

Geochemical Implications of CO₂ Sequestration in Arkosic Sandstone Reservoirs

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Abstract:

Geologic sequestration of CO₂ is an attractive option for mitigating the buildup of anthropogenic CO₂ in the earth's atmosphere. Part of the uncertainty stems from the complex geochemical interactions of subsurface processes. For example, the pH falls and bicarbonate concentrations increase when high pressure CO₂ comes in contact with formation waters. These changes, in turn, can initiate rock-brine interactions with the potential for altering the transport properties of the rock. A related issue is the extent to which such interactions transform the CO₂ to carbonate, thus fixing it in a nongaseous form as dissolved bicarbonate or carbonate minerals.

In this study we report on how these changes affected a Permian arkosic sandstone from southeastern New Mexico, the Queen Formation sand. This work was performed in support of a DOE/NETL sponsored field demonstration in which CO₂ was injected into the Queen sand. Both modeling and experimental studies were carried out in conjunction with this investigation. As expected, the experiments revealed the rapid removal of essentially all the carbonate cement. After 19 months the growth of clays and the corrosion of plagioclase feldspar (but not K-feldspar) was also observed. Changes in brine chemistry reflected these mineralogic changes. The experimental dataset provides a standard against which it is possible to calibrate the predictions of "reaction path" models. With the appropriate adjustments the models reflected both the long and short-term changes observed experimentally.

Over the longer term, the models indicate that, if the pressure of CO₂ is maintained, the complete feldspar inventory of rock would be converted to clays and that part of the carbonates which were initially removed would reappear. However, in spite of its pervasive impact on the rock, these processes only roughly double the dissolved bicarbonate level in the brine. Even with this, the amount of bicarbonate in the brine is small compared with amount CO₂ that remains as dissolved gas. Sensitivity studies also revealed similarly stringent limits on the amounts of CO₂ that could be scavenged by the dissolution of calcite and dolomite. Thus, reactions with the formation minerals do not provide a sink that will permanently fix in place a large percentage of the injected CO₂. However, the pervasive growth of clays would significantly impede any long-term leakage from the formation. With regard to the ongoing field test near Hobbs, NM, it seems likely that the dissolution of carbonate grains may be responsible for the essentially constant injection rate observed during the placement phase of the test. Finally, this study illustrates how laboratory and modeling studies can be generalized to provide a cost-effective strategy for judging the suitability of sites where the rocks and groundwaters differ from those in the Queen formation.

Introduction:

One school of thought holds that the continued large-scale use of fossil fuels will elevate atmospheric CO₂ levels and lead to global warming. One carbon sequestration strategy by which CO₂ generated at point sources, such as power plants, could be safely disposed of is by direct injection into geologic reservoirs. The subterranean pore space vacated by the production of hydrocarbon fuels is a particularly attractive reservoir since, in addition to having the requisite volumes, many of these sites have the demonstrated ability to trap high-pressure gas and liquids for “geologic” periods of time.

That CO₂ can successfully be injected into such structures is not at issue. CO₂ injections have been used for years to stimulate oil production by virtue of its ability to dissolve in, and then lower the viscosity of crude oil. There is, however, far less understanding of how the CO₂ is distributed during (and after) an injection, and how it reacts with the rocks into which it is injected. These questions must be resolved before a case can be made that placing CO₂ in such locations permanently prevents the gas from returning to the earth’s atmosphere.

The US DOE/NETL has undertaken a small (relative to enhanced oil recovery efforts) field test to obtain a more comprehensive understanding of the fate of CO₂ that is injected into subsurface environments (Westrich et al., 2002; Krumhansl et al., 2002). In addition to demonstrating CO₂ injection at a particular site, the overall project encompasses: (1) monitoring the advancing CO₂ plume by geophysical methods, (2) multiphase flow modeling of the injection process, (3) regional geologic studies directed at documenting fracture orientations and the variable stratigraphy of the formation, (4) laboratory investigations into the flow properties of the reservoir rock at different CO₂ to brine ratios, and (5) geochemical investigations (both modeling and experimental) into the impact of exposing brine saturated rock to high pressure CO₂. To date, the injection phase of the experiment has been completed (with the placement of 2100 tons of CO₂) and geophysical characterization is underway. *This report, however, focuses on the supporting geochemical studies.*

The site being evaluated lies in the West Pearl Queen field near Hobbs, NM. The wells are owned and operated by the Strata Production Company, which graciously, has given the project access to the site. About 250,000 barrels of oil have been produced from the field since 1984. Although production decreased in recent years, the field has not been subjected to any enhanced oil recovery operations. Oil production, and the main CO₂ injection zone, is the Shattuck Sandstone member of the (Permian) Queen Sand at a depth between 4500 and 4550 feet. At this depth, the formation consists of fine-grained arkosic sandstone confined between shale-rich strata. The gross texture and lithologic setting of this unit is similar to many strata from which hydrocarbons have been extracted, and which might potentially be used to sequester CO₂.

Mineralogy and Brine Chemistry:

The program was fortunate in that core samples from the production horizon had been preserved and were available for laboratory studies. This material was characterized by both X-ray diffraction and by using a scanning electron microscope (SEM) equipped with an X-ray energy dispersive system (EDS) for assessing the gross composition of phases imaged under the SEM. For the most part the rock is composed of subangular to subrounded grains of quartz with minor amounts of potassium feldspar and

plagioclase (rough modal percentages are Quartz - 67%, Albite - 26%, K-feldspar-5%). The surfaces of these grains are partially coated with overgrowths of carbonate cement (rounded crystals, Fig. 1 - 3) and euhedral authigenic feldspars (angular rhombs in Fig. 1-3). The carbonate grains can be divided into those which are essentially pure calcium carbonate and those where the Mg:Ca ratio exceeds 0.1. Clays were entirely absent from the rock. They were probably initially present and subsequently reacted with formation brines to produce the authigenic potassium feldspars that coat the sand grains throughout the rock. It is not clear if this happened while the carbonate overgrowths were forming or whether multiple episodes of diagenesis have effected the formation.

Brine samples from the formation have also been obtained (Table 1). The brine is dominantly a sodium chloride fluid with minor additions of potassium, calcium, magnesium and sulfate. It is much less saline than the more concentrated brines that occur lower in the Permian (evaporite) section, and it is unusual for its relatively high Ca:Mg ratio.

Experimental Studies:

One approach to understanding the chemical changes that will result when CO₂ is injected into the Queen formation is to experimentally simulate the situation in the laboratory. This was done by placing sandstone chips (1-2 grams) in small stainless steel autoclaves with about 2.5 grams of formation brine under 700 psi (~ 48 atm) CO₂ pressure at 40° C (the ambient formation temperature at the injection depth). One autoclave was disassembled after 6.5 months and the other after 19 months. Fluids were analyzed by ion chromatography for anions. Cation analyses were obtained by either direct current emission spectroscopy (early samples) or inductively coupled plasma mass spectrometry (later samples). As with the original core, post-test samples were characterized using SEM/EDS and by X-ray diffraction.

Several significant changes took place during these tests. Fig. 1a illustrates typical pre-treatment material; with rounded sand grains overgrown by angular K-feldspars and rounded carbonate (both Mg-rich and nearly pure calcium carbonate) overgrowths. Clays, and indeed all sheet silicates including the micas, are absent from the pre-test core. After 6.5 months of treatment (Fig. 1b) almost all of the carbonate mineral grains are gone but, occasionally, a Mg-rich carbonate grain can be found (Fig.2a). It is also possible to find rare instances where clay overgrowths are displayed along the edges of the grains (also in Fig. 2a). After 19 months the clay overgrowths are much more common and well developed (Fig. 2b). It is also evident that the plagioclase feldspars have become etched (Fig. 3a), which provides the silica and aluminum needed for clay growth. At this point, even the Mg-rich carbonate grains have dissolved.

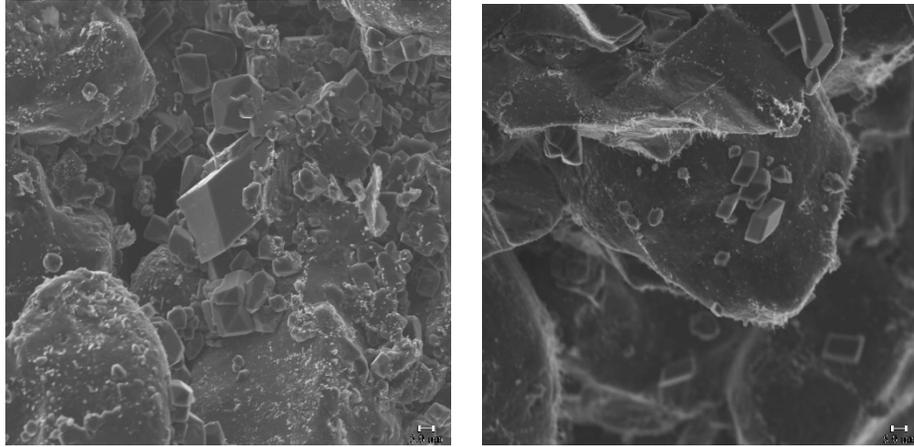


Fig. 1(a -left, b-right): Left - Pre-test sample not exposed to CO₂
 Right- Appearance after being exposed to 700 psi CO₂ for 6.5 months

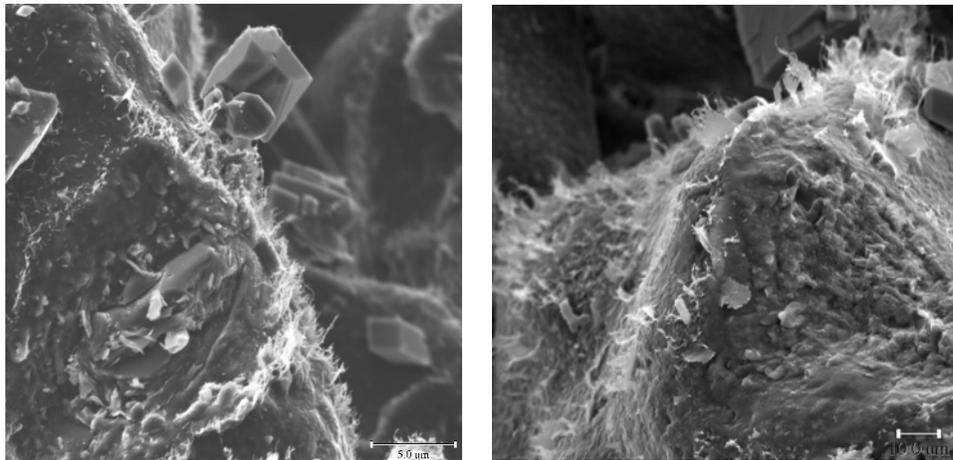


Fig. 2(a -left, b-right): Left – 6.5 months CO₂ exposure, Note high-Mg carbonate crystal at top of the picture and incipient clay growth on the edge of the grain.
 Right- Well developed clays formed after 19 months exposure to 700 psi CO₂.

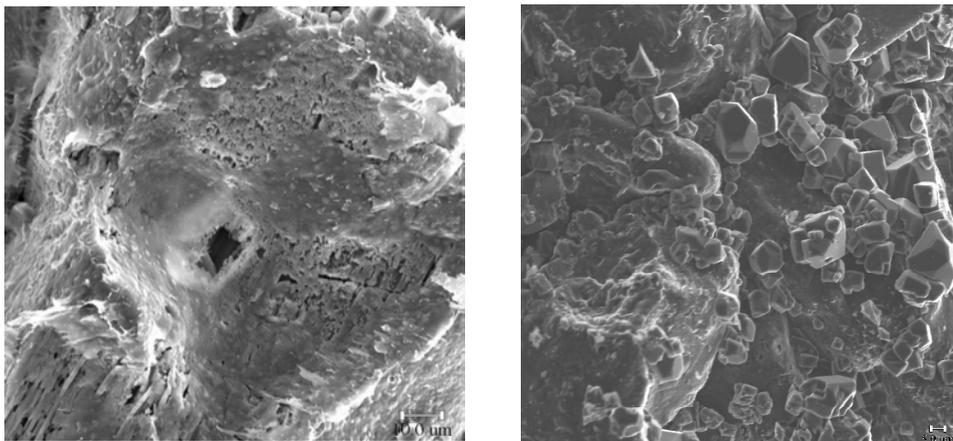


Fig. 3(a -left, b-right): Left- Etched plagioclase grain formed after 19 months exposure to 700 psi CO₂. Right-Post-test sample from flow-through experiment.
 Note: short-term exposure removes little carbonate (Krumhansl et al., 2002).

By virtue of the very high magnifications employed, SEM examinations can only evaluate changes in a very small percentage of a sample. In contrast, changes in fluid chemistry characterize the bulk interactions between solid and fluid. Fortunately, in this case the fluid chemistry confirms the trends identified using the SEM. Aluminum, initially in very short supply, has risen as feldspars dissolved and silica has fallen to reflect the subsequent precipitation of clays. The largest changes are the increases in Ca and Mg, which is consistent with the dissolution from the carbonate cements. In spite of the increase in calcium, the sulfate did not decrease. This is consistent with the absence of either gypsum or anhydrite from the SEM observations. Neither sodium nor chloride concentrations changed appreciably. This confirms the absence of new minerals containing large amounts of Na or Cl, as well as precludes widespread formation of new hydrated minerals that would have withdrawn water from the solution.

Table 1. Pre and post test brine chemistry.

	<u>Al(ppm)</u>	<u>Si(ppm)</u>	<u>Na(ppt)</u>	<u>K(ppt)</u>	<u>Mg(ppt)</u>	<u>Ca(ppt)</u>	<u>Cl(ppt)</u>	<u>SO₄(ppt)</u>	<u>HCO₃ (ppt)</u>
Pre-Test	0.05	12.3	52.4	1.6	3.1	3.1	109	1.8	0.12
Post Test*	0.33	3.6	53.5	1.6	4.2	3.8	104	1.8	-----

19 Months at 40° C, CO₂ pressure of 47.6 atm, starting fluid, “Pre-Test”, from Stivason Federal wells #4,#5

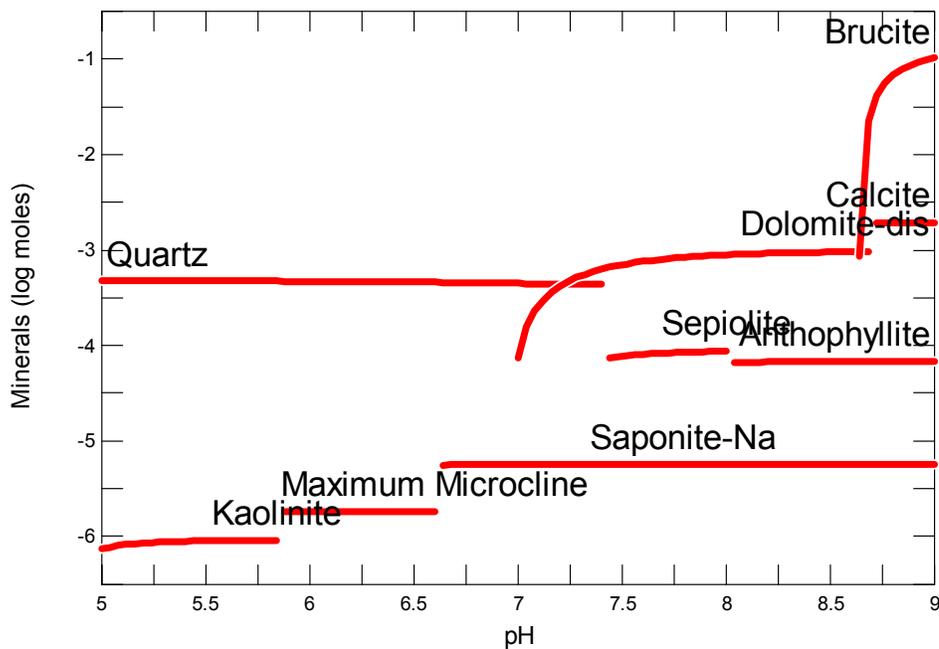
Geochemical Modeling:

The preceding section illustrated that exposure to high pressure CO₂ could initiate mineralogic changes with the potential for altering the porosity and, presumably, the permeability of a potential host formation. Unfortunately, it is not practical to initiate long-term laboratory studies, or expensive field tests, for every reservoir setting that might be considered as a CO₂ sequestration site. A way around this is to develop “reaction path” computer models (which can run many times at minimal cost) to evaluate the impact of changing formation mineralogy and indigenous brine chemistry. These models computing the equilibrium state of an assemblage of components. Inherent in this approach is the inability to evaluate formation of metastable phases unless the most stable phase(s) are manually “suppressed” before starting the computation. This approach can also be used to simulate reaction kinetics if outside information exists (as shown above) indicating whether reactions progress quickly or take a long time. Most of what follows is based on results from a commercially available reaction path-modeling package called REACT (Bethke, 1998) that employs extended Debye-Huckel activity coefficients. However, the discussion concludes with a comparison between these results and a parallel computation using the EQ3/6 (public domain) program and recently developed Pitzer coefficients for CO₂ in high ionic strength brines.

Since phase suppression is done manually it is best to start by calibrating the model on a simple system. In this case we asked what was needed to produce a model of the brine chemistry that predicted compatibility with the minerals actually observed in the core samples at the nearly neutral pH that was measured for the brine. Simply “plugging in” the brine chemistry (Table 1) suggested numerous minerals, some plausible and others which clearly are absent from the formation; notably well crystallized micas (muscovite, phlogopite, paragonite), magnesium silicates of dominantly metamorphic

origin (antigorite, chrysotile, tremolite, talc clinochlore), and two carbonates (magnesite, well ordered dolomite). This, then, was the initial list of suppressed phases. Once these minerals were removed, the model predicted minerals that were in reasonable agreement with the actual formation mineralogy at pH values near neutrality. (Fig. 4).

The predicted occurrence of Na-saponite above pH 6.5 represents a special problem. This is a magnesium-rich smectite clay and a legitimate sedimentary mineral though, in fact it is absent from the pre-test core. The principal effect of suppressing Na-saponite in Fig. 4 would be to extend the upper limit of potassium feldspar (“maximum microcline”) to a pH of 7.8, rather than having it drop out at around a pH of 6.6. Another problem is that calcite only appears above a pH of 8.8, where brucite formation extracts magnesium from the mixed carbonate phase. However, in this particular system (but not those evaluated later) there is just a trifling difference between the saturation state of calcite and disordered dolomite. Thus, here a better interpretation would be that above pH 7 both phases coexist. It is also noteworthy that although albite does not actually appear it almost reaches saturation between pH 5.8 and 6.7. Overall, the pH range that comes closest to providing a mineral assemblage that mimics the actual formation lies between pH 6.5-pH 7.0. This agrees with the nearly neutral pH measured on the brine.



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Fig. 4 Minerals predicted to be compatible with Pearl Queen brine as a function of pH. (Suppressed minerals include: antigorite, muscovite, phengite, phlogopite, chrysotile, dolomite-ord, tremolite, magnesite, saponite-Ca, saponite-Mg, saponite-H, saponite-K, talc, paragonite, clinochlore-14A, diopside, dawsonite, clinochlore-7A, amesite-14A.)

The above calculation only assumes the presence of components in the brine, which, in fact, contains only minuscule amounts of silicon and aluminum. The next step is to equilibrate the brine with an excess of the minerals present in the formation (per liter: 0.26 moles of albite, 0.67 moles of quartz, 0.01 moles of dolomite, 0.03 moles of calcite, 0.03 moles of potassium feldspar). When this is done a mineral assemblage of quartz, kaolinite, saponite, albite, calcite and potassium feldspar is predicted. The effect of suppressing saponite is to add disordered dolomite to the final phase assemblage and greatly decrease the amount of kaolinite predicted to be present.

Finally, increasing the CO₂ partial pressure (Fig. 5) to that of the experiment drops the pH, quickly eliminating calcite, saponite and albite. Potassium feldspar persists until the pH has fallen to 5.6, which corresponds to a CO₂ pressure of about 65 psi or about 10% of the experimental CO₂ pressure. At about 70% of the final CO₂ pressure calcite reappears because the bicarbonate increases so that saturation is again achieved.

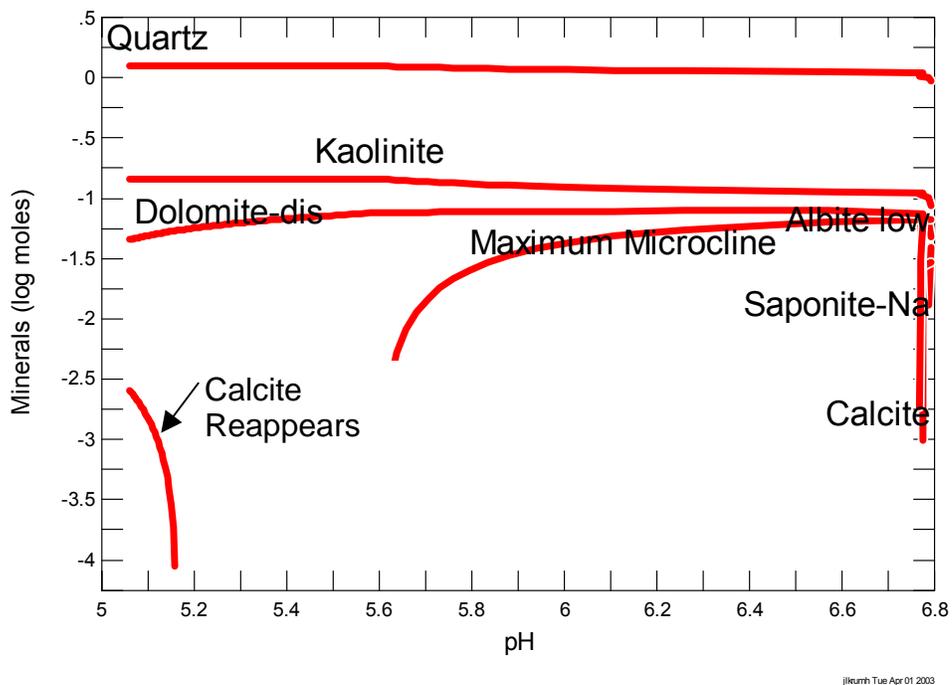
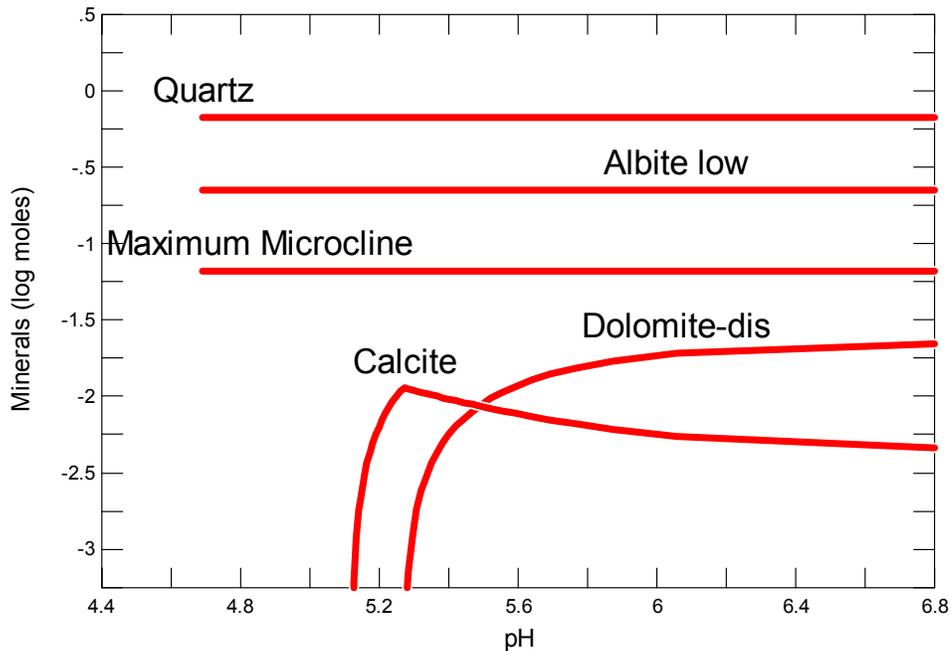


Fig 5. Impact of reacting CO₂ with Pearl Queen brine plus minerals: Prior to adding CO₂ (right side of figure) the pH was about 6.8. When the CO₂ partial pressure reaches 700 psi (far left of figure) the pH is about 5.1. Curve in lower left of figure marks reappearance of calcite. (Suppressed species: antigorite, muscovite, phengite, phlogopite, chrysotile, dolomite, dolomite-ord, tremolite, magnesite, saponite-Ca, saponite-Mg, saponite-H, saponite-K, talc, paragonite, clinochl-14A, diopside, dawsonite, clinochlore-7A, amesite-14A, gibbsite and alunite.)

The utility of such models lies not in their ability to mimic a particular experiment or natural setting, but in what they can tell about the behavior of related systems. In this study one concern is comparing the short and long-term responses of the formation.

Fig. 5 illustrates the expected long-term response when clays form while Fig. 6 illustrates the contrasting short-term behavior when all clays are suppressed. In the absence of clays, a lower pH is attained and carbonate removal is complete once a few atmospheres of CO₂ pressure are present in the system. Complete carbonate removal is consistent with the experimental observations.

Contrasting Fig. 6 with Fig. 5 provides considerable insight into how this particular host formation would evolve over time. Once clays form to a significant degree the pH rises (from pH 4.6 to pH 5.1 once argillization is completed) and the mineralogy alters dramatically. Ultimately, large-scale argillization is predicted to consume the entire feldspar inventory in the rock, assuming the CO₂ pressure can be maintained above 65 psi. At the highest CO₂ pressures one might also anticipate the reappearance of carbonate minerals. Unfortunately, all of these chemical changes only about doubles the level of dissolved bicarbonate in the brine. At this concentration the dissolved bicarbonate is still a factor of six less than that of aqueous (e.g., dissolved) CO₂. Thus, argillization is not a significant CO₂ fixation mechanism.



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Fig. 6: Effect of reacting CO₂ with Pearl Queen brine plus minerals while suppressing the appearance of all clays. The model was the same as that which produced Fig. 5 except that kaolinite and Na-saponite were also suppressed. Prior to adding CO₂ (right side of figure) the pH was about 6.8. When the CO₂ partial pressure reaches 700 psi (left side of the figure) the pH is about 4.6.

With Permian sediments (such as are the focus of the present study) another key variable is the availability of sulfate, and whether calcium liberated by carbonate dissolution will initiate precipitation of anhydrite or gypsum. The models used in generating Fig. 5 and 6 were run iteratively while varying the level of sulfate. These results suggest that when all clays are suppressed about 12 g/l sulfate would be needed to initiate calcium sulfate precipitation. If clays are allowed to form about 23 g/l sulfate is needed to accomplish this result. One might also consider a system that starts out with enough anhydrite to maintain calcium sulfate saturation throughout the ramp-up in CO₂ pressure. In this case essentially none of the carbonates present initially dissolve if clays are allowed to form, but they have all disappeared by the end of the pressure buildup if clay formation is completely suppressed. An immediate application of these results would be to rule out the possibility that injecting high pressure CO₂ into the Queen sandstone is likely to clog the pores by forcing the precipitation of calcium sulfate. However, at a site with slightly more sulfate in the groundwater this could occur quickly and seriously impede the injection process.

One can also use such models to investigate the effects of changing the proportions of the major rock-forming minerals in the rock. For example, the same two models were run again except, this time, the amounts of both disordered dolomite and calcite were increased by a factor of 5. Even in the absence of clay formation, the calcite persists along with the disordered dolomite to the lowest pH attained (a little above 4.8 in this case, as compared with about 4.6 with less carbonate). When clays are allowed to form essentially none of the original carbonates dissolve. It was shown previously that argillization was not a significant CO₂ fixation mechanism. In this example only small amounts of calcite and dolomite were needed to maintain carbonate mineral saturation across the board. Thus, stringent limits also apparently exist on the amount of CO₂ that can be fixed by interactions with limestone, dolomite and carbonate cements.

The preceding discussion illustrates how the utility of reaction path modeling can be significantly enhanced through the judicious use of the mineral suppression option. A second refinement of the technique would be to switch from the use of extended Debye Huckel activity coefficients (used by REACT) to those computed using a Pitzer formalism. Activity coefficients are the correction factors needed to transform bulk dissolved concentrations into thermodynamic activities needed for computing the equilibrium configuration for the system (e.g., they essentially allow one to derive effective concentrations for components that account for all the interferences from the other components dissolved in the same solution). It is generally recognized that when solutions with ionic strengths in excess of 0.5 molar are involved the use of Pitzer activity coefficients will improve the reliability of a model. However, a much larger supporting database is needed to develop Pitzer coefficients for evaporite systems (Greenberg, and Møller, 1989; He and Morse, 1993; Pabalan and Pitzer, 1987; Pitzer, K. S. 1991); one that is only now being slowly assembled by the geochemical community for CO₂-rich systems.

To assess the importance of such an improvement the authors reran the basic model (Fig. 5) using the EQ3/6 reaction path program with Pitzer coefficients. Activity coefficients from this run were then compared with those predicted with REACT (Table 2). For ions such as Na⁺, K⁺, SO₄⁻, and HCO₃⁻ the differences are not large, and the

REACT activity coefficients only slightly under-predict the effective concentrations of these components relative to their Pitzer counterparts. However, the Pitzer activity coefficients for Ca^{++} are roughly twice as great as those obtained from REACT, while for magnesium the situation is reversed. Thus, the predicted stabilities for Ca and Mg-containing minerals would differ somewhat depending on which model is used.

In practical terms, dolomite solubility (e.g. the dissolved concentrations of the constituent components in equilibrium with the mineral) calculated with EQ3/6 would be about half that calculated with REACT, while for anhydrite the number is closer to a third. In an example presented above, REACT predicted anhydrite precipitation would occur in brines with 12 g/l (clay free) and 23 g/l (with clays: kaolinite, saponite) dissolved sulfate but, the Pitzer coefficient approach suggests these values might be reduced by a half to two thirds. However, neither model suggests that the indigenous sulfate concentrations in the Pearl Queen brine would lead to calcium sulfate precipitation (or a subsequent decrease in formation permeability) as CO_2 is being injected during the current field test.

Table 2 Comparison of activity coefficients from REACT and EQ3/6 using a Pitzer database: EQ3/6 (top) and REACT (bottom)

Cl ⁻	Na ⁺	CO ₂ (aq)	Mg ⁺⁺	Ca ⁺⁺	K ⁺	SO ₄ ⁻	HCO ₃ ⁻	
Gamma	Gamma	Gamma	Gamma	Gamma	Gamma	Gamma	Gamma	
0.937346	0.702425	1.715537	0.444017	0.093972	0.537898	0.087801	0.651178	EQ3/6
0.625893	0.712689		1	0.30662	0.210426	0.625749	0.111199	0.748859
								REACT

Gamma EQ3/6 divided by Gamma REACT

Cl ⁻	Na ⁺	CO ₂ (aq)	Mg ⁺⁺	Ca ⁺⁺	K ⁺	SO ₄ ⁻	HCO ₃ ⁻	
Gamma	Gamma	Gamma	Gamma	Gamma	Gamma	Gamma	Gamma	
1.497614	0.985598	1.715537	1.448105	0.446581	0.859607	0.789587	0.869561	

Summary and discussion:

For CO_2 sequestration in geologic formations, the two most important questions are: (1) can we get it into the ground and (2) will it stay there? The issue is complex and geochemical studies can only give a part of the answer. Studies of this nature can provide information on changes in the bulk porosity of a potential host formation, identify minerals that are likely to appear (or disappear) as injected CO_2 interacts with the host formation (and indigenous groundwaters), and ultimately identify (or disprove) the presence of long-term sinks for sequestered CO_2 .

Relating these studies to this specific field project suggests that the first impact of injecting the CO_2 will be dissolution of the carbonate cement. In the field, it was noted that over the six-week injection period the flow into the formation (at a fixed injection pressure) remained essentially constant. This contrasts sharply with the short-term increased resistance to flow noted when CO_2 -brine mixtures were forced through cores (Westrich et al., 2002, Krumhansl et al., 2002) during which, apparently, no dissolution of the carbonate cement occurred (compare Fig 3-b with Fig. 1-a vs. 1-b). The underlying cause for the short-term resistance is still subject to discussion, but the

lodging of fine carbonate particles where the flow channels narrow is certainly a plausible explanation. In the field, the subsequent dissolution of these particles may provide an explanation for why it was possible to maintain a steady flow into the formation, rather than having the flow fall off as would be predicted based on the laboratory flow tests.

If one were to ask whether a steady input flow might be maintained for many years (e.g., as would be necessary at an “industrial scale” sequestration site) the answer would probably be “no”. The onset of incipient clay growth was observed experimentally after less than two years, and our models indicate that (eventually) argillization will become a pervasive theme in the mineralogic evolution of the formation. The new clays will certainly block the pore throats and should greatly impede the flow of fluids into the rock. However, this development has a positive side in that the clays will also greatly impede CO₂ leakage out of the formation, thus improving the long-term performance of the site. This is particularly important since our models also suggest that CO₂-rock-pore fluid interactions are unlikely to transform a large percentage of CO₂ into a non-gaseous form that could be permanently fixed in the rock.

Finally, with regard to other potential sites, one concern would be the onset of calcium sulfate precipitation. This could, in short order, significantly decrease the permeability of a potential host rock and create real problems in getting the gas into the ground. Our models suggest that this problem is unlikely at our field test site. However, one might plausibly encounter enough sulfate elsewhere for this to be a real problem. Another general observation is that only very limited amounts of carbonate minerals dissolve even at high injection pressures. In addition to further limiting the ability of a formation to permanently “fix” the CO₂, this also implies that the development of an increased volume of new pore space would not be anticipated, even though a potential host rock might contain a high proportion of carbonate minerals.

References:

1. Bethke, C. M., *The Geochemist's Workbench (Release 3.0): A users software guide to Rxn, Act2, Tact, React, and Gtplot*, p. Pages, Hydrogeology Program, University of Illinois, (Urbana-Champaign) (1998).
2. Greenberg, J. P.; and Møller, N. 1989. “The Prediction of Mineral Solubilities in Natural Waters: A Chemical Equilibrium Model for the Na-K-Ca-Cl-SO₄-H₂O System to High Concentration from 0 to 250 °C.” *Geochimica et Cosmochimica Acta*, 53, 2503–2518.
3. He, S.; and Morse, J. W. 1993. The Carbonic Acid System and Calcite Solubility in Aqueous Na-K-Ca-Mg-Cl-SO₄ Solutions From 0 to 90°C. *Geochimica et Cosmochimica Acta*, 57, 3533–3554.
4. Krumhansl, J.L., R. Pawar, R. Grigg, H. Westrich, N. Warpinski, D. Zhang, C. Jove-Colon, P. Lichtner, J. Lorenz, R. Svec, B. Stubbs, S. Cooper, C. Bradley, J. Rutledge, and C. Byrer, Geological Sequestration of Carbon Dioxide in a Depleted Oil Reservoir, In Proceedings of the SPE/DOE 13th Symposium on Improved Oil Recovery, Tulsa, OK, April 13-17, 2002.

5. Pabalan, R.T., and Pitzer, K.S., 1987, Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO₄-OH-H₂O, *Geochimica et Cosmochimica Acta*, v. 51, p. 2429-2443.
6. Pitzer, K. S. 1991. "Ion Interaction Approach: Theory and Data Correlation." Pages 75–153 of *Activity Coefficients in Electrolyte Solutions*. 2nd Edition. Pitzer, K. S., ed. Boca Raton, Florida: CRC Press.
7. Westrich, H.R., J. Lorenz, S. Cooper, C. Jove Colon, N. Warpinski, D. Zhang, C. Bradley, P. Lichtner, R. Pawar, B. Stubbs, R. Grigg, R. Svec, C. Byrer, Sequestration of CO₂ in a Depleted Oil Reservoir: An Overview, *J. of Energy and Environmental Research*, v. 2, No. 1, p. 64-74, 2002.