperature tests.

![Figure 3.6: pH and EC versus experiment duration for four core flood experiments. Narrow data spikes and erratic EC data are considered spurious measurements resulting from system pressure fluctuations or free-phase CO2 passing the EC probe.](image)

The ICP-MS measurements of major cations are normalized such that the ionic concentration at time = 0 represent the starting brine chemistry. Geochemical analysis of discrete fluid samples shows varied response in concentrations of Ca^{2+}_{(aq)} and Na^{+}_{(aq)} and
overall increase in $\text{Mg}^{2+}_{\text{(aq)}}$ for each experiment (Figure 3.7). $\text{Ca}^{2+}_{\text{(aq)}}$ increased overall for both 0.5 g L$^{-1}$ brine experiments but did not change significantly for the 5 g L$^{-1}$ experiments. $\text{Na}^{+}_{\text{(aq)}}$ increased in the 0.5 g L$^{-1}$ 90ºC experiments but did not change significantly for the other three experiments.

Core analysis did not show significant trends relating exposure to CO$_2$ to changes in rock properties (Figure 3.8). Overall, samples with higher porosity generally had higher permeability, and in general post-flood samples had higher porosity and permeability than unchallenged samples, but this was not the case for all samples. The three highest porosity values were in flooded samples (21.96, 19.46 and 18.63%) but the
The highest measured permeability was for an unflooded core plug (57.5 mD).

Figure 3.8: Porosity versus permeability for four unflooded samples and eight flooded samples (open and closed icons, respectively).

**Discussion**

Injecting brine and CO₂ into Madison Formation rock cores resulted in a smaller change in pH than observed for the experiments without a rock core; a change of ~3.5 and ~3 pH units for 0.5 and 5 g L⁻¹ experiments with no core and ~1.8 and ~1.05 pH units for 0.5 g L⁻¹ core experiments at 50°C and 90°C and ~1.5 and 1 pH units for 5 g L⁻¹ core experiments at 50°C and 90°C (Figures 3.3 and 3.6). EC data were more erratic, showing a greater increase in brine conductivity than in prior tests and showing experimental artifacts not previously observed (Figure 3.6).
The subdued pH reduction and increased brine solute concentrations are due to dissolution of the rock core partially buffering the highly acidified brine thus increasing the concentration of ionic species in the brine. Erratic EC measurements occurred either just after discrete fluid sampling, signifying that the in situ EC probe is highly sensitive to system pressure changes, or for prolonged periods of up to multiple days, most likely due to a bubble of free supercritical CO2 near the EC probe causing unpredictable measurements. No pressure change was observed in the collected pressure data to match the prolonged erratic EC measurements. Minor short-lived (less than 30 seconds) decreases in system pressure (~10-30 psi) accompanied the smaller artifacts likely due to liquid sample extraction.

Experiments with a rock core in line produced a higher minimum brine pH under all tested conditions of 4.8 and 5.0 versus 3.1 and 3.9 for 0.5 and 5 g L\(^{-1}\) experiments and a larger change in pH with increasing temperature, 0.7 and 0.5 pH units for 0.5 and 5 g L\(^{-1}\) core experiments versus 0-0.1 pH units for experiments without inline cores. The higher minimum pH observed in the core experiments is due to mineral dissolution from the carbonate cores buffering part of the brine acidity increase caused by adding CO2 to the brine. The larger change in pH observed in the core experiments with increasing temperature may be due to more rapid solid phase dissolution kinetics at higher temperature. At a higher temperature, mineral dissolution occurs at a higher rate (Deutsch, 1997) and may increase the rate at which the core can buffer the increased brine acidity.
Additionally, the core experiments showed significant differences in brine chemistry as a function of increased brine TDS. In the 0.5 g L⁻¹ experiments, Ca²⁺(aq) and Mg²⁺(aq) increased whereas only Mg²⁺(aq) increased significantly in the 5 g L⁻¹ experiments. Further, Mg²⁺(aq) reached similar final concentrations in the 5 g L⁻¹ experiments but final brine pH was ~1 pH unit higher at the end of the 90°C experiment relative to the 50°C experiment.

Varied temperature and brine concentration produced greater effects in these experiments than in the prior CO₂-brine only reaction studies. In the prior studies, differences of about 1 pH unit and no measurable changes in EC were observed for varied brine concentration and temperature. Core experiments at 50°C and 90°C produced differences in pH (~0.75 and ~0.5 pH units higher than for CO₂ and brine alone for 0.5 g L⁻¹ and 5 g L⁻¹ brines respectively) and brine chemistry (lower final Ca²⁺(aq) and higher Mg²⁺(aq) concentrations at higher temperatures for each of the brine concentrations). This indicates that in experiments at 90°C CO₂ solubility was likely decreased resulting in higher pH values compared to the 50°C experiments. The smaller change in pH at 90°C with both 0.5 and 5 g L⁻¹ brines indicates production of a brine with lower acidity and thus solid-phase reactivity than the larger pH change at 50°C; the higher pH resulted in reduced dissolution and thus reduction in part of the increases in Ca²⁺(aq) and Mg²⁺(aq) observed at 50°C.

The increasing concentration of Ca²⁺(aq) and/or Mg²⁺(aq) through time in all experiments likely indicates dissolution of dolomite in the cores. Ca²⁺(aq) increased more than Mg²⁺(aq) for the 0.5 g L⁻¹ experiments but the reverse was true for the 5 g L⁻¹
experiments (Figure 3.9). Saturation indices (SI) for relevant calcium and magnesium containing minerals were calculated at time 0 in equilibrium with ambient concentrations of CO\textsubscript{2} (1 atm) in PHREEQC to aid analysis (Table 3.4). Input variables are tabulated in Table 3.1. Calculated SI indicate that the brine is significantly undersaturated with respect to dolomite much more so than with respect to aragonite, calcite, anhydrite, and gypsum for all experiments. This effect is enhanced to a greater degree for the 0.5 g L\textsuperscript{-1} brine than the 5 g L\textsuperscript{-1} brine. Therefore at ambient conditions one would predict dolomite dissolution should be preferred over dissolution of those other mineral phases (Table 3.4). Ca\textsuperscript{2+} and Mg\textsuperscript{2+} showed similar increases in concentration for the 0.5 g L\textsuperscript{-1} experiments which is consistent with congruent dolomite dissolution (Figure 3.9; Table 3.5).

<table>
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<tr>
<th>Mineral</th>
<th>0.5 g L\textsuperscript{-1} brine</th>
<th>5 g L\textsuperscript{-1} brine</th>
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<td></td>
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<td>Gypsum</td>
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Figure 3.9: Change in $\text{Mg}^{2+}_{(aq)}$ and $\text{Ca}^{2+}_{(aq)}$ concentrations for four core flood experiments illustrating differential cation dissolution between experiments utilizing 0.5 g L$^{-1}$ and 5 g L$^{-1}$ brines.

However, $\text{Mg}^{2+}$ concentrations were 2.6 and 2.5 mmol L$^{-1}$ greater than $\text{Ca}^{2+}$ concentrations by the end of the 50ºC and 90ºC 5 g L$^{-1}$ experiments. The final $\text{Ca}^{2+}_{(aq)}$ concentrations were actually lower than the starting concentrations implying that there may have been some precipitation of $\text{Ca}^{2+}$ potentially as CaCO$_3$$_{(s)}$ given the lack of aqueous sulfate in the brine (Figure 3.9; Table 3.5) and incongruent dissolution of dolomite. However, the exact mechanism for this is unclear at this time. Although the 5 g L$^{-1}$ brines are closer to saturation with respect to aragonite and calcite than the 0.5 g L$^{-1}$ brines in the ambient pressure equilibrium scenario modeled in PHREEQC there is no indication that there should be $\text{Ca}^{2+}$ precipitation. PHREEQC is limited to low-pressure simulations and likely does not appropriately model the supercritical CO$_2$ phase as highlighted in this comparison with the experimental data. It and other geochemical
models will benefit from further characterization of high-pressure supercritical CO₂ data produced by our apparatus.

Comparative analyses of the CO₂-brine only and CO₂-brine-rock experiments highlights some interesting reaction kinetics. The predicted amount of CO₃²⁻ dissolved to account for the ΔpH at equilibrium (difference between CO₂-brine and CO₂-brine-rock) is calculated for each 24 hour time step (Table 3.5). This value is subtracted from the actual concentration measured for each time step in the CO₂-brine-rock experiments and the resulting difference between the measured values reflecting kinetic reaction processes and the equilibrium value is tabulated (Table 3.5). The calculations indicate that an excess of solid carbonate material was liberated in the core floods compared to the H⁺(aq) necessary to produce the observed pH change in CO₂-brine experiments. This is likely due to drawdown of freephase supercritical CO₂ into the brine promoted by partial buffering of the solution acidity via carbonate dissolution. This highlights the importance of the reaction kinetics that require accurate parameterization in geochemical models that may be developed to incorporate supercritical CO₂.
Table 3.5: Mass balance calculations for the core flood experiments. Mg and Ca concentrations are normalized to the input brine such that concentrations at t = zero are zero. ΔpH is the difference between the pH measured in the brine CO₂ only experiments relative to those measured in the experiments with cores inline. It is assumed the brine-CO₂ values measured over a 10-hour experiment (Figure 3.3) would remain unchanged over a 120-hour experiment.

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<th>Time (hrs)</th>
<th>pH</th>
<th>Mg(^{2+}) (aq) mmol L(^{-1})</th>
<th>Ca(^{2+}) (aq) mmol L(^{-1})</th>
<th>ΔpH</th>
<th>Predicted CO(_3^{2-}) (mmol L(^{-1})) to account for ΔpH at equilibrium</th>
<th>Actual moles CO(_3^{2-}) dissolved</th>
<th>Difference between calculated and actual moles CO(_3^{2-})</th>
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Mass balance calculations (assuming 1” diameter 4” length rock core, 2.8 g cc\(^{-1}\) grain density, 10 % porosity, and 1 L day\(^{-1}\) solute flow) indicate between 0.32-0.39 % of rock material was removed in the CO\(_2\)-brine core flood experiments. However, rock core analyses yielded no significant trends in porosity and permeability, but this may be less a reflection on the experiments than on natural rock heterogeneity. This interpretation is supported by the work of Henriette et al. (1989) who found that permeability for 1” core plugs taken from the same rock block varied significantly (from 4 to over 400 mD), to a higher degree than the variability observed in these analyses. Altering the core reactor system to allow for porosity and permeability assessment before, during, and after experiments would provide more robust data. This could be most feasibly achieved by installing high precision in-line flowmeters or using a pump to inject CO\(_2\) and brine that is capable of constant flow injection. This, with differential pressure data across the core, could be used to calculate permeability change during experiments. Cores could be analyzed via magnetic resonance imaging before and after experiments to evaluate porosity change.

**Summary**

The experiments with version two of the experimental system showed the following relative to Hypotheses 2-4:

2) Increased brine TDS will decrease CO\(_2\) solubility. (True)
Decreased CO₂ solubility at higher brine TDS was indicated by a smaller change in pH with higher brine concentration in experiments with and without cores in line (~0.8-1.0 pH unit with no core and ~0.5 pH units with core in line).

3) Increased temperature will decrease CO₂ solubility. (True)

CO₂ solubility decreased with increasing temperature as indicated by smaller pH change for both brines at 90°C than at 50°C. A difference in pH reduction of ~0.7 and ~0.5 pH units for 0.5 and 5 g L⁻¹ brines was observed for the 40°C temperature increase.

4) Reduced brine pH resulting from addition of CO₂ will promote solid-phase dissolution of rock cores. (True). However, the experimental results do not show a clear relationship between net dissolution and temperature or net dissolution and fluid TDS. Greatest net dissolution was in the 50°C, 0.5 g L⁻¹ experiments, followed by 90°C, 5 g L⁻¹, then 90°C, 0.5 g L⁻¹, with 50°C, 5 g L⁻¹ showing the lowest net dissolution.

While some of the differences observed may result from core composition heterogeneity these results highlight the need for further studies to better understand the effects of primary variables such as temperature and TDS on supercritical CO₂-brine-rock interactions.
SUMMARY AND FUTURE DIRECTIONS

Summary

The key outcomes of this thesis are:

1) The successful development and testing of laboratory core-flooding technology for experimentally assessing potential effects of geologic carbon storage, including novel inline, in situ measurements of variable such as temperature, pressure, pH and EC.

2) Mixing supercritical CO₂ and brine significantly reduced brine pH under all tested conditions, however, this effect was partially buffered by an in line carbonate rock core. The buffering effect from dissolution of the carbonate core promoted further CO₂ dissolution into the brine.

3) Increasing brine TDS and temperature reduced CO₂ dissolution into brine without the rock core inline.

4) The experimental results do not show a clear relationship between net dissolution and temperature or net dissolution and fluid TDS.

These findings should be incorporated into improving geochemical models and in considering aquifer geochemistry prior to CO₂ injection.

Our apparatus provides the first reported in situ characterization of important aqueous phase geochemical properties (pH and EC) under simulated subsurface environmental conditions for the brine-rock-CO₂ system. Initial experiments for each experiment condition showed good reproducibility, demonstrating the robustness of this
new system. Overall the experimental apparatus performed as designed and is considered a successful evolution of high-pressure, high-temperature supercritical CO₂ core reactor technology as it expands on the types of data available for supercritical CO₂ core-flooding reactors.

The *in situ* monitoring demonstrated that *in situ* pH values resulting from supercritical brine CO₂ mixtures are up to 1 pH unit lower than either the bench top or modeled values at ambient conditions. The data indicate dissolution of Ca²⁺ and Mg²⁺ from the dolostone when using a 0.5 g L⁻¹ brine and preferential dissolution of Mg²⁺ when using the 5 g L⁻¹ brine. This highlights different dissolution behavior depending on brine concentrations, and/or possibly core composition heterogeneity, demonstrating the importance of experimentation in evaluating potential sequestration targets. The United States Environmental Protection Agency (US EPA) currently considers aquifers in excess of 10,000 ppm TDS permissible for CO₂ injection (US EPA, 2002) and thus may limit injection into the Madison Formation in the Powder River Basin. However, since increasing brine TDS altered the dissolution characteristics in these experiments, experimentation could be used to characterize the effects of CO₂ injection on Madison Formation rock and brine where TDS exceeds the EPA limit, for example in the Williston Basin, MT (Busby et al., 1995).

Dissolution and precipitation reactions in response to supercritical CO₂ addition to subsurface waters/brines has the potential to impact the deep saline aquifer geochemistry and may affect fluid flow characteristics. For example, mobilized ions dissolved in low pH solutions will likely precipitate away from CO₂ injection sites after the pH change has
been buffered, e.g. in carbonate systems. They may precipitate in formation pore throats and restrict flow in parts of the aquifer which may be compensated for by activation of unexpected flow paths in other parts of the aquifer system. These geochemical changes may be accompanied by geomechanical changes to the rock formations. While it is unrealistic to experiment every potential target for subsurface carbon storage experimentally, emphasis should be placed on experimentation in the near term to improve the applicability and efficacy of geochemical models. Improved geochemical models are key to evaluating the impacts of geological carbon sequestration on larger (basin wide) scales.

**Recommendations for Future Work**

While the core reactor system improves upon previous technology, further advances can be made. The current system cannot accurately assess very low flow rates. This could be improved by incorporating either an in-line flow-meter or redesigning the fluid delivery and collection systems to incorporate a high-accuracy, high-pressure, constant flow-rate pump, such as a Teledyne Isco model. Altering the system to accommodate multiple pH and EC probes could provide additional insight into chemical kinetics before, during, and after fluid injection into the rock cores. Incorporating pre- and post-experiment magnetic resonance imaging would provide insight into changes in porosity resulting from experimental CO\textsubscript{2}-brine exposure. Altering the system to allow for in situ permeability assessment, through high-resolution flow-rate and pressure drop measurements across the core, would provide more insight into the geomechanical effects
of reaction with supercritical CO₂. Such data would be important for larger scale carbon sequestration. The apparatus would also benefit from more frequent standard application and probe calibration.

Further experiments using additional rock-brine combinations in the core reactor system would help evaluate the efficacy of potential carbon storage targets as well as potential long-term effects, such as leakage potential, geomechanical effects, and formation brine chemistry changes. Longer-term experiments would help assess buffering capacity and dissolution/precipitation dynamics of the CO₂-brine-rock system. Our relatively short experiments indicate predominantly dissolution over five days, however some precipitation did appear evident in the higher temperature experiments.
REFERENCES CITED


APPENDICES
APPENDIX A

BRINE PREPARATION
Brines were prepared from the salts NaCl, MgSO₄, MgCO₃, and CaCl₂. HCl (0.1 M) was used to acidify brines to the desired final pH. Concentrated stock solutions of NaCl (3 M), MgSO₄ (1 M), and CaCl₂ (3 M) were prepared initially. The stock solutions were then used to make the final brine solutions. The following instructions were followed to produce brines used in Chapter 3. However, due to an omission during preparation, MgSO₄ was not added to the brines resulting in final brine concentrations of 0.5 and 5 g L⁻¹ measured by ICP-MS instead of the proposed 1 and 10 g L⁻¹.

The 5 g L⁻¹ brine was prepared as follows:-

- To a 1 L flask, add 500 mL water
- Add 11 mL NaCl stock solution, stir for 20 minutes
- Add 4 mL 0.1 M HCl, stir for 20 minutes
- Add 42.4 mg MgCO₃, stir for 20 minutes
- Add 11 mL CaCl₂ stock solution, stir for 1 hr
- If 5 g L⁻¹ brine is to be used as stock to make 0.5 g L⁻¹ brine, add 442 mL water to bring total to 1 L; otherwise add 432 mL water, acidify to pH 6.5, then add water to bring to 1 L

Target pH = 6.5 and EC = 15.5 mS cm⁻¹

To make 0.5 g L⁻¹ brine

Dilute 5 g L⁻¹ brine stock 1:10, acidify to pH 6.5

Target pH = 6.5 and EC = 1.55 mS cm⁻¹
Table A.1: Summary of laboratory produced brine chemistry. 5 g L\(^{-1}\) was made from concentrated stock solutions of NaCl, MgSO\(_4\).7H\(_2\)O, and CaCl\(_2\).2H\(_2\)O. Solid MgCO\(_3\) was added directly to the 5 g L\(^{-1}\) mix rather than using concentrated aqueous solution due to its low solubility. 0.5 g L\(^{-1}\) brine was made with a 1:10 dilution of the 5 g L\(^{-1}\) brine.

### Stock solutions

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<th>Species</th>
<th>Molarity</th>
<th>Molecular weight</th>
<th>Nonhydrous molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>3</td>
<td>58.50</td>
<td>58.50</td>
</tr>
<tr>
<td>CaCl(_2).2H(_2)O</td>
<td>3</td>
<td>147.07</td>
<td>129.05</td>
</tr>
<tr>
<td>HCl</td>
<td>0.1</td>
<td>45.57</td>
<td>45.57</td>
</tr>
<tr>
<td>MgCO(_3)</td>
<td>n/a</td>
<td>84.32</td>
<td>84.32</td>
</tr>
</tbody>
</table>

### 1 L 5 g L\(^{-1}\) brine

<table>
<thead>
<tr>
<th>Stock</th>
<th>mL stock added for 1 L of brine</th>
<th>TDS (g L(^{-1}))</th>
<th>Molarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.011</td>
<td>1.81</td>
<td>0.032</td>
</tr>
<tr>
<td>CaCl(_2).2H(_2)O</td>
<td>0.011</td>
<td>3.17</td>
<td>0.032</td>
</tr>
<tr>
<td>HCl</td>
<td>0.004</td>
<td>0.019</td>
<td>4E-4</td>
</tr>
<tr>
<td>MgCO(_3)</td>
<td>n/a</td>
<td>0.042</td>
<td>5E-5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>5.04</strong></td>
<td></td>
</tr>
</tbody>
</table>

### 1 L 0.5 g L\(^{-1}\) brine dilute 5 g L\(^{-1}\) brine 1:10

<table>
<thead>
<tr>
<th>Species</th>
<th>TDS (g L(^{-1}))</th>
<th>Molarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.18</td>
<td>0.003</td>
</tr>
<tr>
<td>CaCl(_2).2H(_2)O</td>
<td>0.32</td>
<td>0.003</td>
</tr>
<tr>
<td>HCl</td>
<td>0.002</td>
<td>4.E-05</td>
</tr>
<tr>
<td>MgCO(_3)</td>
<td>0.0042</td>
<td>5.E-06</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>0.56</strong></td>
</tr>
</tbody>
</table>

The 0.9 g L\(^{-1}\) brine used in the concept proof experiments was made with the salts NaCl, MgSO\(_4\), CaSO\(_4\).2H\(_2\)O, CaCl\(_2\), and MgCO\(_3\) in the following concentrations:

<table>
<thead>
<tr>
<th>Brine Solution</th>
<th>pH</th>
<th>Na(^+) (mmol)</th>
<th>Cl(^-) (mmol)</th>
<th>SO(_4^{2-}) (mmol)</th>
<th>Mg(^{2+}) (mmol)</th>
<th>Ca(^{2+}) (mmol)</th>
<th>HCO(_3^-) (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9 g L(^{-1})</td>
<td>6.5</td>
<td>1.0</td>
<td>0.7</td>
<td>6.4</td>
<td>1.6</td>
<td>4.1</td>
<td>0.05</td>
</tr>
</tbody>
</table>
APPENDIX B

IC DATA
Table B.1: IC cation data for experiments using version one of the experimental apparatus. Values are in mg L⁻¹. Triplicate analyses of single samples were analyzed as series labeled “a”, “b”, and “c.” The deionized water used to make brines and for all dilutions was analyzed as “DI H₂O blanks.” Initial brine chemistry was analyzed as “Stock.” NIST traceable standards were analyzed as “XX ppm NIST.”

<table>
<thead>
<tr>
<th>Label</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI H₂O blank</td>
<td>0</td>
<td>0.06</td>
<td>0.09</td>
<td>0.05</td>
</tr>
<tr>
<td>Stock 1:10 a</td>
<td>22.32</td>
<td>0.00</td>
<td>166.94</td>
<td>39.08</td>
</tr>
<tr>
<td>Stock 1:10 b</td>
<td>22.58</td>
<td>0.00</td>
<td>162.31</td>
<td>38.56</td>
</tr>
<tr>
<td>Stock 1:10 c</td>
<td>22.01</td>
<td>2.43</td>
<td>166.94</td>
<td>38.14</td>
</tr>
<tr>
<td>Day 1 a</td>
<td>138.72</td>
<td>9.70</td>
<td>144.90</td>
<td>117.93</td>
</tr>
<tr>
<td>Day 1 b</td>
<td>138.80</td>
<td>7.65</td>
<td>144.71</td>
<td>124.18</td>
</tr>
<tr>
<td>Day 1 c</td>
<td>137.48</td>
<td>11.07</td>
<td>144.93</td>
<td>119.39</td>
</tr>
<tr>
<td>Day 2 a</td>
<td>94.02</td>
<td>8.92</td>
<td>72.56</td>
<td>182.45</td>
</tr>
<tr>
<td>Day 2 b</td>
<td>93.45</td>
<td>8.96</td>
<td>67.10</td>
<td>180.16</td>
</tr>
<tr>
<td>Day 2 c</td>
<td>93.81</td>
<td>9.36</td>
<td>71.84</td>
<td>185.59</td>
</tr>
<tr>
<td>Procedure blank</td>
<td>0</td>
<td>0.00</td>
<td>1.26</td>
<td>1.22</td>
</tr>
<tr>
<td>10 ppm NIST</td>
<td>11.64</td>
<td>9.97</td>
<td>9.43</td>
<td>10.33</td>
</tr>
<tr>
<td>Day 3 a</td>
<td>28.47</td>
<td>4.00</td>
<td>159.66</td>
<td>266.11</td>
</tr>
<tr>
<td>Day 3 b</td>
<td>28.29</td>
<td>4.22</td>
<td>160.91</td>
<td>271.97</td>
</tr>
<tr>
<td>Day 3 c</td>
<td>28.85</td>
<td>4.92</td>
<td>156.07</td>
<td>0.82</td>
</tr>
<tr>
<td>Day 4 a</td>
<td>29.08</td>
<td>3.28</td>
<td>252.96</td>
<td>269.38</td>
</tr>
<tr>
<td>Day 4 b</td>
<td>29.81</td>
<td>4.20</td>
<td>251.45</td>
<td>276.31</td>
</tr>
<tr>
<td>Day 4 c</td>
<td>29.23</td>
<td>3.60</td>
<td>245.46</td>
<td>273.23</td>
</tr>
<tr>
<td>Day 5 a</td>
<td>28.14</td>
<td>2.91</td>
<td>143.76</td>
<td>257.25</td>
</tr>
<tr>
<td>Day 5 b</td>
<td>28.38</td>
<td>2.96</td>
<td>151.57</td>
<td>264.38</td>
</tr>
<tr>
<td>Day 5 c</td>
<td>28.43</td>
<td>2.61</td>
<td>147.88</td>
<td>261.01</td>
</tr>
<tr>
<td>Procedure blank</td>
<td>0</td>
<td>0.00</td>
<td>0.07</td>
<td>0.03</td>
</tr>
<tr>
<td>1 ppm NIST</td>
<td>1.12</td>
<td>0.92</td>
<td>0.83</td>
<td>0.91</td>
</tr>
</tbody>
</table>
Table B.2: IC anion data for experiments using version one of the experimental apparatus. Values are in mg L⁻¹. Label convention follows Table A.2.

<table>
<thead>
<tr>
<th>Label</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI H₂O blank</td>
<td>0</td>
<td>0.10</td>
</tr>
<tr>
<td>Day 1 a</td>
<td>237.47</td>
<td>621.27</td>
</tr>
<tr>
<td>Day 1 b</td>
<td>237.48</td>
<td>621.26</td>
</tr>
<tr>
<td>Day 1 c</td>
<td>237.37</td>
<td>620.70</td>
</tr>
<tr>
<td>Day 2 a</td>
<td>153.20</td>
<td>600.40</td>
</tr>
<tr>
<td>Day 2 b</td>
<td>153.17</td>
<td>600.91</td>
</tr>
<tr>
<td>Day 2 c</td>
<td>153.69</td>
<td>602.68</td>
</tr>
<tr>
<td>Day 3 a</td>
<td>37.41</td>
<td>553.67</td>
</tr>
<tr>
<td>Day 3 b</td>
<td>37.49</td>
<td>554.38</td>
</tr>
<tr>
<td>Day 3 c</td>
<td>37.59</td>
<td>555.14</td>
</tr>
<tr>
<td>Day 4 a</td>
<td>39.00</td>
<td>574.93</td>
</tr>
<tr>
<td>Day 4 b</td>
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<td>574.99</td>
</tr>
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<td>Day 4 c</td>
<td>39.12</td>
<td>575.24</td>
</tr>
<tr>
<td>Day 5 a</td>
<td>32.27</td>
<td>592.11</td>
</tr>
<tr>
<td>Day 5 b</td>
<td>32.40</td>
<td>594.51</td>
</tr>
<tr>
<td>Day 5 c</td>
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<td>591.51</td>
</tr>
<tr>
<td>Procedure blank</td>
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<td>0</td>
</tr>
<tr>
<td>Stock a</td>
<td>2.56</td>
<td>61.34</td>
</tr>
<tr>
<td>Stock b</td>
<td>2.56</td>
<td>61.30</td>
</tr>
<tr>
<td>Stock c</td>
<td>2.57</td>
<td>61.45</td>
</tr>
<tr>
<td>5 ppm NIST</td>
<td>4.27</td>
<td>4.66</td>
</tr>
<tr>
<td>1 ppm NIST</td>
<td>0.78</td>
<td>0.90</td>
</tr>
<tr>
<td>DI H₂O blank</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table B.3: Change in ion concentration data used in Figure 2.3. These are averages of triplicate analyses in mg L⁻¹ and normalized to the initial concentration of the solution to plot as deviations rather than measured values.

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>24</td>
<td>125.83</td>
<td>-25.63</td>
<td>277.42</td>
<td>168.38</td>
<td>1.62</td>
</tr>
<tr>
<td>48</td>
<td>77.49</td>
<td>-118.35</td>
<td>488.20</td>
<td>101.54</td>
<td>-2.67</td>
</tr>
<tr>
<td>72</td>
<td>6.76</td>
<td>-8.13</td>
<td>780.53</td>
<td>9.45</td>
<td>-12.85</td>
</tr>
<tr>
<td>96</td>
<td>7.67</td>
<td>105.46</td>
<td>793.85</td>
<td>10.71</td>
<td>-8.37</td>
</tr>
<tr>
<td>120</td>
<td>6.52</td>
<td>-22.02</td>
<td>752.89</td>
<td>5.32</td>
<td>-4.54</td>
</tr>
</tbody>
</table>
APPENDIX C

ICP-MS DATA
Table C.1: ICP-MS data. Only Na\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) are reported. Values are in µg L\(^{-1}\). “Bql” denotes analyses that were below the apparatus quantification limit. “N.d” denotes analytes were not detected. Procedural blanks were analyzed labeled “blank.” Standards were analyzed as “aa/bb Optima.”, where aa = concentration in ppm and bb = concentrations in ppb. Experiment samples were labeled “Xg YY ZZ” where X denotes brine concentration, YY denotes experiment temperature, and ZZ denotes sample number.

<table>
<thead>
<tr>
<th>Element</th>
<th>Na(^+)</th>
<th>Mg(^{2+})</th>
<th>Ca(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit</td>
<td>1.4</td>
<td>25</td>
<td>3.4</td>
</tr>
<tr>
<td>lower quantification limit</td>
<td>10.3</td>
<td>31</td>
<td>25</td>
</tr>
<tr>
<td>upper quantification limit</td>
<td>55000</td>
<td>55000</td>
<td>55000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>Na(^+)</th>
<th>Mg(^{2+})</th>
<th>Ca(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>13</td>
<td>n.d.</td>
<td>35</td>
</tr>
<tr>
<td>blank bql</td>
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<td></td>
<td></td>
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<tr>
<td>blank n.d.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01/1 Optima</td>
<td>10</td>
<td>n.d.</td>
<td>bql</td>
</tr>
<tr>
<td>0.1/10 Optima</td>
<td>34</td>
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<td>bql</td>
</tr>
<tr>
<td>0.5/50 Optima</td>
<td>44</td>
<td>71</td>
<td>60</td>
</tr>
<tr>
<td>1/100 Optima</td>
<td>93</td>
<td>134</td>
<td>124</td>
</tr>
<tr>
<td>5/500 Optima</td>
<td>518</td>
<td>489</td>
<td>495</td>
</tr>
<tr>
<td>10/1000 Optima</td>
<td>1051</td>
<td>988</td>
<td>1024</td>
</tr>
<tr>
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<td>4820</td>
<td>4801</td>
<td>4850</td>
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</tr>
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<tr>
<td>0.5g 90 02</td>
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<td>407</td>
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<tr>
<td>0.5g 90 03</td>
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<td>299</td>
<td>6472</td>
</tr>
<tr>
<td>50/5000 Optima</td>
<td>5035</td>
<td>5006</td>
<td>5201</td>
</tr>
<tr>
<td>----------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
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</table>
Table C.2: ICP-MS data used for Figure 3.6. Data were converted to mg L\(^{-1}\) and normalized to the initial concentration of the 0.5 and 5 g L\(^{-1}\) solutions respectively to plot as deviations rather than measured values. Label convention follows Table C.1.

<table>
<thead>
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APPENDIX D

APPARATUS PARTS LIST
Table D.1: Major experimental apparatus components grouped by supplier

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<th>Item</th>
<th>Part number</th>
<th>Quantity</th>
<th>Description</th>
<th>Vendor</th>
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<tr>
<td>EC sensor</td>
<td>BV CX 547 S</td>
<td>1</td>
<td>Sensor for EC probe</td>
<td>Barben Analyzer Technology</td>
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<tr>
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<td>2402COND</td>
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<td>EC meter and transmitter</td>
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<td>pH sensor cartridge</td>
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<td>pH meter and transmitter</td>
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<td>1 L high pressure fluid accumulators</td>
<td>Calkins Fluid Supply</td>
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<td>Gas chuck flow controller assembly</td>
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<td>Adapters for accumulator thread to NPT</td>
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<td>ACL-1</td>
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<td>COM310</td>
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<td>Voice synthesizer for alarm system</td>
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<td>Logger multiplexer</td>
<td>AM16/32A</td>
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<td>PS100-SW</td>
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