Experimental and Geochemical Modeling Evidences of Mineral Sequestration of CO2 in Saline Siliciclastic aquifers

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The validity of mineral sequestration in saline siliciclastic aquifers in sedimentary basins is assessed in this paper. *Mineral sequestration* is the precipitation of carbonates due to the dissolution of silicates upon the injection of CO_2 in deep geological formations, while *solubility trapping* is the dissolution of CO_2 in the formation water. Saline reservoirs in sedimentary basins seem to constitute one of the best targets for the storage due to their huge storage capacity, low importance in terms of natural resources and wide availability and in close proximity to power generation plants. Siliciclastic aquifers are predicted to have the best potential for trapping CO_2, by precipitating carbonate minerals, when they contain an assemblage of basic aluminosilicate minerals such as fledspars, zeolites, illites, chlorites and smectites. Precipitation of carbonate minerals due to the dissolution of silicate are generally not observed in laboratory experiments conducted at low temperature and pressure due to the slow dissolution rates of silicates, or the absence of significant amount of divalent cations in the rock composition. However, carbonate precipitation is observed in work conducted under relatively high pressure and temperature. On the other hand, although carbonate perception is predicted by computer simulation for larger timeframes as reported in several studies, yet laboratory and geochemical modeling work suggests that the injection of supercritical CO_2 in deep saline aquifers may show limited reactivity with reservoir rocks. Thus, the dominant trapping mechanisms will be more based on the dissolution of CO_2 in the formation water rather than on mineral sequestration. Accordingly, this article concludes that apart from the physical conditions such as temperature and pressure, mineral sequestration in saline siliciclastic aquifers of sedimentary basins may behave differently due to differences in brine compositions and rock types, and thus the degree of mineral sequestration is case specific.

Keywords

Geological sequestration of carbon dioxide, solubility storage, mineral sequestration, saline aquifers, siliciclastic aquifers, sedimentary basins, precipitation, dissolution, laboratory experiments, geochemical modeling

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Mineral chemical formula

Mineral	Example Mineral Formula	Remarks
Albite	$NaAlSi_3O_8$	Feldspar mineral
Anhydrite	$CaSO_4$	
Anorthite	$CaAl_2Si_2O_8$	
Calcite	$CaCO_3$	
Chlorite	ClO_2^-	Sodium
Chlorite	$Mg(ClO_2)_2$	Magnesium
Dawsonite	$NaAlCO_3(OH)_2$	
Dolomite	$CaMg(CO_3)_2$	
Halite	$NaCl$	
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)$	Phyllosilicate
K-Feldspar	$KAlSi_3O_8$	
Kaolinite	$Al_2Si_2O_5(OH)_4$	
Magnesite	$MgCO_3$	
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O.$	Phyllosilicate
Quartz	SiO_2	
Siderite	$FeCO_3$	
Smectite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$	Clay minerals
Zeolites	$Na_2Al_2Si_3O_{10}\text{-}2H_2O$	Aluminosilicate

1.0 Introduction

In response to the current global climatic changes, laboratory, field and computer experiments are being conducted over the two decades to study the storage of CO_2 in deep geological formations such as saline aquifers, depleted petroleum reservoirs and coal deposits as a mean of decreasing the CO_2 concentration in the atmosphere. It is estimated the that capacity in deep sedimentary aquifers and depleted carbon reservoirs is sufficient to store up to 1000 years worth of CO_2 emissions (Oelkers and Schott 2005). Saline reservoirs in sedimentary basins seem to constitute one of the best targets for the storage due to their huge storage capacity, low importance in terms of natural resources (Gaus et al., 2008) and wide availability and in close proximity to power generation plants (Hitchon et al., 1999).

Geological storage of CO_2 is the injection of gas or supercritical fluid into deep geological reservoirs with three different storage techniques being *hydrodynamic trapping* of CO_2 below a low permeability caprock, *solubility storage* by dissolution of CO_2 in deep brine or oil, and *mineral sequestration* by precipitation of carbonate minerals specially in siliciclastic aquifers or adsorption specially in carbonate aquifers (Hitchon et al., 1999). Broadly speaking, sequestration implies the tying up of carbon in a geologically stable form, while storage implies a potentially shorter term method (Kaszuba 2005).

Mineral sequestration appears as an attractive permanent fixation mechanism for CO_2 in the form of carbonate minerals. The major natural pool of carbon is carbonate minerals, which develop largely from the interaction of water with silicate rocks enriched in calcium and magnesium. Once alkaline-earth metals are released from the silicates via dissolution, leaching or other mineral-alteration reactions, they can react with dissolved CO_2 to precipitate carbonates, which is thermodynamically stable and hence act as immobile storage for CO_2 as proposed by Seifritz (1990). Consequently, siliciclastic aquifers are predicted to have the best potential for trapping CO_2 by precipitating carbonate minerals when they contain an assemblage of basic aluminosilicate minerals such as fledspars, zeolites, illites, chlorites and smectites (Gunter et al., 1997).
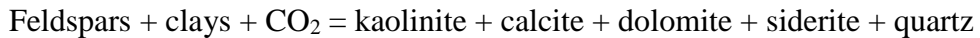
In laboratory experiments aimed at evaluating the CO_2-brine-rock interaction in saline siliciclastic aquifers, precipitation of carbonate minerals as a consequence of dissolution of primary silicates is generally not observed except in work conducted under relatively high pressure and temperature, while geochemical models on the contrary generally estimate considerable mineral sequestration over larger timeframe. The results of these laboratory experiments and computer simulations are presented in this study to assess the validity of mineral sequestration and the effect of CO_2 storage on the repository porosity.

2.0 Theoretical background

The two possible chemical trapping mechanisms are solubility storage and mineral sequestration. Reaction with brine can trap CO_2 as a dissolved phase in the form of $H_2CO_3^*$, and further reactions with minerals can result in pH buffering, which leads to further enhancement of the solubility trapping by the formation of bicarbonate ions and complexes such as HCO_3^-, $CaHCO_3^+$, $MgHCO_3^+$, $NaHCO_3^0$, … (Czernichowski-Lauriol et. al 2006). Further reaction of dissolved CO_2 with certain non-carbonate Ca-, Mg- or Fe- rich minerals can sequestrate CO_2 as carbonate precipitates such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), siderite

($FeCO_3$), dawsonite ($NaAlCO_3(OH)_2$), … (Czernichowski-Lauriol et. al 2006). This later mechanism known as mineral sequestration will immobilize the CO_2 for geological time periods (Gunter et. al 2004).

Although the geochemical reactions induced by the reaction of CO_2-brine-rock system are function of interdependent thermodynamic, kinetic, flow and transport processes, which are determined by the physical and chemical parameters of the CO_2-brine-rock system, yet the general hypothesis of mineral sequestration assumes that the breakdown of silicate minerals due to lowering the pH of the brine by the dissolution of CO_2 will results in the precipitation of carbonates and kaolinite as shown by the following simple and complex over all reaction equations:

$$2H_2O + CO_2 + anorthite (CaAl_2Si_2O_8) = kaolinite (Al_2Si_2O_5(OH)_4) + calcite (CaCO_3)$$

$$Feldspars + clays + CO_2 = kaolinite + calcite + dolomite + siderite + quartz$$

where the role of the silicate minerals in these reactions is to neutralize the acid added to the formation water from the dissolution of CO_2 (Hitchon et al., 1999). The formation of other carbonate minerals such as dolomite, magnesite, siderite… flow similar reactions.

The silicate minerals dissolution are the rate-limiting reactions, since their rate constant is slow ranging from 10^{-9}-10^{-12} moles/m^{2}s (Gunter et al., 1997) compared to carbonate precipitation. The dissolution rate is a function of temperature, pressure and reactive area. Oelkers and Schott (2005) conclude that silicate dissolution rates can be accurately determined by simply taking account of the presence of CO_2 on solution pH. Pokrovsky et al. (2005) observe that dissolution rates increase with increasing CO_2 pressure from 1 to ~10 atm, but remain constant with further CO_2 pressure increase to at least 60 atm. An equation for the total rate of dissolution for each mineral is formulated by Gunter et al., 1997 as shown in Annex III.

3.0 Experiment design

Several complex chemical systems are designed in batch or column experiments to study the interaction between CO_2, brine and reservoir rock and assess the overall chemical carbon storage process. Generally, the aim of these experiments is to study the key geochemical reactions at the reservoir temperature and pressure and/or validate numerical codes before using them for long term prediction.

According to Czernichowski-Lauriol and his co-works, batch experiments can show the reaction of CO_2-brine-rock system at different time scales, while column experiments aims to model the actual reservoir conditions especially during injection to elucidate the inter-relationships between geochemical and hydrodynamic processes (2006). Gunter et al. (1997) batch experiment is conducted in an autoclave at 105°C, and the pressure of CO_2 is raised to 105 bars by injecting water by a high pressure syringe pump. After 4 weeks the aqueous phase is extracted by pumping CO_2, and the pressure and temperature are maintained through the extraction process to ensure that no mineral perception will occur as a result of depressurization. The carbon dioxide is collected quantitatively from the sample tube by slowly depressurizing into a Brooks Gas Meter. In Bateman et al. (2005) a column of 100 cm long and with an internal diameter of 3.6 cm is used. The initial total weight of the synthetic mineral mixture is 1604 g.   The reactant fluid is equilibrated with CO_2 at a temperature of 70ºC and a pressure of 100 bars, before being pumped into the column held

under the same conditions. Fluid is passed along the column at a constant flow rate of 1.25 cm^3/h for approximately 7.5 months. Fluid samples are collected using the titanium pressure sampler at intervals throughout the duration of the experiment.

Analytical methods do not vary significantly from one experiment to another. In Gunter et al. (1997) laboratory experiment, the sand is rinsed with de-ionized water, dried and analyzed by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) to determine the extent of reaction, and the remaining aqueous sample is analyzed for cations by inductively coupled plasma (ICP), chloride and sulphate by ion chromatography (IC) and alkalinity by titration. Analytical methods for both aqueous and solid phases can vary depending on the liquid or rock composition.

4.0 Results

Solubility trapping in saline siliciclastic aquifers is successful. Dissolution of supercritical carbon dioxide in brine is observed. Laboratory and geochemical modeling findings as presented in the Annex I and II indicate a sudden decrease in pH upon the injection of CO_2 followed by a pH increase after reaching saturation with CO_2. Generally, bicarbonate concentration is seen to be increasing overtime. Thus to evaluate the storage capacity through solubility trapping, bicarbonate ions and complexes can be quantified. Portier and Rochelle (2005) developed an equation that allow the prediction of CO_2 solubility as a function of temperature, pressure and brine composition, and provide an example of how solubility can be used to estimate the storage capacity of a potential aquifer.

Mineral sequestration predicted by geochemical models is not observed in many laboratory experiments. The pH changes are expected to lead to several dissolution and precipitation reactions. Although Kaszuba et al. (2005) undoubtedly indicate the occurrence of rock dissolution through the injection of CO_2 in brine, and Gunter et al. (1997) show that the water-rock reactions are proceeding slowly, yet Bateman et al. (2005) conclude that even with such a long reaction time mineralogical observations are difficult as the degree of reaction is small. In laboratory experiment, the precipitation of carbonate is even less prominent than dissolution reactions, and is only reported by Pearce et al. (1996) and Kaszuba et. al (2005). On the other hand, geochemical modeling results indicate substantial sequestration of CO_2 through the precipitation of siderite, calcite (Gunter et al., 1997) and large quantity of dawsonite (Bateman et al., 2005) as presented in detail in Annex II.

5.0 Discussion

Mineral sequestration in saline siliciclastic aquifers is tentative. The high sequestration capacity estimated by Gunter et al. (1997 and 2000) is challenged by Xu et al. (2000 and 2004) through considering different proxy minerals (Marini 2007). Dawsonite, which is one of the most prominent sequestration mineral expected to form in large quantity is unstable. Thermodynamic calculations indicate that although dawsonite is favored to form at the high CO_2 pressures associated with the CO_2 injection into sandstone reservoirs, Hellevang et al. (2005) shows that the dawsonite rapidly dissolves following the decrease of CO_2 pressure. In addition, the quantity of CO_2 trapped in carbonate minerals depends generally on the rock composition. For example, carbonate formation is not observed during in Wigand et al. (2008) laboratory and modeling study due to the fact that the sandstone sample used in their experiment contained K-feldspar and albite, so the potential source for Ca is not available to form the calcite and kaolinite assemblage.

The effects of the reactions that take place in the CO_2-brine-rock system, which differ from the brine–rock system, are case specific. If dissolution occurs without precipitation porosity will increase. In Wigand et al. (2008) experiment, directly after the injection of CO_2 into the sandstone, dissolution of carbonate cement (dolomite) occurs without any precipitation occurring. While porosity is expected to increase in this example, other studies suggest that changes in porosity will be limited. For example, Gunter et al. (1997) predicates that dissolution is the predominant process in the early stages of geochemical reaction and precipitation will take place in the far region from the well over a very long time period, and concluded that porosity decrease would depend on the amount of reaction, but is expected to be small even when substantial amounts of the basic aluminosilcate minerals react out. On the other hand, other studies predict a decrease in porosity. According to Pearce et al. (1996), the precipitation of extensive halite efflorescences from the brine on the external sandstone block surfaces and the apparent interaction between brine and the clay minerals present in the sandstones by exchanging sodium from the seawater with calcium present in the minerals, leads to the formation of Na-smectites which have much greater swelling characteristics. This results in blocked pore throats and a reduction in porosity. Other studies are uncertain about the exact effect on porosity. Bertier et al. (2006) concludes that dissolution of carbonates might increase porosity, which will facilitate injection, yet precipitation of carbonates and of K-rich clays as observed may hamper the injection at later stages.

6.0 Conclusions
Although in principle the mineral sequestration is a valid technique for reducing the amount of carbon dioxide in the atmosphere, yet the laboratory and modeling evidences are somehow diverse. While geochemical modeling results (e.g. Gunter et al., 1997) and laboratory results (e.g. Kaszuba et. al 2005) suggest substantial sequestration of CO_2 through carbonate precipitation, other laboratory and modeling work (e.g. Wigand et al., 2008) shows limited reactivity of CO_2 with reservoir rocks. However, mineral sequestration cannot be discarded as an ineffective CO_2 storage mechanism, and a broader conclusion could be that mineral sequestration in saline siliciclastic aquifers of sedimentary basins behaves differently due to differences in brine compositions and rock types, and thus the degree of mineral sequestration is case specific.

The results presented in this study generally tend to confirm Wigand et al. (2008) conclusion that dominant chemical storage mechanisms will be solubility trapping rather than on mineral sequestration. Although mineral sequestration in saline siliciclastic aquifers has most storage security due to the formation of immobile carbonate minerals, yet solubility trapping will general have the major storage contribution for at least the non-geological periods.

At this point, it is essential to point out that a major inadequacy in most of the current laboratory experiments aimed at studying the CO_2-brine-rock system is that they are batch experiments. Such closed-box experiments can be conducted to study the reaction kinetics, yet to assess the fluid-rock interaction under real aquifer conditions a closed system assumption is invalid. Although the design of column experiments and periodical sampling techniques under high pressure and temperature are complex, yet to reach valid results the integration of flow and transport is inevitable. The same applies for the numerical codes. Although the design of numerical models is not discussed in this article, yet the geochemical model should be coupled to a multiphase transport model in order to simulate the fluid-rock interaction under the real aquifer conditions.

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Supplementary Materials

A1. Experimental Evidences

Precipitation of carbonate minerals due to the dissolution of silicate are generally not observed in laboratory experiments conducted at low temperature and pressure due to the slow dissolution rates of silicates (Gunter et al., 1997, Bateman et al.,2005) or absence of significant amount of divalent cations in the formation rock (Wigand et al., 2008). Yet carbonate precipitation is observed in work conducted under relatively high pressure and temperature (Pearce et al., 1996, Kaszuba et al., 2005 and 2003, Bertier et al., 2006).

Gunter et al. (1997) conducted a one month long experiment at 105°C and 90 bar of P_{CO2} on a glauconitic sandstone aquifer in Alberta sedimentary basin to test the validity of CO_2 trapping, which is unsuccessful due to slow kinetics, and Gunter and his coworker concluded that the increased alkalinity of the produced water indicates that water-rock reactions are proceeding slowly.

Bateman et al. (2005) conducted a 7.5 month long experiment at 70°C and 100 bars on Utsira sand aquifer. Fluid samples are taking at specific intervals during the experiment for chemical analysis, and an intact column is recovered at the end of the experiment to examine the mineralogical changes. The pH of the un-equilibrated fluid is ≈ 7.1. The initial pH of the equilibrated fluid pH ≈ 5.1, which rises to pH ≈ 6.6 during the first 300 h of reaction before falling to pH ≈ 6.2 after 1500 h reaction. The pH then remains at pH ≈ 6.2 for the remainder of the duration of the experiment. The bicarbonate concentration is seen to be increasing overtime. Generally, Bateman et al. (2005) conclude that even with such a long reaction time mineralogical observations are difficult as the degree of reaction is small.

Wigand et al. (2008) simulated the in-situ effect of supercritical CO_2 on reservoir rock from deep (1500-2000m) saline aquifer via a laboratory experiment and geochemical modeling. Dry sandstone samples are mounted in a triaxial cell and autoclave system, evacuated, and saturated with 1 M NaCl solution. The brine-rock system is allowed to react at 300 bars confining pressure, 150 bars pore fluid pressure at 60°C. The experiment is conducted for a period of two month, during which fluids are periodically sampled and analyzed. The result shows changes in aqueous chemistry relative to the starting brine. The pH decreases from 7.0 to 4.3 in 9 days and finally reaching 5.1 after saturation with CO_2 with small variations in the pH in the later stage of the experiment that could be related to the dissolution of aluminosilicates such as K-feldspar and albite after 28.5 days. The formation of montmorillonite from albite is observed, yet no formation of kaolinite from K-fledspar and albite is observed. Most importantly carbonate formation is not observed during this study due to the fact that the sandstone sample used in this experiment contained K-feldspar and albite and potential source for Ca is not available to form the calcite and kaolinite assemblage. In addition, low cation concentrations with acidic pH are observed which shows that dissolution prevails over carbonate precipitation. Moreover, the injection of CO_2 into the brine results in dissolution of carbonate cement (dolomite) directly after the injection of CO_2 into the sandstone.

Pearce et al. (1996) conducted batch experiments for 3 and 8 months at 80°C and 200 bars pressure, which are the typical conditions of southern North Sea gas fields. The experiments are performed in two sets of de-ionized water and synthetic water equilibrated with supercritical CO_2 with a variety of sandstones and mudstones rocks. Reactions observed in the experiments are dissolution of dolomite, fledspars and anhydrite with secondary precipitation of calcite, halite and semectitic clay is only very tentatively identified. It appears that most reaction occurred within the first three months of the experiment since no significant increases in the amount of K-feldspar and dolomite corrosion are detected in the eight-month experiments. The most obvious differences between the sandstones reacted with seawater and those reacted with de-ionized water are the precipitation of extensive halite efflorescences from the seawater on the external sandstone block surfaces and the apparent interaction between seawater and the clay minerals present in the sandstones by exchanging sodium from the seawater with calcium present in the minerals .This have two effects: first, release of calcium into solution which may then contribute to the precipitation of calcite; second, the formation of Na-smectites which have much greater swelling characteristics, which will results in blocked pore throats and a reduction in permeability.

In Kaszuba et al. (2005) a 5.5m of NaCl brine–rock system is held at 200°C and 200 bars for 32 days to approach steady state, then is injected with CO_2 and allowed to react for an additional 45 days, while the control experiment no CO_2 is injected during the 77 days. The supercritical carbon dioxide–brine–rock experiment is performed in a gold reaction cell (108 cm^3) with the initial brine to rock mass ratio being 15.5:1 and the initial brine to carbon dioxide mass ratio being approximately 9.5:1. The rock is arkose (1:1:1:0.3 quartz/ plagioclase/microcline/biotite) as an aquifer and shale chips as an aquitard. By comparing the experiment with the control, it is clear that the addition of supercritical carbon dioxide into the experimental brine–rock (aquifer plus aquitard) system decreased brine pH and precipitated carbonate minerals. The pressure decrease following injection of carbon dioxide indicates a decrease in the volume of the system due to the phase change of supercritical carbon dioxide, to dissolved carbonate, to mineral carbonate. In addition to pH decrease and carbonate mineral precipitation, a diversity of other fluid–rock reactions takes place between the mixed fluid (immiscible supercritical carbon dioxide plus brine) and rock that differ from the brine–rock system. For example, the brine is enriched with Mg (74x), Fe (188x) and Mn (5x) in the CO_2-brine-rock system relative to the brine-rock system, which undoubtedly indicate the occurrence of rock dissolution through the injection of CO_2 in brine.

Bertier et al. (2006) conducted an 8 month long experiment at 80°C and 150 bars on sandstones at the Campine basin in NE-Belgium. The carbonate dissolves with transitions coinciding with a small drop of Ca, Mg and Fe concentrations, which probably represents the initiation of carbonate precipitation. Carbonate dissolution/reprecipitation is confirmed by a petrographic study. Reactions involving Al-silicates are also observed, although they are less prominent. Analysis of the precipitates reveals the presence of newly formed K-rich clays. Bertier et al. (2006) concludes that dissolution of carbonates might increase porosity/permeability, which will facilitate injection and could increase storage capacity. However, precipitation of carbonates and of K-rich clays as observed can hamper the injection on one hand, yet permanent CO_2 disposal could be assured on

the other hand. Other newly formed phases are gypsum, Fe-oxides/hydroxides, albite and amorphous silica are observed in lesser quantities and are unlikely to affect the reservoir properties.

A2. Geochemical modeling evidences

Geochemical modeling is generally carried out to evaluate the long term geological processes. According to Marini, the available codes cannot accurately predicate the reactions paths, since the formation of a secondary phase rather than another depends on their different kinetics of growth, yet geochemical modeling is the only available tool to at the present to evaluate the long-term geochemical processes (2007). The insufficient accuracy of the geochemical modeling evaluation can be summarized from Marini (2007) as follows:
1. Available codes utilize (B-dot) Deye-Hückel equation instead of Pitzer's approach for activity calculation
2. The thermodynamic properties of some mineral phases such as clay minerals are unknown or poorly known
3. The kinetics data base is less complete than the thermodynamic database
4. The available codes cannot accurately describe the precipitation processes such as nucleation and crystal growth
5. Possible variation of reactive surface area with reaction progress cannot be described

Bateman et al. (2005) suggests that laboratory experiments should be conducted to validate the geochemical models, since the use of geochemical modeling without constraints from such experiments is not reliable because the results are not consistent in all cases with the results of experimental studies.

Despite these limitations numerous modeling exercises are carried out to evaluate the geological sequestration of CO_2 for larger time scales, since the laboratory experiments are limited in their prediction duration. Few computer experiments are discussed in this section to illustrate the effect of CO_2 injection on the evolution of saline siliciclastic aquifers of sedimentary basins under high pressure and temperature.

Gunter et al. (1997) extended the time scale of the experiment on a glauconitic sandstone aquifer in Alberta sedimentary through the use of the computer code PATHARC.94 at a pressure of 260 bars. A substantial sequestration of CO_2 through the precipitation of siderite and calcite and solubility trapping are predicted to slowly take place at least on the order of tens to hundreds of years, yet in time considerably smaller than the residence time of the water in the sedimentary basin aquifer. Generally, Gunter et al. (1997) predicated that dissolution is the predominant process in the early stages of geochemical reaction and precipitation will take place in the far region from the well over a very long time period, and concluded that porosity decrease would depend on the amount of reaction but is expected to be small, even when substantial amounts of the basic aluminosilcate minerals react out.

Bateman et al. (2005) modeling exercise of the laboratory experiment using PRECIP code concludes that the model tends to overestimate the degree of reaction compared

with the results of the experiment. Some mineral phases important for CO_2 mineral sequestration such as dawsonite that are predicted to form in large quantities by the model are not seen at all in the experimental system due to mainly the quality of equilibrium and kinetics data. Bateman et al. (2005) suggests that laboratory experiments should be conducted to validate the geochemical models.

Wigand et al. (2008) numerically modeled their laboratory experiments to reproduce long-term trends. The geochemical model indicates limited rates of dissolution as the system remained strongly undersaturated with most minerals, including carbonates. The Geochemical simulations are conducted with PHREEQC (version 2.12.1) and the databases are modified to more accurately calculate CO_2 solubility at high pressure by adding a special CO_2 species that reproduces experimental solubilities at constant pressure as a function of temperature. The geochemical modeling shows that the solutions are significantly undersaturated with respect to carbonates and most minerals. This cannot be due simply to slow kinetics of dissolution because the concentration of Ca, Mg and K decrease with time, indicating that a precipitation or cation-exchange process occurred. However, the geochemical model did not yield any precipitation and lacked adequate cation- exchange capacity to explain these compositional trends. Generally, the paper concludes that the libratory and modeling work suggests that the injection of supercritical CO_2 in deep saline aquifers may show limited reactivity with reservoir rocks and that the dominant trapping mechanisms will be more based on the dissolution of CO_2 in the formation water of the sandstone rather than on mineral sequestration. The authors add that in real reservoirs mixing of fluids of different compositions may allow for additional reaction.

A3. Silicate Dissolution

The silicate minerals dissolution are the rate-limiting reactions, since their rate constant is slow ranging from 10^{-9}-10^{-12} moles/m^2s (Gunter et al., 1997) compared to carbonate precipitation. The presence of CO_2 has no direct effect on the dissolution rate of silicate minerals that can supply earth metal. The dissolution rate is a function of temperature, pressure and reactive area. Carroll and Knauss (2005) and Golubev et al. (2005) find no evidence of a direct effect of CO_2 on the dissolution rates. Oelkers and Schott (2005) conclude that silicate dissolution rates can be accurately determined by simply taking account of the presence of CO_2 on solution pH. Pokrovsky et al. (2005) observe that dissolution rates increase with increasing CO_2 pressure from 1 to ~10 atm, but remain constant with further CO_2 pressure increase to at least 60 atm. In addition, dissolution rate depend on the reactive area, which is surface area of the mineral in contact with aqueous phase. The total rate of dissolution for each mineral can be formulated as follows (Gunter et al., 1997):

$$R = A(k_a[H^+]^x + k_n + k_{co_2}[P_{CO_2}]^z)(1-\Omega^n)^m$$

where A is the reactive surface area and the second term is the summation of the overall kinetic terms with x and z being the order of the reaction, and "k"s being the rate constant of dissolution, and the third term is the saturation quotient.