

The importance of considering rock-water interaction when studying potential impacts of geological CO₂ sequestration on drinking water resources

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Summary

It is of fundamental importance that water-rock reactions be taken into account in the interpretation of ground water chemistry. Not considering the rock contributions to the rock-water-CO₂ reactive system can lead to incorrect extrapolations and overemphasize the risk to water.

Conclusions of modeling exercises must also be seriously weighted by the soundness of the model assumptions. For example, we think that the role of sulfides in terms of risk to water as a consequence of CO₂ leakage in the report of Birkholzer et al. (2008) has been overemphasized, as these species are not the minerals commonly observed in fresh-water aquifers.

Introduction

Researchers from the Bureau of Economic Geology (BEG) at the University of Texas at Austin are conducting experimental and modeling studies relevant to geologic sequestration of CO₂ (CO₂GS) with specific regard to potential impacts to shallow groundwater resources. In addition, BEG researchers have recently completed a field-based groundwater sampling study at the SACROC oilfield in west Texas and are continuing research on CO₂GS at the Cranfield oilfield in Mississippi. Other researchers in the field of geologic carbon sequestration have recently published work on potential impacts to water resources as a result of CO₂ injection directly into deep brine formations, or by accidental release of injectate CO₂ into drinking water resources either through laboratory experiments or groundwater modeling studies.

Themes we want to emphasize as being critical to studies of potential impacts to drinking water resources from CO₂ injection are:

- CO₂ occurs naturally in shallow aquifers. CO₂ concentrations in a single aquifer can vary temporally and spatially as a result of agricultural and industrial practices. For example, Scanlon et al. (2005, 2007) have documented enhanced recharge from land use changes. Enhanced recharge of groundwater through the vadose zone can potentially change CO₂ concentrations in the saturated zone.
- The capacity for carbonate minerals (carbonate rocks and carbonate cement in clastic rocks) to buffering changes in pH with influx of CO₂ is under represented in the literature (i.e. Carroll et al., 2009). An exception to this statement is Keating et al. (2009) who documented nicely the buffering capacity of carbonate cement in a high-CO₂ concentration natural analog system in New Mexico.
- Realistic rock-water reactions are critical to accurate prediction of impacts to groundwater as a result of CO₂ injection (numerous articles referenced herein). For example, Romanak et al. (in preparation) have also documented the importance of carbonates but in a more complex fashion through the incongruent

dissolution of dolomite as a process dominating the hydrochemistry of the Dockum aquifer that overlies the SACROC oilfield in west Texas.

The following text is a review of recently published studies on potential impacts to groundwater from GS with some examples from BEG's on-going and soon to be published work. We start by citing published work on the importance of rock-water interactions in both deep and shallow aquifers for interpreting results of groundwater modeling. We then focus on one specific study (Birkholzer et al., 2008) that has been completed by researchers at the Lawrence Berkeley National Laboratories (LBNL).

CO₂-water-rock interactions discussed in literature

Rock-water reactions are ubiquitous in groundwater systems and cannot be excluded from models used to predict impacts to groundwater from introduction of CO₂. Work of Kaszuba et al. (2003) concludes that because of the importance of rock-water reactions in potential geologic sequestration systems, much more than simple aqueous dissolution of CO₂ in water must be factored into any realistic model of potential impacts to deep formation fluids or freshwater aquifers from introduction of anthropogenic CO₂.

Earlier work by Zhu and Burden (2001) states that the complexity of aquifer fluid chemistry is defined by the degree of interaction with aquifer mineralogy, which includes solid matrix, grain-coatings and colloids. They are critical of groundwater modeling efforts that only consider pore-fluid compositions and ignore or greatly simplify aquifer mineralogy. Conclusions from Zhu and Burden (2001) are that contaminant fate and transport model predictions depend upon mineral composition of the aquifer. In fact, they state that the amount of calcite in the aquifer matrix determines the distance of contaminant plume migration.

Wigand et al. (2008) go on to state that not only does introduction of supercritical CO₂ into geologic systems affect brine composition through aqueous dissolution, it also affects the intensity of rock-water interactions. The phenomenon of increased rock-water interaction with increase in dissolved CO₂ in brine is becoming common knowledge through DOE/NETL- and EPA-sponsored research on geologic sequestration (i.e., Keating et al. 2009).

Review of LBNL shallow groundwater modeling

LBNL (Birkholzer et al., 2008) evaluated mobilization of a set of trace elements (called hazardous constituents in the report¹), such as arsenic, barium, cadmium, mercury, lead, uranium and zinc from a set of mineral species that may potentially be mobilized in the event of CO₂ leak from the deep storage reservoirs using a comprehensive computational model. The mineral assemblages in the aquifer rocks were selected indirectly upon evaluation of 38,000 groundwater samples from aquifers throughout the United States, retrieved from the United States National Water Information System (NWIS). The report concluded that some trace elements may be mobilized and exceed the maximum

¹ We disagree with the term "hazardous constituents" used in the Birkholzer et al., (2008) report because the trace elements occur in groundwater naturally even if their concentrations may increase owing to CO₂ intrusion.

contamination levels (MCL) resulting from enhanced dissolution of the mineral assemblages caused by CO₂ intrusion into shallow groundwater aquifers. However, the model results rely on a fundamental assumption with large uncertainties in model parameters. We disagree with the assumption for constructing the EQ3/6 models and the methodology they used for investigating mobilization of trace elements from the aquifer rocks. We believe that this report illustrates the trappings of solely using groundwater compositions to estimate impact of CO₂ on the system.

The fundamental assumption in the Birkholzer et al. (2008) report for constructing the EQ3/6 models is that mobilization of trace elements is mainly dominated by enhanced dissolution of a set of specific mineral assemblages (for instances, sulfides in Table 3.6, p37 in the report). This set of specific mineral assemblages was selected from mineralogical analysis of coal seam aquifers, which formed in very strong reducing environments. Based on such an assumption, the authors calculated saturation indices of the selected mineral assemblages over chemical analyses of 38000 groundwater samples and determined whether a specific mineral phase would be present in a rock in equilibrium with the water sample. In a second step, assuming this phase is present, the authors computed the amount of trace elements that could be released under addition of CO₂. This assumption is unreasonable and not well supported at all in the literature. There are many other factors that could affect mobilization of the tracer elements, such as aqueous complexation (by ligands), ad/desorption from metal oxide and clay surfaces, and solid solutions in common minerals (carbonates, feldspars, and clay minerals). For instance, behavior and contribution of arsenic in natural water are related to MeOx (either simple desorption in oxidizing conditions or reducing conditions) (for example, Smedley and Kinniburgh, 2002, Scanlon et al. 2009).

BEG researchers did a set of batch experiments by reacting rock samples taken from major aquifers in Texas with water and CO₂ gas at a pressure of 1 atm (Lu et al., 2009, Smith et al. 2009). They found that concentrations of some trace elements may be elevated after CO₂ intrusion, such as arsenic (Figure 1). However, no evidences of XRD and SEM analysis indicated that arsenopyrite existed in the rock samples. Lead, which according to the Birkholzer (2008) could be the most problematic element after CO₂ intrusion, however, is non-detectable in the 10 batch experiments. Of the 114 analyses of potable groundwater in the vicinity of the SACROC oilfield in west Texas, 100 samples (88% of the total samples) had Pb concentrations below a detection limit of 0.0002 milligrams per liter (mg/L) (Smyth et al., in preparation). Our experiences indicate that Pb in drinking water resources commonly comes from corrosion of submersible water pumps and accompanying conduit pipes and not from the aquifer rocks.

In conclusion, the methodology employed in the Birkholzer (2008) report on potential impacts of CO₂ addition to shallow groundwater resources by using only numerical modeling techniques is questionable and may be misleading if the controlling minerals/or controlling phases assumed in the numerical models are not the right ones. In addition, large uncertainties in the model parameters, such as Eh values and solubility constants may lead to wrong conclusions. Regulations of CCS based on such conclusions drawn

from the model results presented in the Birkholzer (2008) report could be biased and may be impractical when applied to actual sites.

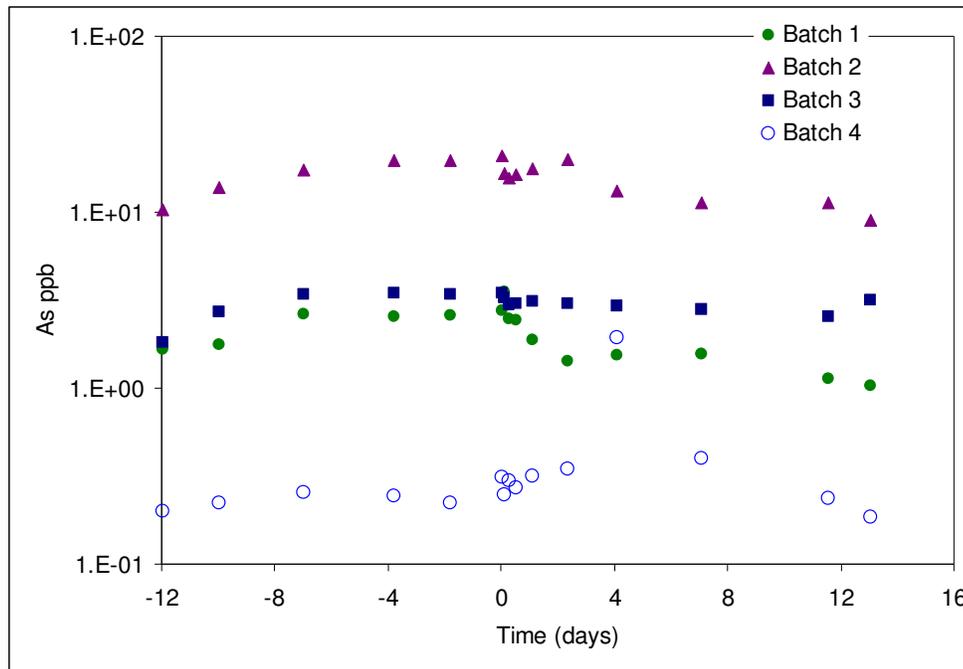


Figure 1. Evolution of arsenic concentration in four batch experiments (time 0 represents introduction of CO₂ into the batch reactor)

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