

Geochemical Impacts of Sequestering Carbon Dioxide in Brine Formations

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The purpose of this chapter is to lay out potential geochemical impacts of geologic sequestration. Injection of supercritical carbon dioxide into a brine aquifer shifts rock-dominated reaction systems to fluid-dominated systems controlled by acid-generating reactions and mixed-fluid equilibria. Increased carbonic acid content in the brine reduces the pH of *in-situ* brine by approximately 1.5 to 4 pH units, depending on brine chemistry, formation lithology, and temperature, to a pH value between 3.5 and 4. Alkalinity is also produced by reaction of carbonic acid with reservoir minerals, but alkalinity of *in-situ* brine cannot overcome the acidity produced by dissolution of supercritical carbon dioxide fluid. Analysis suggests that displacement of brine as injection proceeds will lead to separation from supercritical carbon dioxide fluid and loss of saturated carbon dioxide, wherein alkalinity can neutralize the acidity, yielding near-neutral to alkaline pH. Silica concentrations and dissolution rates will become enhanced and silica precipitation inhibited in acidic brine. Acidified brine will also react with both reservoir rock and caprock, enriching the brine in metal cations and creating alkalinity. As silica-supersaturated, metal-laden brine migrates into areas without CO₂, *in-situ* monitoring can be used to indicate repository performance. Return of silica super-saturated brine to a rock-dominated reaction system buffered to neutral pH conditions may enhance precipitation of quartz, chalcedony, or amorphous silica. Reaction kinetics among supercritical carbon dioxide, brine, and rock are comparable to rates in systems containing gaseous carbon dioxide.

1. INTRODUCTION

A promising approach to the problem of managing anthropogenic carbon is to dispose of CO₂ in deep brine formations. As discussed in other chapters of this volume, retention of CO₂ presumably occurs by one or more mechanisms [*Bachu et al.*, 1994]: hydro stratigraphic trapping, solubility trapping (dissolution) residual gas trapping, and mineral trapping (precipitation). This chapter focuses specifically on mineral trapping and related processes.

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A geologic repository for CO₂ will be a complex structural and stratigraphic package exhibiting diverse geochemical environments, groundwater chemistries, reservoir and caprock lithologies, facies transitions, *etc.* It will span a range of depths for emplacement and subsequent movement of CO₂ and therefore a range of pressures and temperatures. Pressures may range from a few MPa where CO₂ has migrated into a shallow formation, to several tens of MPa within the initial zone of emplacement, depending on in situ porosity, permeability, and injection rate. Temperatures may range from approximately 40°C to as high as 150 or 200°C, depending on local and regional geothermal gradients [Bachu, 2002, 2003].

The world's first anthropogenic geologic repository for CO₂ was Statoil's commercial-scale Sleipner project in the North Sea [Portier and Rochelle, 2005]. Nearly a million tons of CO₂ from natural gas production has been injected annually into a brine aquifer, the Utsira Formation. Seismic surveys and other technologies are used to monitor the disposition of the injected CO₂. In a sequestration pilot project in the U.S. Gulf Coast [Kharaka *et al.*, 2006], approximately 1600 tons of CO₂ was injected into a brine aquifer, the Frio Formation. Geochemical data were collected to assess reactions and processes associated with the injected CO₂. With few field examples to draw on, enhanced oil recovery (EOR) using CO₂ offers a reasonable means to evaluate multiphase (CO₂-H₂O) fluid-rock reactions and processes. While CO₂-hydrocarbon interactions complicate matters, no other field examples provide reasonably quantitative yet temporally comprehensive geochemical datasets. EOR will also provide initial commercial-scale sequestration until brine formations can be developed. Two examples of EOR projects that use CO₂ and have suitable geochemical datasets are the Weyburn Oil Field in Saskatchewan, Canada [Emberley *et al.*, 2005] and the Rangely field in Colorado, USA [Hefner and Barrow, 1992].

The purpose of this paper is to evaluate potential geochemical impacts of sequestering CO₂ in brine formations. The geochemical behavior of this system will defy simple assumptions and predictions because the reactions and kinetics involve two immiscible fluid phases, supercritical CO₂ and brine, as well as a variety of minerals in the aquifer and the caprock. Laboratory and computational experiments provide a means to evaluate the reactive behavior of the mixed fluid-rock system. We combine insight gleaned from published and ongoing laboratory and computational experiments as well as published field studies of the Frio Formation and the Weyburn and Rangely EOR projects.

2. GEOCHEMICAL PROPERTIES OF SUPERCRITICAL CARBON DIOXIDE

Geologically relevant fluids may exist in a supercritical state above a unique critical temperature and pressure. In this state, the fluid possesses properties of both gas and liquid. H₂O is a supercritical fluid above 374.2°C and 22.05 MPa, whereas CO₂ is a supercritical fluid at much lower conditions (31.1°C and 7.38 MPa) [Span and Wagner, 1996]. In mixtures of CO₂ and H₂O, single and multiple phases comprised of gas-, liquid-, and supercritical-rich regions can exist in equilibrium. At the temperatures, pressures, and CO₂-rich conditions necessary for a carbon repository, two phases will predominate: a supercritical fluid rich in CO₂ and a coexisting liquid rich in H₂O (Figures 1 and 2). A one-phase region in which a single CO₂-H₂O supercritical fluid exists will occur at extreme CO₂-H₂O compositions, high temperature, or high pressure. NaCl (and other salts) in the aqueous fluid will shift the phase boundaries to higher temperature and pressure [Takenouchi and Kennedy, 1965; Bowers and Helgeson, 1983a, 1983b; Gehrig *et al.*, 1986; Portier and Rochelle, 2005], expanding the stability field at which two fluids co-exist.

The mutual solubility of CO₂ and H₂O (Figures 1 and 2) may initiate physical-chemical processes such as brine desiccation and enrichment in dissolved metals [Kaszuba *et al.*, 2003]. Concomitant density contrasts and ensuing gravitational instability and convective mixing are now being scrutinized [Xu *et al.*, 2006]. Chemical fractionation within brine and localized micro-environments of high ionic strength at the supercritical CO₂-brine interface are also possible. Fluid-rock reactions at these interfaces may differ from reactions in the bulk system.

3. GEOCHEMICAL CHANGES IN BRINE FORMATIONS

3.1. Rock- vs. Fluid-Dominated Reaction Systems

Deep, brine formations are generally not exposed to fresh recharge or sources of acidity. The aqueous geochemistry of these deep formations is therefore controlled by reaction with the component minerals (carbonate, silicate, and alumino-silicate) of the aquifer. These types of formations are known as rock-dominated systems [Langmuir, 1997]. On the other extreme are aquifers replenished by fresh water recharge. The fluid is the predominant control of aqueous geochemistry in these systems, known as fluid- or water-dominated systems.

Brine formations that are candidates to host a carbon repository will be rock-dominated reaction systems prior to adding anthropogenic CO₂. Following emplacement of supercritical CO₂, these rock-dominated brine aquifers will

become fluid-dominated reaction systems in which acid-dominated and related reactions are controlled by mixed-fluid ($\text{CO}_2\text{-H}_2\text{O}$) equilibria. This fundamental change from rock to fluid control triggers almost all of the emergent geochemical phenomena in a brine-hosted carbon repository. For a brine-rock system into which anthropogenic CO_2 is abruptly introduced, perturbation of on-going reactions will profoundly change the manner in which the geochemistry of the system ultimately evolves.

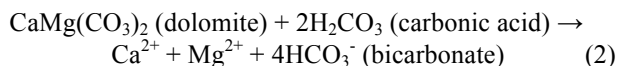
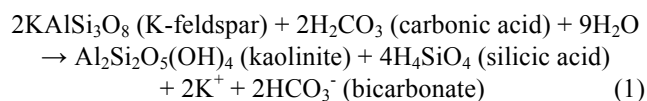
3.2. pH and Alkalinity

Emplacing supercritical CO_2 into a brine formation shifts the carbonic acid equilibria of the fluid-rock system. Computational [Gunter *et al.*, 2000] and laboratory [Kaszuba *et al.*, 2003, 2005a] experiments demonstrate that adding supercritical CO_2 to a brine-rock (siliciclastic aquifer plus aquitard) system increases the aqueous carbonic acid content, thereby decreasing the pH of the *in-situ* brine (Figure 3). The pH decreases to a value between approximately 3.5 and 4, depending on brine chemistry, formation lithology, and temperature.

In computational experiments [Gunter *et al.*, 2000], brine pH subsequently increases once simulated injection stops, supercritical CO_2 fully dissolves, and aqueous CO_2 is consumed by mineral reactions. Brine pH also increases in laboratory experiments [Kaszuba *et al.*, 2003, 2005a] after brine separates from supercritical CO_2 , depressurizes, cools, and exsolves saturated CO_2 , such as would happen with migration of acidified brine into areas without CO_2 present. In both computational and laboratory experiments, pH becomes approximately 0.5 to 1 pH units greater than pH in the starting (pre-injection) brine (Figure 3). This counterintuitive pH behavior is illustrated in Figure 4, wherein brine pH is separately plotted as a function of aqueous CO_2 and temperature. In this example, *in-situ* brine equilibrated with supercritical CO_2 and rock at reservoir conditions contains approximately 300 millimolar (mM) aqueous CO_2 . The pH of this brine increases from 3.5 to 5.7 upon separation of brine from supercritical CO_2 and subsequent release of dissolved CO_2 , then to 6.7 as the degassed brine cools to 25°C (equivalent to less than 1 km depth in most areas). This pH behavior is in marked contrast with brine that has equilibrated with rock, but not supercritical CO_2 , at reservoir conditions. Significantly less aqueous CO_2 is dissolved in this brine, approximately 0.09 mM. The pH of this brine (4.9) increases to 5.5 with the release of its dissolved CO_2 , then to 5.9 as the brine cools to 25°C .

Why does pH exhibit this seemingly anomalous behavior? That is, why does the pH of acidified, carbonated brine rebound to a value that is higher than pre-injection pH? Supercritical CO_2 fluid provides a reservoir for generating carbonic acid that is orders-of-magnitude

greater than comparable volumes of CO₂ gas. Subsequent reaction with aluminosilicate or carbonate minerals produces significant alkalinity, for example:



Alkalinity of the *in-situ* brine cannot overcome the acidity within the repository that was produced by dissolution of supercritical CO₂ fluid. But separating brine from the supercritical CO₂ and the prevailing chemical potential of carbonic acid, imposed by multi-phase conditions, permits alkalinity in the brine to neutralize the acidity, yielding near-neutral pH.

Are the processes predicted by these laboratory and computational experiments observed in the field? Enhanced oil recovery (EOR) in the Rangely field, a clastic sandstone reservoir (Permian Weber Sandstone), began in October 1986 with a water-alternating-CO₂ process [Bowker and Shuler, 1991; Hefner and Barrow, 1992; Klusman, 2003a; 2003b]. The average reservoir temperature is 56°C and reservoir pressure since CO₂ injection began is a minimum of 17.9 MPa. *In-situ* brine pH of 3.5 was measured at the injection well during injection [Bowker and Shuler, 1991], a value consistent with laboratory and computational predictions. Pre- and post-CO₂ injection pH measured at the wellhead are not in good agreement with predictions, as these were measured at 7.0 to 7.5 (pre-injection) and 6.5 (post-injection) [Bowker and Shuler, 1991]. Bicarbonate increased from a pre-CO₂ injection concentration of about 500 milligrams per liter (mg/L) to about 1250 mg/L within 6 months after CO₂ injection began [Bowker and Shuler, 1991] to about 4000 mg/L about 12 years after injection began [Klusman, 2003b].

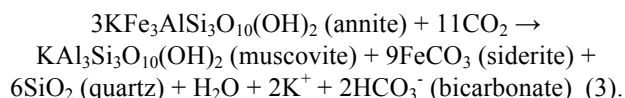
In the Weyburn Oil Field, a carbonate reservoir (Mississippian Midale Formation), EOR began in 2000 with a water-alternating-CO₂ injection process [Emberley *et al.*, 2005]. Reservoir temperature and pressure prior to CO₂ injection were 60°C and 14.6 MPa. Brine samples were collected immediately prior to CO₂ injection and 6, 10, and 12 months after injection began. *In-situ* brine pH was not measured, but baseline wellhead pH ranged from 6.5 to 7. Wellhead pH in samples collected at 6 months decreased by about 0.5 to 0.6, to a pH of 5.9 to 6.4. Wellhead pH in samples collected at 10 and 12 months increased to 6.8 to 7.6, trends consistent with laboratory and computational predictions. Baseline alkalinity ranged from 300 to 700 mg/L, with up to 50% of this alkalinity due to dissolved sulfide. Alkalinity increased in samples

collected at 6 months (500 to >1400 mg/L), then decreased in samples collected at 10 and 12 months (400 to 900 mg/L). This trend suggests continued reaction with reservoir minerals.

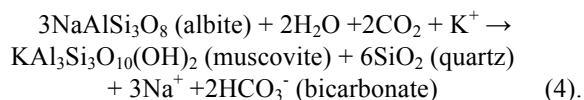
CO₂ injection in the Frio Formation, a subarkosic sandstone, spanned 10 days in 2004 [Kharaka *et al.*, 2006]. In wellhead samples collected at an observation well located 30 meters from the injection well, pH decreased from 6.7 to 5.6 about 3 days after injection began. Bicarbonate in these same samples increased from about 100 to 3000 mg/L.

3.3. Silica

Acid-dominated and related reactions will consume silicate minerals, produce secondary silicate assemblages, and liberate silica. Computational and experimental simulations [Perkins and Gunter, 1995; Gunter *et al.*, 1997; Gunter *et al.*, 2000] of the siliciclastic Glauconitic Sandstone brine aquifer (ionic strength 2.9 molal), Alberta Basin suggest that CO₂ injection produces carbonate and quartz from aluminosilicate:



Ca- or Mg-bearing aluminosilicates would react in similar fashion to consume CO₂ and precipitate calcite, dolomite, or magnesian carbonate minerals plus quartz [Gunter *et al.*, 2000]. Other reactions will consume albite or K-feldspar plus CO₂ to produce quartz, for example:



In addition to liberating silica, the acidity of these fluid-dominated systems accelerates fluid-silicate reaction rates, enhances silica solubility, and inhibits quartz precipitation (Figure 5).

Silica super-saturation and inhibition of quartz precipitation at low pH are also observed in the mixing of high-temperature hydrothermal fluid and seawater at mid-ocean ridge vents [Janecky and Seyfried, 1984]. These phenomena were attributed to kinetics of silica polymerization and precipitation under low pH conditions, assumptions consistent with experimental results [Icopini *et al.*, 2005] and the analytical practice of dilution to below amorphous silica saturation and acidification. Vent fluids at ultramafic rock-hosted, mid-ocean ridge hydrothermal systems exhibit relatively high aqueous silica (2 to 5 mM) and low pH (5 to 5.3) despite olivine-undersaturation that would presumably yield low silica. In comparison, within

the carbonate reservoir at Weyburn, CO₂ injection increased aqueous silica from 0.2 to 0.8 mM silica to 0.4 to 2 mM [Emberley *et al.*, 2005], a trend consistent with experimental predictions (Figure 5).

Metastable silicate reactions and buffering by silica-rich phases are clearly important in disparate geochemical systems, from mid-ocean ridge hydrothermal systems to carbonate oil reservoirs, in which silica is generally perceived as insignificant. Reaction of silica supersaturated brine with a rock-dominated reaction system buffered to neutral pH may occur by displacement of brine to a shallower crustal level. Even without such mass transfer, reactions will consume CO₂ on geologic time scales and the rock will ultimately reassert geochemical control. Consequent precipitation of quartz, chalcedony, or amorphous silica as veins or permeability-altering cements underscores the importance of understanding the role of silica in a multiphase (CO₂-H₂O) fluid-rock system.

3.4. Metals

In laboratory experiments, carbonated acidified brine reacts with siliciclastic reservoir rock and caprock to enrich the brine in Ca, Mg, and Mn by approximately one order-of-magnitude, and Fe by two orders-of-magnitude, as measured in the sampling event held 72 hours after injection of CO₂ [Kaszuba *et al.*, 2003, 2005a]. In the Rangely EOR project, CO₂ injection produced notably similar increases for these metals [Bowker and Shuler, 1991]. The CO₂ sequestration pilot project in the Frio Formation exhibited similar increases for Fe and Mn within 3 days after CO₂ injection began [Kharaka *et al.*, 2006].

Could heavy metals be dissolved into brine by reaction of rock (aquifer and caprock) with acidic brine and supercritical CO₂? Would trace metals behave in like fashion? Naturally-occurring organic ligands can function as chelating agents and form organometallic complexes, compounds that significantly increase metals solubility in supercritical CO₂ [Burford *et al.*, 1999; Mochizuki *et al.*, 2000]. Since organic compounds and organometallic complexes are important in sedimentary basin waters and oilfield brines [Seward and Barnes, 1997], the brine aquifers and caprock that host a carbon repository may also experience enhanced solubility and result in extraction of metals with supercritical CO₂. The potential for enhanced metals dissolution with organometallic complexes is so great that industrial research focuses on this subject, with the ultimate goal of developing production-scale extraction processes. Supercritical CO₂ fluids also have significant potential to penetrate complex geometries inaccessible to aqueous fluid in order to dissolve and redistribute metals as organometallic compounds [Kaszuba *et al.*, 2005b]. The added complexities that supercritical CO₂ fluids bring to fluid-rock systems remain key research problems.

4. REACTIVITY OF A SUPERCRITICAL CARBON DIOXIDE-BRINE-ROCK SYSTEM

Once supercritical CO₂ is injected into a brine aquifer, how long does it take to carbonate and acidify the brine and induce subsequent chemical reactions within reservoir rock? In other words, how rapid is the shift from a rock-dominated to a fluid-dominated reaction system? In closed system laboratory experiments, we recreated the geochemical conditions of a carbon repository at steady state, wherein brine, rock, and supercritical CO₂ coexist. We estimated relative kinetic rates by measuring the pressure changes accompanying injection of supercritical CO₂ into ongoing brine-rock reactions (Figure 6). Following an initial pressure increase (5.8 MPa) due to injection of CO₂ into a steady state brine-rock (siliciclastic aquifer and illite-rich shale caprock) system at 20 MPa, pressure decreases 2.4 MPa within 40 hours and subsequently remains stable at approximately 23 MPa for the life of the experiment. The pressure decrease is interpreted as consumption of supercritical CO₂ fluid by rapid dissolution into brine. Formation and dissociation of carbonic acid follows, with subsequent, kinetically slower reaction between acidified brine and siliciclastic rocks producing siderite. To enhance reaction at the laboratory scale, experiments were performed at the upper end of the temperature spectrum expected for carbon repositories (200°C). Reaction between supercritical CO₂ and brine exhibits relatively rapid kinetics (Figure 6) that are similar in magnitude to rates of CO₂ gas dissolution in seawater.

Numerical studies of the Glauconitic Sandstone brine aquifer in Alberta emulate the prevailing conditions after injection of CO₂ had ceased [Gunter *et al.*, 2000]. Initial CO₂ pressure decreases from approximately 8.7 to 0.002 MPa, also concurrent with observed siderite precipitation. Carbonate precipitation and concomitant pressure decreases take place within 18 years, even though the system continues to react and requires hundreds of years to reach equilibrium. The details of kinetic reaction rates in these systems are important research needs for general and site specific evaluation of mineral trapping sequestration.

5. SUMMARY AND CONCLUSIONS

Laboratory and computational experiments, in combination with EOR field studies and pilot sequestration projects, provide geochemical data for evaluating the reactive behavior of multiphase (CO₂-H₂O) fluid-rock systems in a carbon repository. Based on our analyses and results we suggest the following potential geochemical impacts of CO₂ sequestration in deep brine reservoirs:

1. Addition of supercritical CO₂ to a brine aquifer changes reactions in the system from rock- to fluid-

dominated. Within a carbon repository, injected CO₂ will exert control over geochemical reactions previously regulated or buffered by host rock. Acid-base reactions and solubility of metals will depend on interactions between supercritical CO₂ and brine, with the rock responding to new equilibrium pressures.

2. Dissolution of supercritical CO₂ generates carbonic acid, thereby decreasing the pH of *in-situ* brine and simultaneously increasing brine alkalinity by reaction with aluminosilicate or carbonate minerals. Eventual migration of acidified brine into areas without CO₂ induces exsolution of CO₂, permitting the alkalinity to neutralize acidity and increasing pH to near-neutral values.
3. The silicate matrix of siliciclastic and mafic rock formations and the small amounts of silicates in carbonate formations are significant reactive components of a carbon repository. Precipitation of crystalline or amorphous silica from silica-supersaturated brine may accompany migration of fluid within and from a repository. Enhancement in silica precipitation could armor and protect flow paths or plug them.
4. Reaction among supercritical CO₂, brine, and rock exhibits relatively rapid kinetics that are similar to rates measured in systems containing gaseous CO₂.
5. To determine repository performance (*i.e.*, monitoring, mitigation, and verification in the vernacular of the CO₂ sequestration community), comprehensive water chemistries must be determined in brine sampled from proximate aquifers and wells, including alkalinity, silica, and metals (major and trace) analyses. Simple pH measurements are potentially misleading because of sampling complexities and counterintuitive pH behavior in brine. In addition, a range of potential mineral reactions may occur along transport paths and affect pH. Such misleading pH measurements are particularly possible if the brine is not sampled with a device that preserves *in-situ* conditions.

6. IMPORTANT DIRECTIONS FOR FUTURE WORK

Success in sequestering CO₂ will depend on understanding, predicting, and measuring a variety of geochemical reactions and processes. We recommend the following as important directions for future work:

1. Characterize geochemical reaction and hydrogeologic transport processes in a multiphase (CO₂-H₂O) fluid-rock system. How do supercritical CO₂ fluids interact with brine, reservoir rock, and caprock to influence fluid-rock reactions? Given that supercritical CO₂ is used as a “green” solvent in industry, can we expect geochemical reactions to take place within

- supercritical CO₂ fluid itself, with and/or without water films?
2. Evaluate historic data for EOR projects as a basis for comprehensive understanding of reaction and transport processes in hydrocarbon-CO₂-brine-rock systems over extended time frames.
 3. Characterize the influence of supercritical CO₂ on the organic geochemistry and biogeochemistry of subsurface systems. Can supercritical CO₂ dissolve and redistribute metals as organometallic compounds? What are the effects, beneficial or deleterious, of supercritical CO₂ on subsurface geomicrobiology?
 4. Characterize cement chemistry and potential mechanisms of cement degradation in well bores under physical-chemical conditions of a carbon repository.
 5. Characterize interrelationships between geochemistry and mechanical properties (rock mechanics) of subsurface systems. Reactions among supercritical CO₂, brine, aquifer, aquitard, and well bores may lead to a number of geomechanically beneficial or deleterious consequences. Can competency contrasts develop between a carapace of reacted material and an unreacted periphery? Would such zones lead to loss of system integrity or would they be inherently self-healing? Can we observe and measure multiphase (CO₂-H₂O) fluid flow in fractures and predict fracture evolution with time? Fundamental laboratory and field observations and underlying theoretical explanations of relevant phenomena are needed.
 6. Translate an understanding of multiphase (CO₂-H₂O) fluid-rock reactions and processes into design of advanced geochemical, hydrological, geomechanical, and geophysical measurement technologies to monitor subsurface processes and verify system behavior for relevant time scales (10s to 1000s of years).
 7. Address challenges of temporal and spatial scaling, both up- and down-scaling, that have plagued the earth sciences for decades. How can we reliably extrapolate results of laboratory and computational experiments to relevant geologic time and distance? What are relevant pore and intermediate (meter) scale processes and how can they be reliably extrapolated to an understanding of basin scale processes?
 8. Determine scientifically-rigorous leakage rates for carbon repositories in the context of a) the weathering cycle and its ability to consume “excess” CO₂; and b) time scales of transition between fluid- and rock-dominated reaction systems.
 9. Identify and evaluate “non-traditional” natural analogues (*e.g.*, thermal aureoles in siliceous carbonate rocks) and natural CO₂ reservoirs for evidence of sequestration mechanisms, CO₂ residence time, and failure modes.

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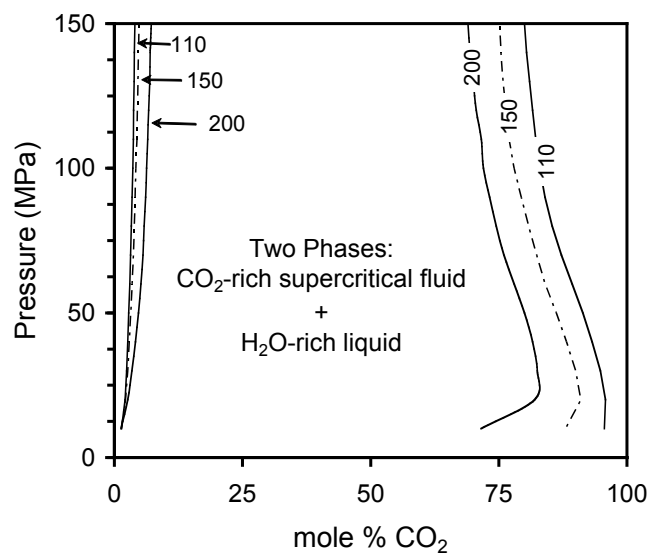


Figure 1. Pressure-XCO₂ diagram depicting fluid compositions for the system CO₂-H₂O [Takenouchi and Kennedy, 1964]. Solvi for maximum pressures (150 MPa) and temperatures (200°C) expected for most carbon repositories are depicted. The data of Takenouchi and Kennedy [1964] was selected as internally consistent for these pressures and temperatures, as discussed by Blencoe *et al.* [2001]. Solvi mark regions where two phases - a supercritical fluid rich in CO₂ and a liquid rich in H₂O - exist. The solvus (consolute curve) at 150°C is presented as a dashed line for clarity.

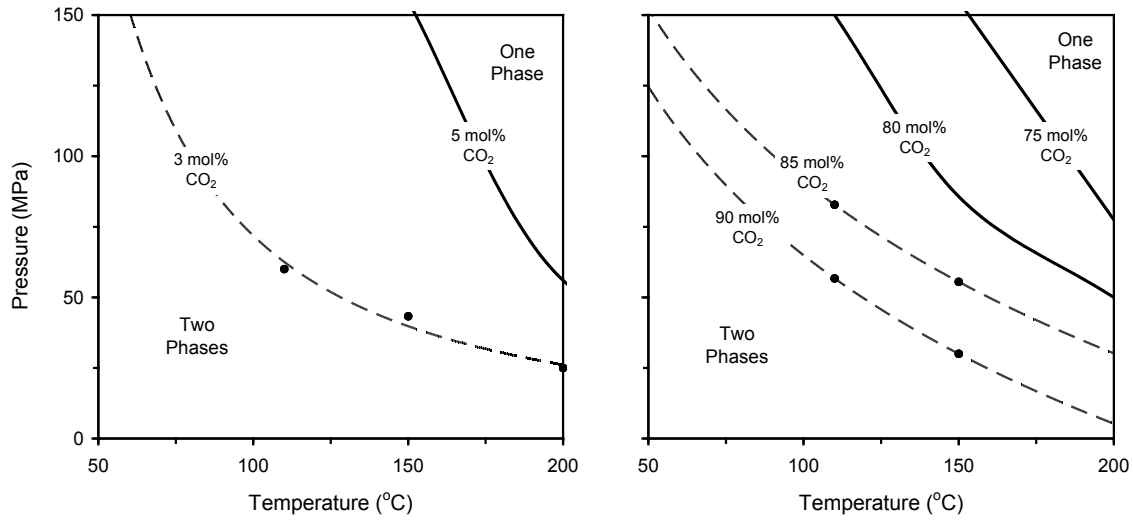


Figure 2. Pressure-temperature diagrams contoured for fluid compositions in the H₂O-rich (left) and CO₂-rich (right) portions of the solvii depicted in Figure 1. Dashed lines denote extrapolations from the *Takenouchi and Kennedy* [1964] dataset. At the range of CO₂ conditions expected for a carbon repository, two phases will predominate, a supercritical fluid rich in CO₂ and a coexisting liquid rich in H₂O.

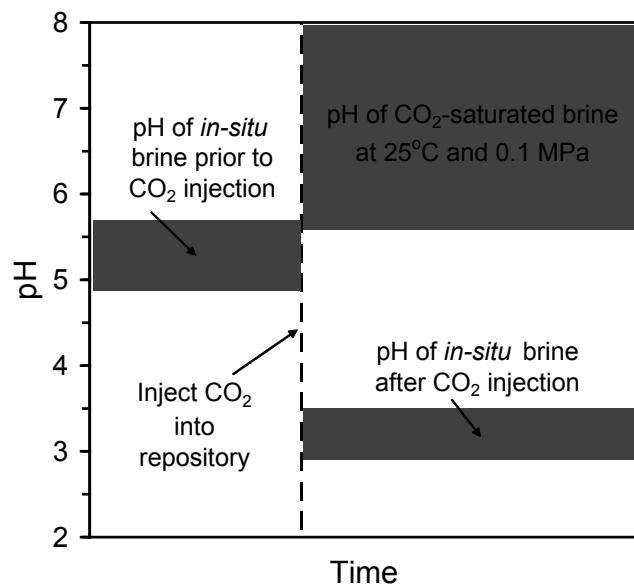


Figure 3. Summary of pH behavior in laboratory analogues of a carbon repository. Injection of supercritical CO₂ into ongoing reactions of brine, reservoir rock (arkose), and caprock (shale) decrease pH of *in-situ* brine from approximately 5.0 to 3.5 or 4 [Kaszuba *et al.*, 2003, 2005a]. CO₂-saturated brine that migrates to shallower crustal levels cools and degasses, yielding near-neutral pH. Analogous behavior is observed in computer simulations of a siliciclastic reservoir in the Alberta Basin [Gunter *et al.*, 2000], where initial reservoir pH of 7.2 decreases to approximately 2.9 after CO₂ is injected, then increases to 8.0 after injected CO₂ is fully dissolved and consumed by reaction.

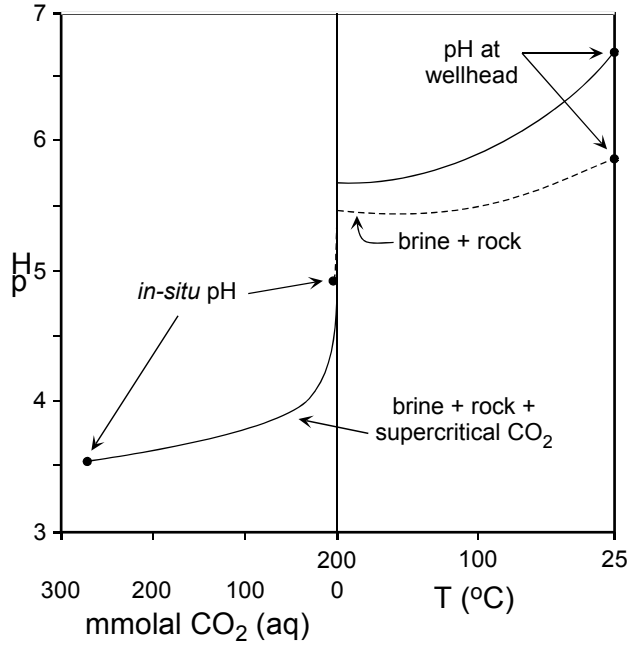


Figure 4. Sequential pH behavior in laboratory analogue for a carbon repository in which brine migrates from the repository into overlying aquifers. The left half of the diagram illustrates changes in brine pH as a function of CO₂ content in the brine, the right half illustrates pH changes as a function of temperature. The solid line represents brine, initially in contact with supercritical CO₂ and the host aquifer (arkose plus shale caprock), that sequentially degasses and cools with emplacement to a shallower crustal level. Brine pH increases from 3.5 to 5.7 with release of CO₂, then to 6.6 with cooling. The dashed line represents brine that is initially at steady state with the same aquifer but without supercritical CO₂. Sequential cooling that accompanies brine migration in this system increases pH from approximately 5.5 to 5.8. Note the largest pH change during cooling occurs between 25 and 75°C, the temperature range expected for most carbon repositories. Changes in brine pH were calculated using the computer code FLOTRAN [Lichtner, 2001], the Pitzer association model [Pitzer, 1987], and brine chemistries from the experimental work of Kaszuba *et al.* [2005a].

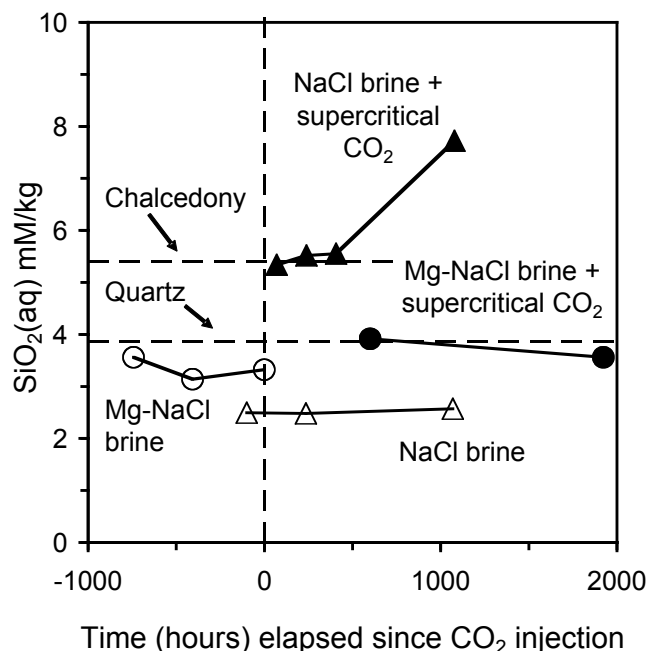


Figure 5. Behavior of silica in laboratory analogues for a carbon repository. Supercritical CO₂ was introduced into a steady state brine-rock reaction at time zero on the abscissa (also denoted by vertical dashed line). The rock is comprised of a siliciclastic aquifer and an illite-rich shale caprock. SiO₂(aq) is illustrated for two different brines representing a range of reaction potential among rock, brine, and supercritical CO₂. Na, Mg, and K are the predominant cations and Cl the predominant anion in the Mg-NaCl brine (open and filled circles), emphasizing reaction between supercritical CO₂ and brine. The NaCl brine (open and filled triangles) initially contains Na and Cl only and is devoid of metal cations, emphasizing reaction among fluids and rock. The solid lines connecting open symbols represent brine that is at steady state with the host aquifer without injection of supercritical CO₂. Solid lines connecting filled symbols represent brine after supercritical CO₂ is injected into the brine-aquifer system at temperature (200°C) and pressure (20 MPa). Horizontal dashed lines are calculated solubilities of chalcedony and quartz. Uncertainties are approximately the thickness of the line connecting the data points. Brine chemistries are from the experimental work of Kaszuba *et al.* [2003, 2005a].

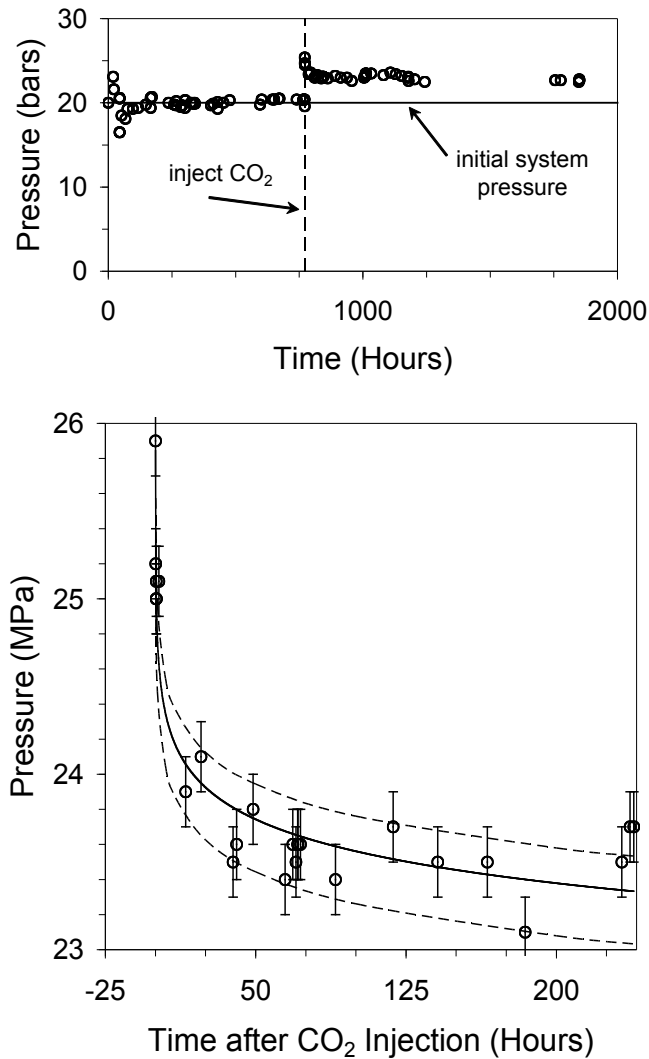


Figure 6. Pressure history for laboratory analogue of a carbon repository. a) The closed system brine-rock (siliciclastic aquifer and illite-rich shale caprock) reaction at 20 MPa (horizontal line) is injected with supercritical CO₂ at 772 hours (vertical dashed line), increasing system pressure to 25.4 MPa and producing a two-phase CO₂-H₂O fluid. b) The 2.4 MPa pressure decrease following injection is due to consumption of supercritical CO₂ by rapid dissolution into brine and subsequent reaction with siliciclastic aquifer to produce siderite. The largest pressure decrease spans approximately 40 hours, after which a relatively stable pressure (23 MPa) is achieved for the duration of the experiment (1040 additional hours). Uncertainty is 0.2 MPa (less than the size of the symbols in a, error bars in b). Experiments were performed in a rocking autoclave [Seyfried *et al.*, 1987] as described in the work of Kaszuba *et al.* [2003, 2005a].