

# **Carbon Dioxide Injection into Shallow Sedimentary Aquifer Systems to Assess Potential Degradation of Groundwater Quality at Geological Carbon Sequestration Sites**

**(Project No. 4265)**

**Periodic Report No. 5, Period covered: May 1, 2011- Oct. 31, 2011**

**Principal Investigator: Bridget Scanlon  
Co-Principal Investigator: Changbing Yang  
Researcher: Patrick Mickler**

Bureau of Economic Geology, University of Texas at Austin

Project Start Date: 5/1/2010      End Date: 5/1/2013

Participating Utilities: Mr. Broussard, Lafayette Utilities, Louisiana; Mr. Coleman, City of College Station, Texas; Mr. Hovsepian, City of Houston, Texas; Mr. Hunsinger, East Bay Municipal Utility District, CA; Ms. Owen, Tampa Bay Water, Florida.

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Project Objectives of this study are to (1) assess impacts of CO<sub>2</sub> leakage on groundwater quality using field studies based on push-pull tests in shallow sedimentary aquifers at a geological carbon sequestration site in the Gulf Coast, (2) conduct laboratory batch experiments to determine impacts of CO<sub>2</sub> on major and trace elements, (3) simulate test results to assess mechanisms dominating mobilization of major and trace elements in the event of a CO<sub>2</sub> leak, (4) evaluate which geochemical parameters are most diagnostic of CO<sub>2</sub> leakage into underground sources of drinking water (USDWs), and (5) communicate study results to water utilities and regulators.

## II. Status Summary

### ***II. 1. Summary of Work Tasks Completed and Accomplishments***

Water samples were continuously collected from the batches during this reporting period. Last samples were collected on September 30<sup>th</sup> 2011, approximately 146 days after the start of the experiment date. These samples were analyzed to compare with data reported in previous reports. Other water samples collected during the current reporting period have not been analyzed yet. Concentrations show obvious changes in some reactive and also nonreactive ions, such as  $\text{Ca}^{2+}$  in the batch experiments of Edwards and Brackenridge samples and  $\text{Na}^+$ . In the batch experiments of Cranfield sand and Cranfield water, changes in reactive solutes ( $\text{Ca}^{2+}$ ) may be due to slow progress of chemical reactions in the batch. Changes in non-reactive solutes could be due to evaporation. However, because only the latest samples were analyzed, measurement errors cannot be excluded before other samples are analyzed.

In the previous report, we presented a model with a 3-D axisymmetric domain. However, that model did not consider the impact of regional groundwater flow on push pull tests. In this reporting period, an improved numerical model, considering regional groundwater flow, was set up to simulate push-pull tests. Five different scenarios were simulated in terms of injection rate, injection period, hydraulic conductivity, and regional groundwater flow. We found that hydraulic conductivity and regional groundwater flow show an obvious impact on time evolution of pH,  $\text{Br}^-$ , and  $\text{HCO}_3^-$  in the well. Model results are sensitive to total amount of water injected into the aquifer (equal to injection rate times injection duration). Low hydraulic conductivity will slow down transport of injected water in the aquifer during the injection or push phase and from the aquifer to the well during the extraction or pull phase. With a high regional groundwater flow gradient, water injected into the well may be flushed downstream and may not be pumped out during the pull phase as is shown in the Run 4 simulation results.

Therefore, the model results provide important information for designing and conducting the push-pull tests.

## ***II.2. Assessment of actual versus planned progress for each task***

Table 1 lists the research status of this project. Lab experiments for Task 1 have been completed. Task 2 on modeling design of the push-pull tests was scheduled to be finished in the third reporting period and will be completed in the sixth reporting period. Because of issues related to regulation of CO<sub>2</sub> injection into the shallow aquifer at Cranfield, MS, after discussing with the program manager, we were permitted to postpone Task 3 for 6 months. During the current reporting period, no major progress has been made on Tasks 3, 4, and 5. We have been working on obtaining permission to conduct the field push pull tests.

**Table 1** Research status of project 4265

Tasks		Past				Current	Ongoing			
		05/2010-07/2010	08/2010-10/2010	11/2010-01/2011	02/2011-04/2011	05/2011-10/2011	11/2011-01/2012	02/2012-04/2012	05/2012-09/2012	10/2012-04/2013
		Reporting Period 1	Reporting Period 2	Reporting Period 3	Reporting Period 4	Reporting Period 5	Reporting Period 6	Draft Report	Final Report	Project end
Task 1	Conduct Lab experiments	Scheduled	●—————▶							
		Progressing								
Task 2	Model the design of field push-pull tests	Scheduled		●—————▶		●	.....▶			
		Progressing								
Task 3	Conduct push-pull tests	Scheduled		●—————▶			●	.....▶		
		Progressing								
Task 4	Simulate results of push-pull tests	Scheduled		●—————▶		●	.....▶			
		Progressing								
Task 5	Communication	Scheduled				◆	.....▶			
		Progressing								

## ***II.2. Tasks proposed to be finished in the coming period***

In the coming period, we will continue to analyze the data from the batch experiments conducted in Task 1. The numerical model developed in Task 2 will be improved to account for mineral reactions and adsorption/desorption due to injection of water dissolved with CO<sub>2</sub>. The model will first be calibrated with the batch experiments, and then used to help design and conduct field push-pull tests. For Task 3, we plan to purchase the instruments which will be used for the push-pull tests and we will also communicate with other researchers who are working on similar field experiments. We are scheduling a visit to a research site in Alabama where push pull tests are being conducted in late November. Currently a research team from Southern Company is injecting groundwater saturated with CO<sub>2</sub> into a shallow aquifer at a depth of about 70 m to evaluate how groundwater quality in the shallow aquifer can be impacted by CO<sub>2</sub> intrusion. During this visit, we will discuss the experimental apparatus which is being used for their experiments..

## ***II.2. Problems encountered***

Currently, we haven't encountered serious problems.

## ***II.3. Rational for proposed changes (if any) to the scoped of work***

Currently, we follow the scopes proposed.

## ***II.4. Presentations, papers, reports***

Currently, we haven't presented or published any results related to this project.

### **III. Technical Summary**

#### ***III.1 Methods and materials***

Impacts of CO<sub>2</sub> leakage on groundwater quality will be evaluated using single-well push-pull tests (PPTs) (Figure 1) in a sedimentary aquifer in the Gulf Coast. These controlled field tests allow isolation of impacts of CO<sub>2</sub> leakage into an aquifer without the confounding issues associated with upward migration of brines with CO<sub>2</sub> that can occur when natural systems are evaluated (e.g. Keating et al., 2009). This project includes four tasks: laboratory batch experiments, modeling design of field push-pull tests, conduction of push-pull tests in the field, modeling of field experiments and communication. In this quarterly report, a detailed description of the batch experiments is described in the following. Description of methods for other tasks has been briefly described in the proposal and also in previous quarterly reports and will be given in more detail in future reports.

#### **Task 1. Batch experiments**

After the previous reporting on batch experiments of water-rock-CO<sub>2</sub> interactions, the experiments were kept running and have been periodically sampled. Four sets of sediment/aquifer samples were included in the batch experiments. The samples were obtained from the Cranfield site in Mississippi and the Helena, and Edwards and Brackenridge sites in Texas. The last sampling date was September 30<sup>th</sup> 2011, approximately 146 days after the start of the experiment.

The periodic exposure to low humidity CO<sub>2</sub> atmosphere may have caused evaporative enrichment in major elements. Generally speaking, Na<sup>+</sup>, K<sup>+</sup> and Cl<sup>-</sup> concentrations, as well as Mg<sup>2+</sup> in samples not encountering significant water rock interactions, increased between 15% and 20%. Future data processing will correct for artificial elemental enrichments. The Cranfield sand, Helena, Edwards and Brackenridge samples show an increase in alkalinity, Ca<sup>2+</sup>, and to

a lesser extent  $Mg^{2+}$ , concentrations. These increases were likely the result of evaporative enrichment and continued water-rock- $CO_2$  interactions. There is likely continued calcite, dolomite, and feldspar dissolution. It is not clear if the samples have reached equilibrium with respect to the reactive mineral phases present after 146 days. The experiment was continued with less frequent sampling to conserve water sample volume during this reporting period.

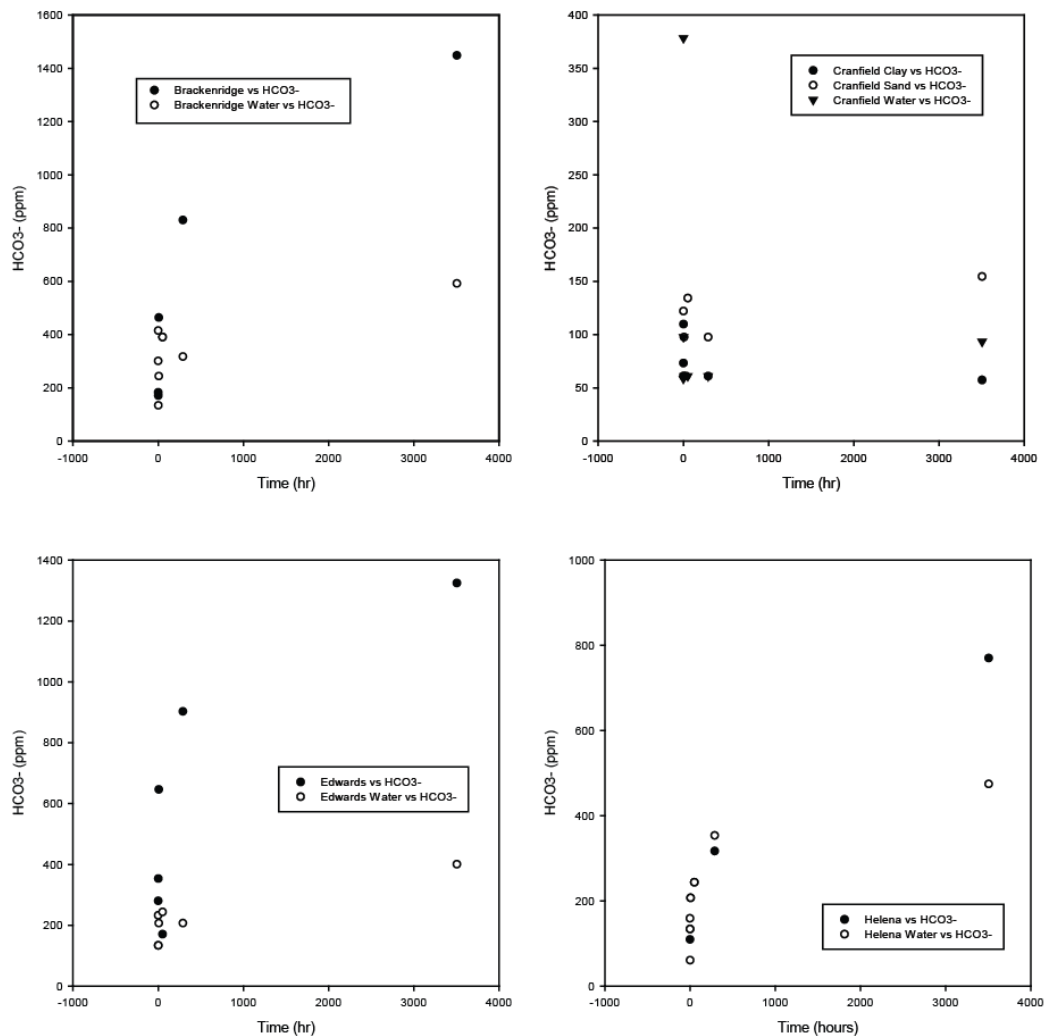


Figure 1. Time evolution of  $HCO_3^-$  concentrations (Samples containing reactive mineral phases (Brackenridge, Edwards and Helena rock samples) show a large increase in alkalinity. Water samples and the Cranfield rock samples do not show large changes in alkalinity and  $HCO_3^-$  concentrations remain low throughout the experiment suggesting a lack of chemically reactive mineral phases.

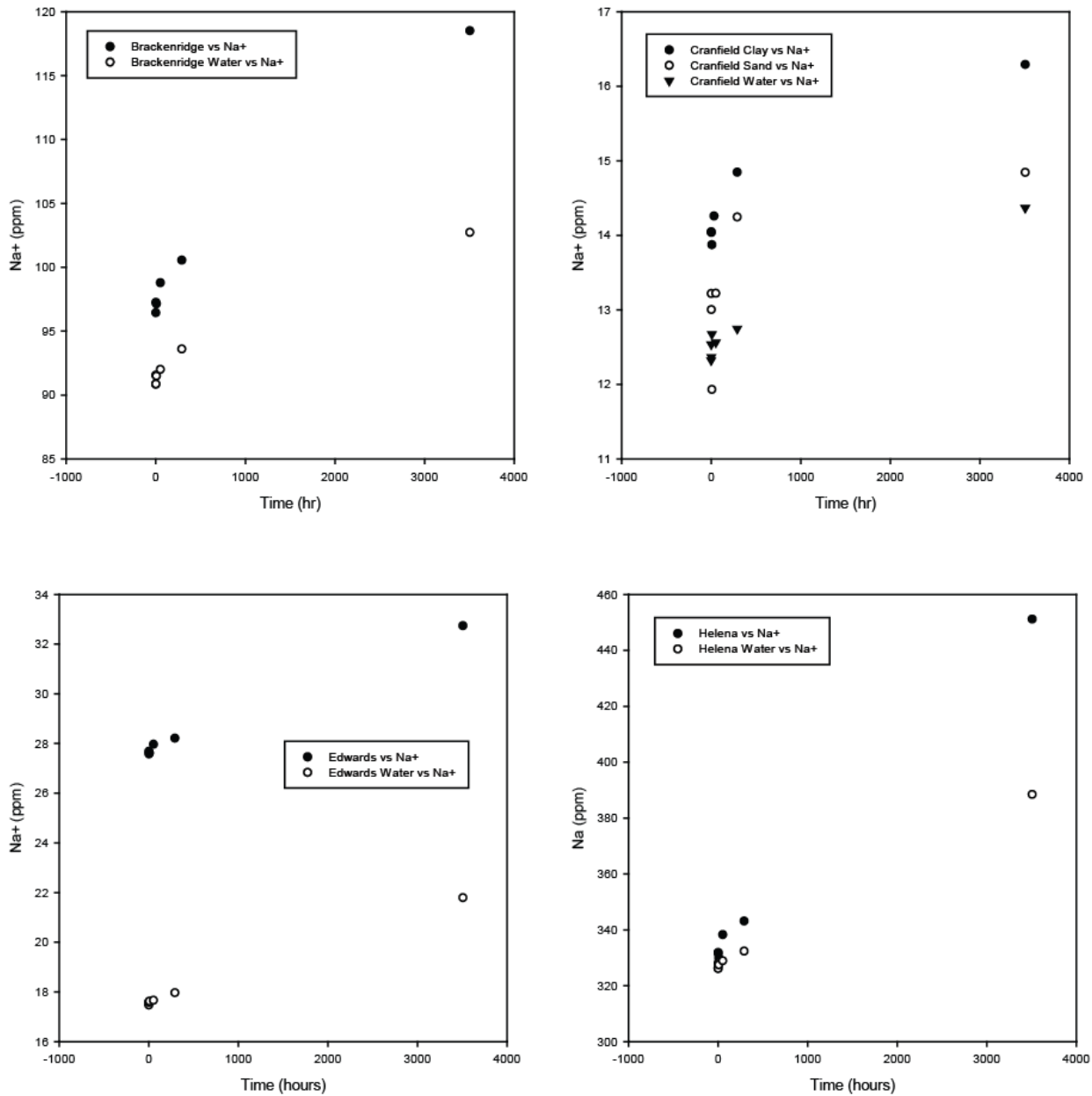


Figure 2. Time evolution of Na<sup>+</sup> concentrations (All samples show an increase in Na<sup>+</sup> concentrations including water samples. It is likely that the Na<sup>+</sup> concentration increases are due to evaporative enrichment of the water samples during the experiment. The Helena and Brackenridge rock samples may show partial Na<sup>+</sup> concentrations increases due to water rock interactions. The Edwards and Cranfield samples appear to exhibit identical Na<sup>+</sup> evaporative enrichments.



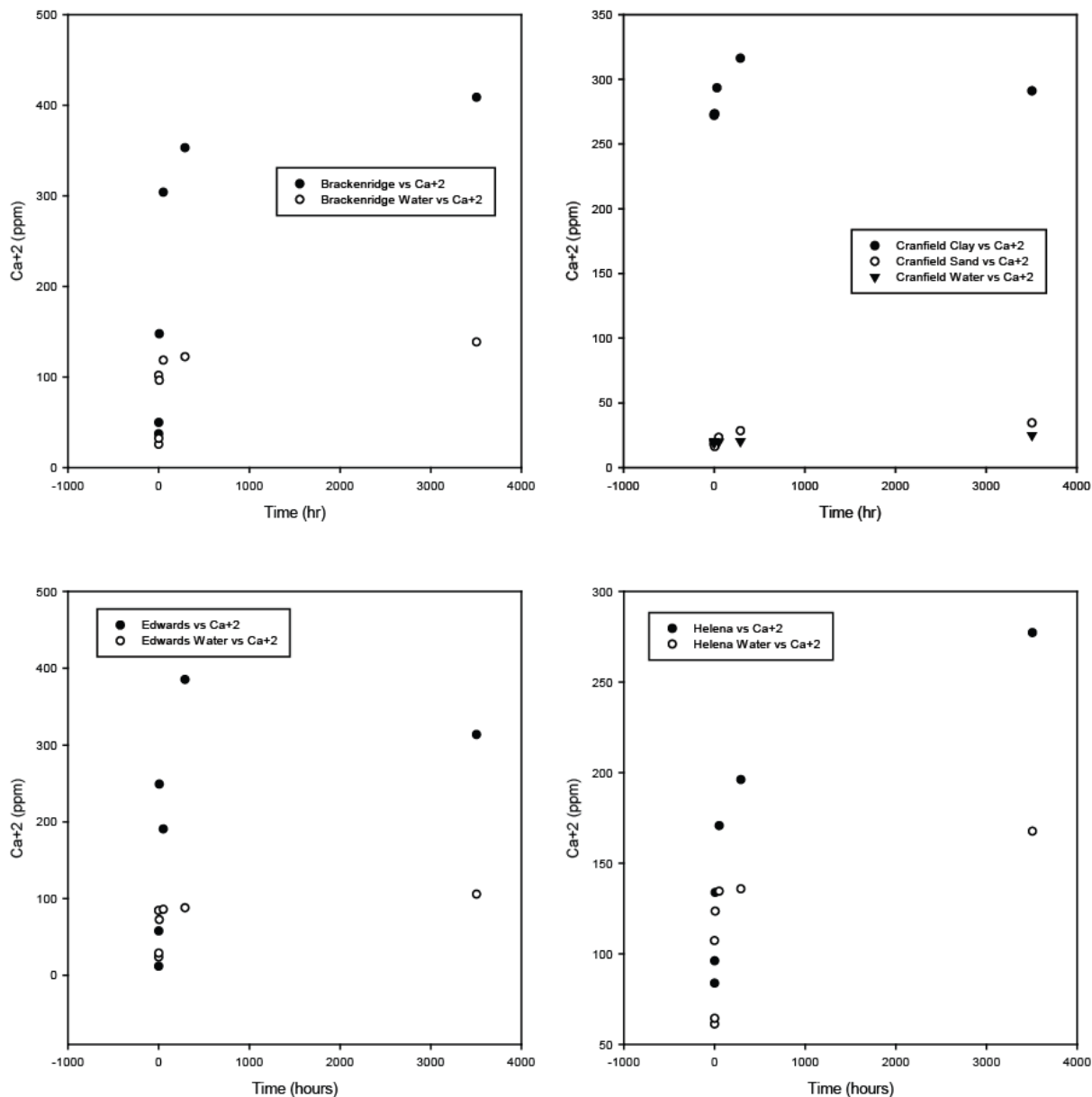


Figure 3 Time evolution of  $\text{Ca}^{+2}$  concentrations. Most samples show an initial increase in  $\text{Ca}^{+2}$  concentrations likely due to carbonate dissolution which also leads to an initial increase in alkalinity. The reactive carbonate phases appear to be quickly depleted and  $\text{Ca}^{+2}$  concentrations stabilize. Later increases in alkalinity may be due to continued, slower, dissolution reactions involving feldspars. Note the lack of reactive sources of  $\text{Ca}^{+2}$  in the Cranfield samples that correspond to a lack of alkalinity increases seen in the other water samples.

## Task 2. Modeling design of push-pull tests

In the previous report, we presented a numerical model for simulating push-pull tests in a 3-D axis-symmetric domain by neglecting the impact of regional groundwater flow on push-pull tests. An improved model was set up to consider regional groundwater flow and provide more reliable predictions for designing and conducting field experiments. A schematic of the conceptual model of the improved numerical model is shown in Figure 4. The water well for push-pull tests is located at the center of the domain with 400 m in length and 400 m in width. Thickness of the aquifer is assumed to be 7 m, the same as in the previous model. Regional groundwater flow with a gradient of 2.5‰ is assumed from the right boundary of the domain to left boundary, shown in Figure 4.

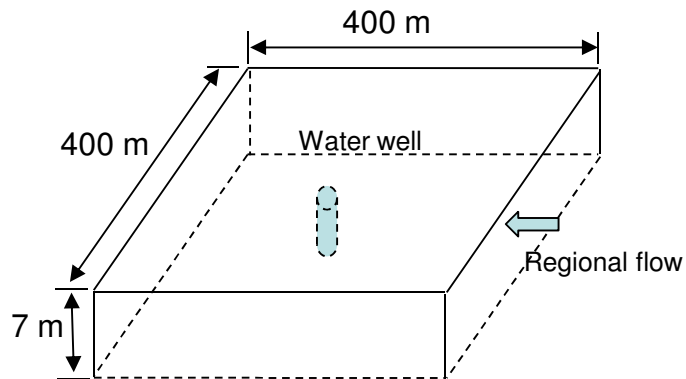


Figure 4. Schematic of conceptual model for simulating push-pull tests

The model domain is discretized into 12362 triangular elements and 6222 nodes in a two dimensional mesh (Figure 5). The elemental size is about 0.01 m near to the well and gradually increases to  $\sim 20$  m near the boundaries. Fixed groundwater heads are imposed on the left and right boundaries of the domain for obtaining a hydraulic gradient of regional groundwater of 2.5‰ at this site (Figure 5) which was roughly estimated from some water level measurements at the Cranfield site. Therefore, sensitivity analysis on the impacts of the regional hydraulic gradient is required to evaluate uncertainty. The other two boundaries are

assumed no-flow boundary conditions. At the well, a time function is imposed upon the pumping rate of the well for representing the three phases: injecting phase, resting phase, and pulling phase. In the numerical model, the pumping rate is calculated to be equal to a pumping rate constant times the time function, pumping rate coefficient,

$$Q=f*q$$

where  $q$  is pumping rate constant ( $m^3/hr$ ) and  $f$  is pumping rate coefficient (positive for water injection into the aquifer and negative for water pulling out the aquifer). An example of pumping rate coefficient as function of time is shown in Figure 6, corresponding to three phases: injection phase with a positive value, resting phase with 0, and negative value for pulling phase of the experiment.

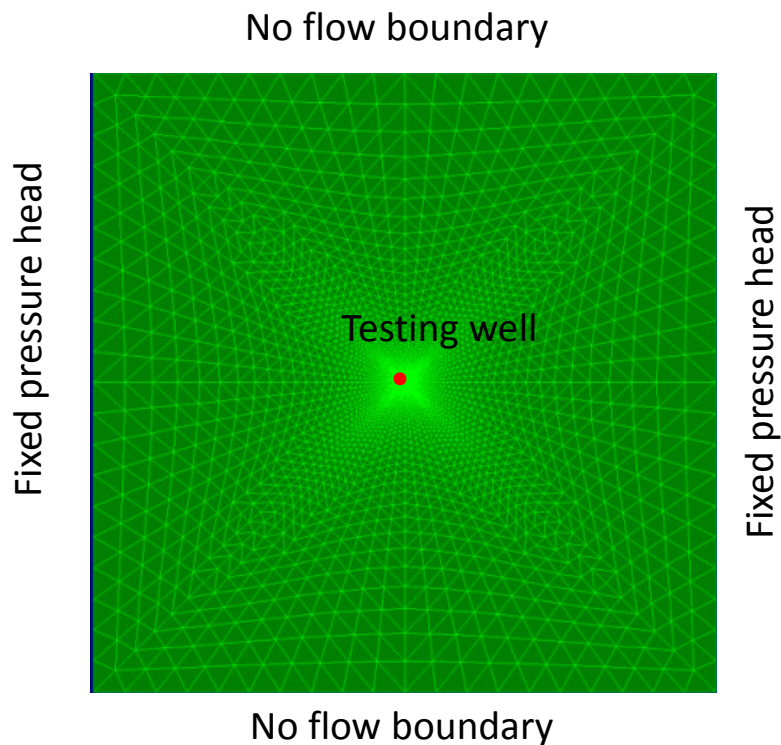


Figure 5. Two-dimensional mesh used in the improved numerical model

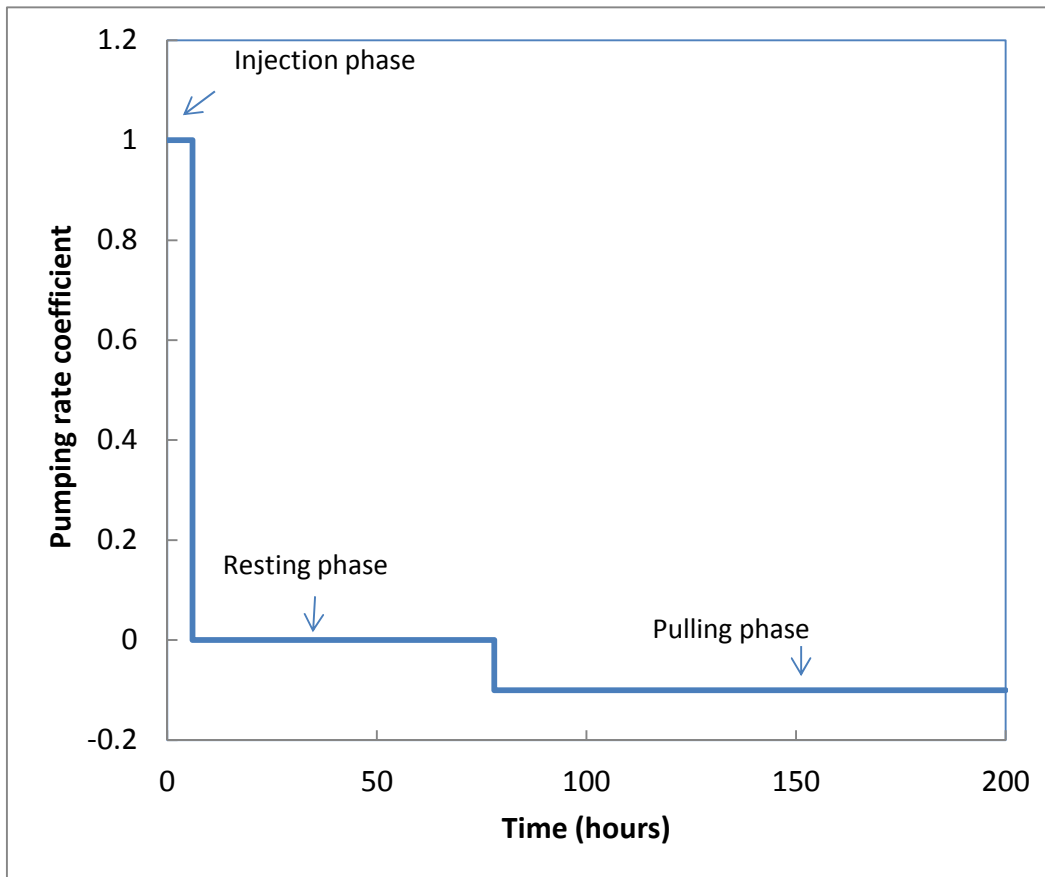


Figure 6. Time function of pumping rate coefficient imposed upon the well in the numerical model (positive for injection phase and negative for pulling phase)

The aquifer is assumed to be homogeneous with hydraulic conductivity of 7.6 m/day and porosity of 0.2 obtained from the literature because no measurements of hydraulic conductivity and porosity are available at this time. Water compositions used in the model are listed in Table 2. The regional groundwater flow into the domain through the right boundary has the same chemical composition as the initial groundwater composition. Composition of the injected water (Table 2) was calculated by equilibrating the initial water with CO<sub>2</sub> gas under a pressure of 1 atm with PHREEQC. Therefore, injected water has a pH of 4.7 and 0.0407 moles/L of HCO<sub>3</sub><sup>-</sup> because of CO<sub>2</sub> gas dissolution into water. NaBr was added to the injected water as a conservative tracer to illustrate the groundwater flow in the aquifer.

Table 2. Water compositions used in the numerical model

	Initial water (moles/L)	Boundary water (moles/L)	Water injected (moles/L)
pH	6.40	6.40	4.76
HCO <sub>3</sub> <sup>-</sup>	1.78E-03	1.78E-03	4.07E-02
Al <sup>+3</sup>	4.76E-07	4.76E-07	4.76E-07
Ba <sup>+2</sup>	8.45E-07	8.45E-07	8.45E-07
Br <sup>-</sup>	1.24E-06	1.24E-06	1.00E-02
Ca <sup>+2</sup>	5.18E-04	5.18E-04	5.18E-04
Cl <sup>-</sup>	8.54E-04	8.54E-04	8.54E-04
F <sup>-</sup>	6.32E-06	6.32E-06	6.32E-06
Fe <sup>+2</sup>	3.67E-06	3.67E-06	3.67E-06
K <sup>+</sup>	4.77E-05	4.77E-05	4.77E-05
Mg <sup>+2</sup>	3.41E-04	3.41E-04	3.41E-04
Mn <sup>+2</sup>	5.63E-07	5.63E-07	5.63E-07
Na <sup>+</sup>	5.03E-04	5.03E-04	1.05E-02
NO <sup>-3</sup>	2.03E-04	2.03E-04	2.03E-04
Pb <sup>+2</sup>	2.81E-08	2.81E-08	2.81E-08
SO <sub>4</sub> <sup>-2</sup>	3.71E-05	3.71E-05	3.71E-05
SiO <sub>2</sub> (aq)	2.04E-04	2.04E-04	2.04E-04
Zn <sup>+2</sup>	2.33E-06	2.33E-06	2.33E-06

This numerical model did not take into account mineral interactions and adsorption/desorption; therefore, there is no buffer for pH in the simulations of the aquifer. The domain processes for ions are mainly advection, dispersion, and mixing. For this preliminary modeling exercise, we wanted to test sensitivity of model results to injection rate and injection within a, regional groundwater flow gradient, and hydraulic conductivity of the aquifer. Therefore, five scenarios were designed for this purpose and summarized in Table 3. Injection rate in Run 2 is two times that in Run 1. Hydraulic conductivity in Run 3 is one tenth of that in Run 1. Run 4 has higher regional hydraulic gradient, 10 times that in Run 1. Injection rate in Run 5 is half of that in Run 1. The injection duration is maintained two times longer than in Run 1 so that the total injection amount of water is the same in both scenarios.

Table 3. Different parameters used in the four scenarios

Runs	Model parameters						
Runs	Injection rate	Duration of injecting phase	Duration of resting phase	Pumping rate at the pulling phase	Duration of pulling phase	Hydraulic conductivity of aquifer	Regional groundwater flow gradient
	(m <sup>3</sup> /hr)	hr	hr	(m <sup>3</sup> /hr)	hr	m/d	‰
1	5.68	6	72	0.568	120	7.62	2.5
2	11.36	6	72	0.568	120	7.62	2.5
3	5.68	6	72	0.568	120	0.762	2.5
4	5.68	6	72	0.568	120	7.6	25
5	2.34	12	72	0.568	120	7.62	2.5

As a tracer, Br<sup>-</sup> was injected with groundwater. At the well location, Br<sup>-</sup> concentration increased because of mixing between the injection water and the background water (initial water) in the aquifer. Br<sup>-</sup> gradually migrated away from the injection well.

Groundwater pH at the well location decreased when the low pH water was injected into the aquifer because of mixing of injected water with initial water in the aquifer. At the end of the injection phase, groundwater pH at the well reached a minimum value (which is mainly the injected water) and then gradually increased during the resting phase because of dispersion and diffusion of H<sup>+</sup> from the injection well to the aquifer. During the pulling phase (pumping rate is about one tenth of the injection rate), groundwater pH continued to increase at a rapid rate (Figure 7). Faraway from the well, no obvious changes in groundwater pH were found, regardless of upstream or downstream position from the well (Figure 7).

Comparison of model results calculated in the five runs is shown in Figures 8 through 10 in terms of time evolution of Br<sup>-</sup>, pH, and HCO<sub>3</sub><sup>-</sup> concentrations at the well. Since Run 1 and Run 5 have the same total amount of water injected, though the injection duration and injection rate are different, Br<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> simulated in the two runs at the well location show slight differences. Values of calculated pH are almost the same in the two runs. This suggests that

time evolution of ion concentrations at the well location may not be sensitive to either injection duration or injection rate, but the total amount of water injected which is equal to the product of the injection rate and duration. This can also be seen from the results of Run 2 where total amount of injection water is two times that in Run 1 (Table 3.) Because more water was injected into the aquifer, concentrations of Br<sup>-</sup>, pH and HCO<sub>3</sub><sup>-</sup> recovered more slowly in Run 2 than in Run 1.

Hydraulic conductivity shows significant impact on time evolution of Br<sup>-</sup>, pH and HCO<sub>3</sub><sup>-</sup> in the well. At the resting phase, concentrations of Br<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> calculated in Run 3 with a lower hydraulic conductivity are much higher than in Run 1 (Figures 9 and 11). The reason for this difference is that low hydraulic conductivity can slow down solute transport from the well to the aquifer during the injecting and resting phases and from the aquifer to the well during the pulling phase. When push-pull tests are conducted in a low permeability aquifer, the modeling results suggest a longer resting phase may be required so that injected water can have sufficient time to migrate into the aquifer to interact with groundwater and rock sediments.

Groundwater with high regional hydraulic gradient could flush away the water injected into the well downstream. Run 3 with a regional hydraulic gradient of 2.5 % (10 times higher than in Run 1), concentrations of Br<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> show a sharp decreasing trend during the resting phase. Concentration of Br<sup>-</sup> in the well computed in Run 3 is about 5% of peak concentration just at the end of first day during the resting phase. At the beginning of the pulling phase, Br<sup>-</sup> concentrations drop to near the background concentration in the aquifer. This is also observed in Figure 10 for HCO<sub>3</sub><sup>-</sup>. The results of Run 4 may suggest that push-pull tests conducted in a high regional hydraulic gradient may not be able to provide the information we need. A system with two wells may be required: one well for injection and the other well at the downstream end for monitoring and sampling. Through the preliminary modeling exercises, it can be seen that hydraulic conductivity of the aquifer and regional hydraulic gradient obviously impact the

results of push-pull tests. This preliminary model will be further improved to consider possible mineral reactions and adsorption/desorption due to CO<sub>2</sub> injection into the aquifer. The model will be calibrated firstly with the results of the batch experiments.

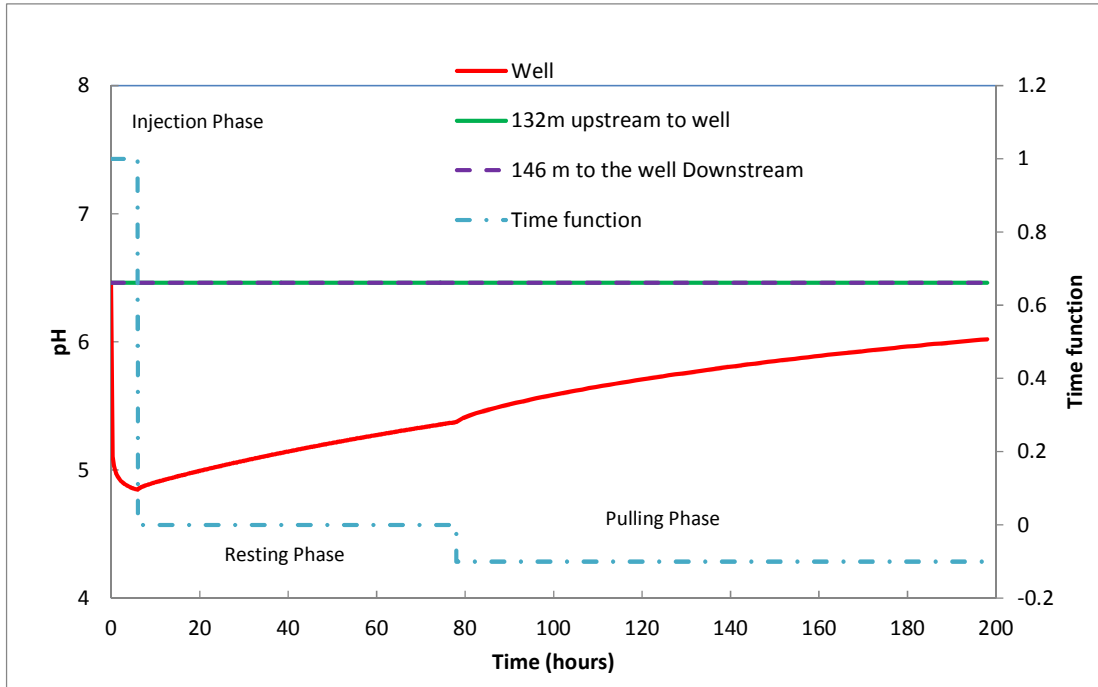


Figure 7. Time evolution of pH simulated in Run 1 at the well, at distances of 132 m upstream and 146 m downstream to the well.

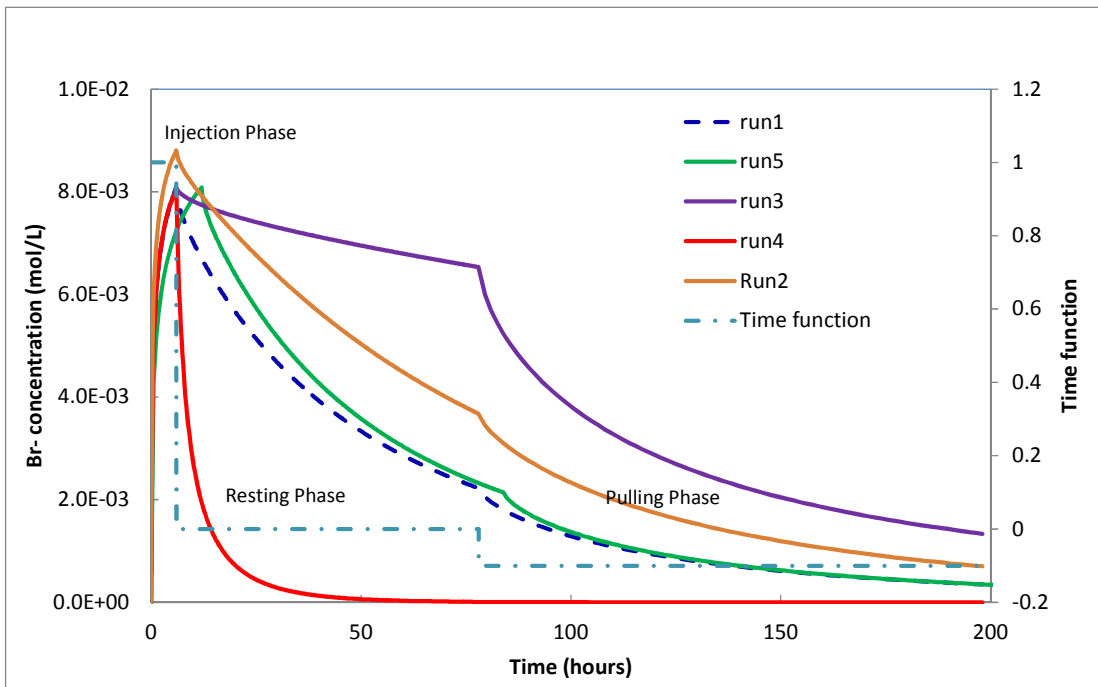




Figure 8. Time evolution of  $\text{Br}^-$  at the water well calculated in the 5 runs.

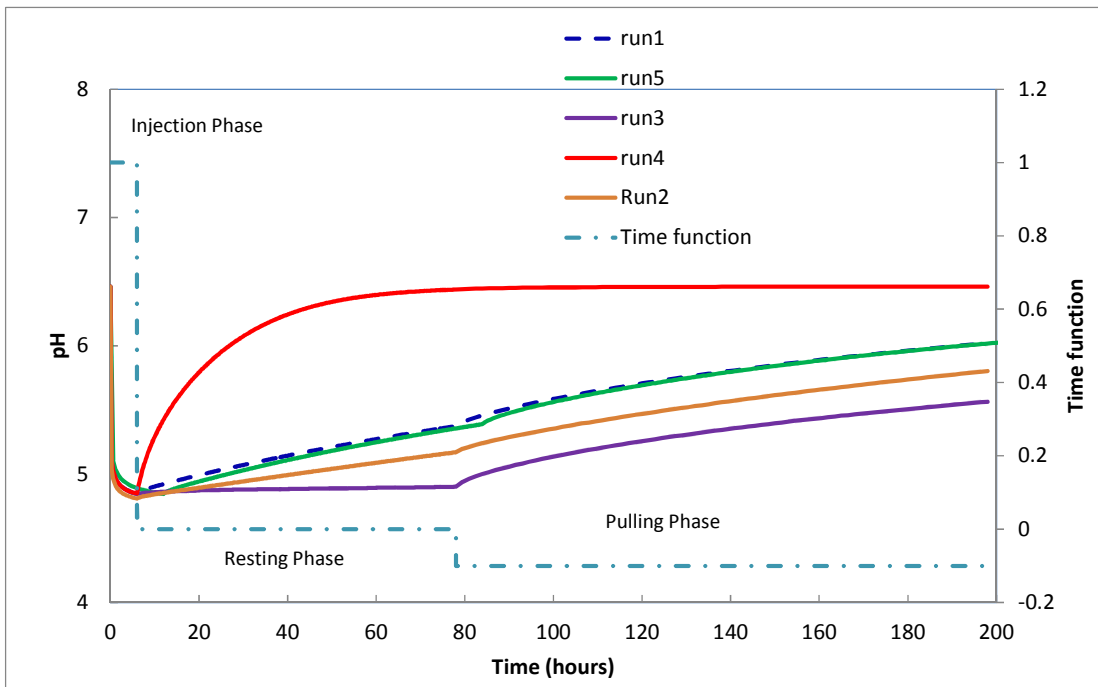


Figure 9. Time evolution of pH at the water well calculated in the 5 runs.

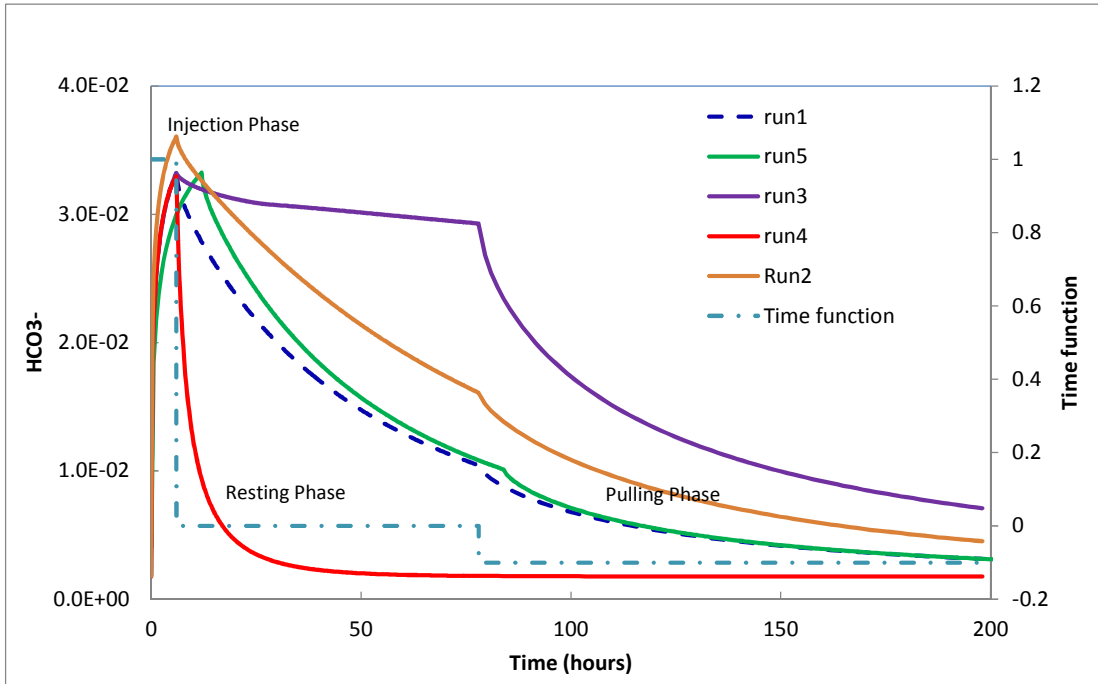


Figure 10. Time evolution of  $\text{HCO}_3^-$  at the water well calculated in the 5 runs.

## IV. Website update

Water Research Foundation Project 4265 — “Carbon Dioxide Injection into Shallow Sedimentary Aquifer Systems to Assess Potential Degradation of Groundwater Quality at Geological Carbon Sequestration Sites”

Principal Investigator: Bridget Scanlon

Co-Principal Investigator: Changbing Yang

Bureau of Economic Geology, University of Texas at Austin

Periodic Report No. 5, Period covered: May 1 2011 – Oct. 31, 2011

### Activities and Progress since Last Update

Batch experiments of water-rock-CO<sub>2</sub> interactions have been completed and preliminary model for designing push-pull tests was initialized.

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