

Scoping Equilibrium Geochemical Modeling to Evaluate the Potential for Precipitate Formation when Sequestering CO₂ in San Juan Basin Coals

Topical Report

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Executive Summary

In October, 2000, the U.S. Department of Energy (DOE), through contractor Advanced Resources International (ARI), launched a multi-year government-industry R&D collaboration called the Coal-Seq project. The Coal-Seq project is investigating the feasibility of CO₂ sequestration in deep, unmineable coalseams, by performing detailed reservoir studies of two enhanced coalbed methane recovery (ECBM) field projects in the San Juan basin. The purposes of the field studies are to understand the reservoir mechanisms of CO₂ and N₂ injection into coalseams, demonstrate the practical effectiveness of the ECBM and sequestration processes and engineering capability to simulate them, and to evaluate sequestration economics. In support of these efforts, laboratory and theoretical studies are also being performed to understand and model multi-component isotherm behavior, coal permeability changes due to swelling with CO₂ injection, as well as potential geochemical reactions between injected CO₂ and coal formation water. This report describes the results of an important component of the overall project, the evaluation of whether geochemical reactions might occur between injected CO₂, the reservoir rock, and coal formation water.

Based on this scoping study, it is concluded that neither calcite dissolution nor subsequent precipitation are likely to occur with CO₂ injection for this reservoir for the conditions evaluated. This conclusion may not be generalized however, and site-specific investigations are required to assess dissolution and precipitation potential for a particular application. Such investigations should include detailed water geochemical analyses as well as rock mineralogy, wellbore and reservoir temperature, and pressure information.

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1.0 Introduction

In October, 2000, the U.S. Department of Energy (DOE), through contractor Advanced Resources International (ARI), launched a multi-year government-industry R&D collaboration called the Coal-Seq project¹. The Coal-Seq project is investigating the feasibility of CO₂ sequestration in deep, unmineable coalseams, by performing detailed reservoir studies of two enhanced coalbed methane recovery (ECBM) field projects in the San Juan basin. The two sites are the Allison Unit, operated by Burlington Resources, and into which CO₂ is being injected, and the Tiffany Unit, operated by BP America, into which N₂ is being injected (the interest in understanding the N₂-ECBM process has important implications for CO₂ sequestration via flue-gas injection). The purposes of the field studies are to understand the reservoir mechanisms of CO₂ and N₂ injection into coalseams, demonstrate the practical effectiveness of the ECBM and sequestration processes, demonstrate an engineering capability to simulate them, and evaluate sequestration economics.

In support of these efforts, laboratory and theoretical studies are also being performed to understand and model multi-component isotherm behavior, coal permeability changes due to swelling with CO₂ injection, as well as potential geochemical reactions between injected CO₂ and coal formation water. This report describes the results of an important component of the overall project, the evaluation of whether geochemical reactions might occur between injected CO₂, the reservoir rock, and coal formation water, which is a little understood area due to the paucity of field studies published in the literature.² If such reactions do occur, they could have important implications for coal permeability reduction, thus affecting CO₂ injectivity and sequestration/ECBM economics.

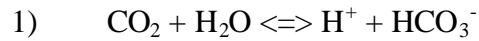
2.0 Discussion of Relevant Reactions

When CO₂ is added to a water-rock system (i.e., a reservoir), the higher pressures encountered near the injection well may cause calcite, if it is present in the reservoir rock, to dissolve. Such a situation is likely to occur if certain conditions exist (i.e., the saturation index for calcite becomes negative with addition of the CO₂). If calcite does dissolve into the water, a second reaction may occur elsewhere in the reservoir. As water flows towards a production well, the pressure will be less than it was near the injection well, and any dissolved calcite may then precipitate if the right conditions exist (i.e., positive saturation index).

Thus, there are two primary reactions involving CO₂, formation water, and reservoir rock that were evaluated for this study:

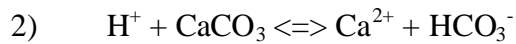
- Dissolution of reservoir rock, primarily any calcite cement that may be present
- Precipitation of calcite from the calcium and bicarbonate in the water

When CO₂ gas comes in contact with water, it dissolves in the water to form carbonic acid (H₂CO₃) which, because it is an acid, tends to dissociate into a hydrogen ion and bicarbonate.



The double-headed arrow indicates that the reaction is reversible, but as long as CO_2 is continuously added to the system, it forces the reaction toward the products on the right-hand side of the equation.

If calcite is present in the reservoir rock that contains this water, the free hydrogen ion will cause the calcite to dissolve:



Again, the double-headed arrow indicates the reaction is reversible. Combining Equations 1 and 2 results in Equation 3:



It is important to note, here, that these reactions involve only pure water. The presence of other dissolved components in the water, as is the case for all formation waters, can potentially drive the reaction back in the reverse direction (thus, again, the double-headed arrow). This doesn't necessarily mean that calcite will precipitate from the water, but it would mean that less calcite dissolution would take place. This phenomenon is referred to as "buffering a reaction," — the bicarbonate "buffers" the effect of the added CO_2 . The presence of substantial amounts of calcium or bicarbonate in the formation water (products in Equation 3), as would occur if calcite had been dissolved near the injection well, may cause calcite to precipitate from the water (the reverse of Equation 2) when the CO_2 pressure drops at some distance from the injection wellbore. This is the second reaction being evaluated for this study:



3.0 Methodology

To perform this assessment, geochemical analyses of three water samples taken from the Tiffany Unit (in May, 1986) were obtained. A summary of the analytic results are provided in Table 1. All three samples have sodium as their dominant cation and bicarbonate as their dominant anion.

Table 1: Water Sample Geochemical Analysis Results, Tiffany Unit

	So. Ute 29-1	Cundiff 34-1	Taichart 32-1
Date	May, 1986	May, 1986	May, 1986
Cations (mg/l)			
Sodium	1955	1380	2679
Potassium	19	9	14
Calcium	28	11	33
Magnesium	13	15	74
Anions (mg/l)			
Chloride	6	24	1
Sulfate	<5	---	<5
Bicarbonate	5362	3322	7690
Total Dissolved Solids (weighed) (mg/l)	7383	4761	10491
pH	8.0	8.5	7.9
Specific Gravity	1.01	1.01	1.01

The samples were first checked for data quality. This includes charge balance, reasonableness of pH, resistivity, and discrepancies between specific gravity and total dissolved solids. All samples appeared suitable for evaluation.

The chemical analyses from these samples were then modeled to determine the effect of injecting CO₂. For this, the program SOLMINEQ.88³ was used to calculate the saturation index (SI) for calcite at various conditions of CO₂ pressure (PCO₂). The saturation index is the stability of a given mineral relative to that particular water composition. A positive saturation index means that the mineral is stable and may precipitate from the formation water. A negative saturation index means that the mineral is unstable and may dissolve if it is in contact with the water at the modeled conditions. The temperature for all the model calculations was 120°F. The total and CO₂ pressure was modeled at 100, 500, and 1,400 psi.

4.0 Results

The calcite saturation index for each sample does not change with changes in pressure except for the sample from the 29-1 well (Table 2). For that sample, calcite becomes only slightly less stable at the highest CO₂ pressure (PCO₂). At the highest level of PCO₂ modeled (1400 psi), calcite saturation indices are still positive for all three samples, and calcite will remain a stable component in the rock-water system in the presence of added CO₂. Therefore, the injection of CO₂ in the Tiffany Unit is unlikely to cause any dissolution of calcite in the reservoir near the injection well.

However, calcite precipitation, not dissolution, is the primary concern, due to its negative effect on permeability. Although all the samples have positive saturation indices for calcite, it is unlikely that calcite will precipitate with the injection of CO₂. The important aspect to note is any change in the calcite saturation index. As can be seen in Table 2, the saturation index changes only slightly for one sample, and that change is in the direction of being less stable (less

likely to precipitate calcite). Therefore, it is the conclusion of this “scoping” study that CO₂ injection is unlikely to cause a decrease in coal permeability for the wells examined or for other wells with similar temperature, pressure, and water composition.

Table 2: Geochemical Modeling Results

Well	Calcium (mg/l)	Bicarbonate (mg/l)	Total dissolved solids (mg/l)	Calcite SI at PCO ₂ =100 psi	Calcite SI at PCO ₂ =500 psi	Calcite SI at PCO ₂ =1400 psi
29-1	28.3	5,362	7,383	1.257	1.257	1.254
32-1	33.1	7,690	10,491	1.221	1.221	1.221
34-1	11.3	3,322	4,761	1.128	1.128	1.128

Several points should be noted regarding the results of this study:

- First, the samples evaluated were taken and analyzed 15 years ago and may not represent the water that is present in the formation now. Water in a formation may change due to coning of water from a lower section or invasion of water from any other section (through fractures, for example)^{4,5}.
- Second, these historical water analyses included only the standard seven components of sodium, potassium, calcium, magnesium, chloride, sulfate, and bicarbonate. Although these are generally the most important, other chemical elements can influence the stability of calcite.
- Third, the mineralogy of the coal itself was not considered. The additional components that may exist within the coal may affect the overall geochemical behavior of the system.
- Fourth, this evaluation was done with an equilibrium model. An equilibrium model determines the direction (towards precipitation or towards dissolution) that a system may go when it is perturbed by adding CO₂. However, it cannot model the timing over which any changes may take place.

5.0 Recommendations

Therefore, we recommend several courses of action for future studies of this nature:

- First, new water samples should be taken, analyzed, and modeled.
- Second, the model scenarios should include detailed temperature and pressure conditions of any planned CO₂ injection schemes.

- Third, the model scenarios should include an analysis of changing temperature and pressure conditions across the field, and up any production wellbore, as well as a knowledge of the coal mineralogy.

6.0 Conclusions

Based on this scoping study, it is concluded that neither calcite dissolution nor subsequent precipitation are likely to occur with CO₂ injection for this reservoir for the conditions evaluated. This conclusion may not be generalized however, and site-specific investigations are required to assess dissolution and precipitation potential for a particular application. Such investigations should include detailed water geochemical analyses as well as rock mineralogy, wellbore and reservoir temperature, and pressure information.

7.0 Acknowledgements

This work was performed using water sample analyses taken from the Tiffany Unit in San Juan basin. Provision of these data by BP America is gratefully acknowledged.

8.0 References

1. Reeves, S.R.: “Geologic Sequestration of CO₂ in Deep, Unmineable Coalbeds: An Integrated Research and Commercial-Scale Field Demonstration Project”, SPE 71749, presented at the SPE Annual Technical Conference and Exhibition, New Orleans, September 30-October 3, 2001.
2. Worden, R.H., and Smith, L.K., in review, “CO₂ Injection into Oil Fields for Enhanced Oil Recovery (EOR): Lessons for the Geological Sequestration of CO₂ in the Subsurface” *in* S. Baines, J. Gale and R.H. Worden, eds., Geological Storage of Carbon Dioxide for Emissions Reduction: Technology. Geological Society of London Special Publication.
3. Kharaka, Y.K., W.D. Gunter, P.K. Agarwall, E.H. Perkins, and J.D. DeBraal, 1988, SOLMINEQ.88: A Computer Program Code for Geochemical Modeling of Water-Rock Interactions: U.S. Geological Survey Water Investigations Report 88-4227.
4. Smith, L.K., 1998, Formation Water as a Tool for Studying Compartmentalization: Example from the Almond Formation in R. Slatt, ed., Compartmentalized Reservoirs in Rocky Mountain Basins: Rocky Mountain Association of Geologists Special Publication.
5. Smith, L.K., and R.C. Surdam, 1998, Reservoir Connectivity Determined from Produced Water Chemistry, Standard Draw-Echo Springs Gas Field, Wyoming, U.S.A. (paper #119), *in* G.B. Arehart and J.R. Hulston, eds., Proceedings of the 9th International Symposium on Water-Rock Interaction, Taupo, New Zealand, March 29-April 3, 1998.