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Evaluating Impacts of CO_2 Intrusion into an Unconsolidated Aquifer: II. Modeling Results†

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ABSTRACT

Large scale deployment of CO_2 geological sequestration requires the assessment of the risks. One of the potential risks is the impact of CO_2 leakage on shallow groundwater overlying the sequestration site.The understanding of the key chemical processes and parameters are critical for building numerical models for risk assessment. Model interpretation of laboratory and field tests is an effective way to enhance such understanding. As part of this investigation, column experiments in which the CO_2 saturated synthetic groundwater flowed through a column packed with materials from the High Plains aquifer, were conducted. Changes in concentrations of several constituents in the column effluent and pH were determined. In this paper, a reactive transport model was developed to describe and interpret the observed concentration changes, attempting to shed light on the chemical reactions and mechanisms and key parameters that control the changes in effluent chemistry. The reactive transport model described fairly well the changes in pH and the concentration changes of Ca, Mg, Ba, Sr, Cs, As and Pb. Calcite dissolution and Ca-driven cation exchange reactions were the major drivers for the concentration changes of Ca, Ba, Sr, and Cs. The pH-driven adsorption/desorption reactions led to a concentration increase of As and Pb. The volume fraction and reactive surface area of calcite, CEC and sorption capacity were key parameters in controlling the magnitude of concentration increase. Model results also showed that Ba, which is an important chemical element released into the aqueous phase during these experiments, may be incorporated into the calcite crystal structure and the dissolution of Ba-bearing calcite could be an alternative pathway to explain the increase in aqueous Ba concentration when sediments are exposed to the CO_2 saturated leaching groundwater.

1. INTRODUCTION

Geological carbon (C) sequestration is a promising new technology to curb global greenhouse gas emissions. It involves capturing the CO_2 gas emitted from fossil fuel burning power plants, and injecting the captured CO_2 gas into deep saline aquifers or depleted oil and gas reservoirs. Geological C sequestration provides a new approach to combat global warming due to ever rising greenhouse gas emissions by storing it permanently underground. However, a critical question that arises from the proposed geological C sequestration is the potential impacts of the CO_2 injection on the quality of drinking water aquifers overlying C sequestration storage sites.

Over the last decade, a number of studies have been undertaken to assess the impacts of potential CO_2 leakage from deep storage reservoirs on the quality of overlying freshwater aquifers (Harvey et al. (2013); Lemieux (2011), and references therein). Numerical modeling has long been used to conduct generic evaluation of the potential groundwater quality change as a result of the hypothetical leakage of CO_2 (Apps et al., 2010; Carroll et al., 2009; Wang and Jaffe, 2004; Wilkin and Digiulio, 2010; Zheng et al., 2009), and more importantly to understand the chemical processes that control the CO_2-induced release of metal via model interpretation of laboratory experiments (Kirsch et al., 2014; Viswanathan et al., 2012; Wunsch et al., 2014) and field tests (Trautz et al., 2013b; Zheng et al., 2012).

In general these models predicted the release of trace metals such as Pb and As (Apps et al., 2010; Wang and Jaffe, 2004; Zheng et al., 2009), which is largely consistent with the observations from laboratory experiments (Humez et al., 2013; Kirsch et al., 2014; Little and Jackson, 2010; Lu et al., 2010; Smyth et al., 2009; Varadharajan et al., 2013; Viswanathan et al., 2012; Wunsch et al., 2014), although the type of metal being released and the severity of release

64 vary among these experiments. In field tests, however, release of trace metals, especially those
65 of environmental relevance such as As, Pb, Ba, and Cd, has not been observed (Cahill and
66 Jakobsen, 2013; Kharaka et al., 2010; Peter et al., 2012; Spangler et al., 2010; Trautz et al.,
67 2013b; Yang et al., 2013). The difference between the observation of laboratory and field tests in
68 terms of the release of trace metals is probably because the laboratory experiment is too
69 aggressive in leaching out trace metal due to the use of DI water, oxidation, high water/solid
70 ratio and longer reaction time. On the other hand, release of alkali and alkaline earth metals,
71 including Na, K, Ca, Mg, Sr and Ba, were commonly observed both in laboratory and field
72 experiments, although the degree of releases were different. The rise in concentrations of
73 dissolved constituents observed during field tests was typically much less pronounced than in
74 laboratory experiments — field tests show increases about an order of magnitude or less
75 compared to pre-CO_2 levels (20% to 700% in the studies cited above), while orders-of-
76 magnitude increases have been observed in laboratory tests.

77 While the increase in concentration of dissolved constituents raises concerns, a lot of
78 efforts have been invested to understand the controlling chemical processes via model
79 interpretation of laboratory experiments (Viswanathan et al., 2012) and field tests (Zheng et al.,
80 2012). These efforts will facilitate the development of numerical models which will have a
81 better predictability. The chemical processes potentially responsible for the mobilization of trace
82 elements (due to an increase in aqueous carbonate concentration and the decrease of pH include
83 the dissolution of carbonates (Birkholzer et al., 2008; Kharaka et al., 2006b; McGrath et al.,
84 2007), sulfides (Apps et al., 2010; Wang and Jaffe, 2004; Zheng et al., 2009) and iron
85 oxyhydroxide minerals (Kharaka et al., 2006a; Kharaka et al., 2009), as well as surface reactions

such as adsorption/desorption and ion exchange (Apps et al., 2010; Kharaka et al., 2006a; Kharaka et al., 2009; Zheng et al., 2009). The release of alkali and alkaline earth metals, including Na, K, Ca, Mg, Sr and Ba, which are most commonly observed both in laboratory and field experiments, is thought to be controlled by the dissolution of calcite and Ca-driven cation exchange reactions (Zheng et al., 2012). The reaction path proposed and kinetic model study conducted by Wilkin and Digiulio (2010) further indicates that the geochemical response of an aquifer to CO_2 leakage is closely related to the aquifer mineralogy. It is thus expected that differences in mineralogy in addition to differences in geology (i.e., aquifer type), and groundwater chemistry at any particular site could lead to different responses to CO_2 leakage. For this reason, experimental laboratory work and field tests coupled with modeling studies are necessary to assess the response of a particular aquifer and evaluate potential changes in groundwater quality and risks related to a CO_2 release.

The objective of this study is to determine the geochemical reactions that occur and influence changes in pH and trace metal mobilizations in groundwater aquifers after the intrusion of the CO_2 gas. Batch and column experiments in which materials from the High Plains aquifer were exposed to CO_2 saturated synthetic groundwater (SGW) were conducted to simulate the impact of an accidental release of CO_2 on a shallow aquifer. These experiments are presented in the first paper of this two paper series (Lawter et al., 2015). A reactive transport model was developed to interpret the observed concentration changes in the column effluent water, attempting to shed light on the chemical reactions and key parameters that control the concentration changes of some constituents. Modeling the batch experiment presented in the first paper of this series (Lawter et al., 2015) would help to improve and/or further consolidate the geochemical

conceptual model and the reactive transport model, but which have been previously developed based on the batch experiments conducted on other sand-based sediment (Zheng et al., 2015).

2. COLUMN EXPERIMENTS

2.1 Materials and Methods

Modeling was based on column experiments conducted on sediments from the High Plains aquifer in Kansas, obtained from the Drill Core Library at the Kansas Geological Survey. Sediments originated from a single well (CNG), but depths varied from 8 feet to 150 feet. The sediments used in this study were from 58'-60' (CNG 60) and 109'-111' (CNG 110). Characterizations were conducted for these sediment samples to determine chemical composition, crystallization, and surface morphology. Acid extractions conducted on the sediments revealed the sediments contained contaminants of concern for groundwater quality, such as As, Sr, and Pb. The SGW with a chemical composition and pH similar to that of the High Plains aquifer [based on USGS groundwater data for the High Plains aquifer (Becker et al., 2002)], was used in all laboratory experiments and as the influent solution in the models. The recipe used to make SGW is given in Lawter et al. (2015); the composition of the SGW is listed in Table 1.

The column experiments are explained in more detail in Lawter et al. (2015), but will be described briefly here. The columns were conducted at room temperature (21 ± 2 °C) and were initially leached with SGW for several days to achieve hydrological equilibrium (i.e., full saturation) and were then leached with CO2 gas-saturated SGW. CO2 gas was continuously purged in the influent bottle at a rate of 0.5 mL/min. Stop flow conditions were used to

130 determine the effect of increased fluid residence time on elemental release to observe time-
131 dependent reactions and processes in the columns. Stop flow conditions were applied after the
132 initial leaching with SGW prior to CO2 injection (time = 70 hours, stopped for 170 hours) then
133 twice more at approximately 250 hours and 350 hours, with the stop flows lasting 122 hours.
134 During the experiment, about one sample per pore volume (PV) was collected, while the effluent
135 samples were collected more frequently after the stop-flow events. The pH was measured
136 continuously online. At the end of the experiments, selected effluent samples were analyzed by
137 both ICP-OES and -MS to determine the aqueous concentrations of major, minor, and trace
138 elements. Column parameters and other related information are listed in Table 2.

139 **2.2 Sediment Characterization: XRD and SEM/EDS**

140 Full results can be found in Qafoku et al. (2013), Shao et al. (2014) and Lawter et al.
141 (2014) but a summary is provided below. Quantitative XRD analyses (QXRD) were conducted
142 for the High Plain aquifer sediments used in this work. The results indicate that quartz and
143 feldspar are the major minerals for the sediments (Qafoku et al., 2013). Small amounts of mica
144 were also detected in the silt fraction of both samples. For the <2mm fraction used in the
145 experiments, CNG 110 contained 1% calcite (the silt and clay fractions contained 35% and 11%
146 calcite, respectively), but no detectable calcite was found in CNG 60. Scanning Electron
147 Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) data shows the presence
148 of Ca bearing phases in CNG 60 (most likely, calcite coatings), which was undetected in the
149 QXRD results (Lawter et al., 2014). These results indicate that the sandy sediments used in this
150 work represent one aquifer type (largely unconsolidated aquifers) overlying potential CO_2
151 sequestration repositories within the continental US.

3. MODELING

3.1 Model setup

A 1-D reactive transport model was developed to mimic the conditions applied to the column tests. A fixed flow rate is applied to one end of the column and open boundary is used for the other end of column. During stop flow events, the flow rate is adjusted to zero. Chemical reactions considered in the model are aqueous complexation, adsorption/desorption via surface complexation, cation exchange (using the Gaines-Thomas convention) and mineral precipitation/ dissolution under kinetic constraints (using published rate laws). The cation exchange reactions are listed in Table 1, with selectivity coefficients from Appelo and Postma (1994) and a CEC of 1.55 meq/100g calibrated based on measured breakthrough curve. The surface complexation reactions are listed in Table 2. In the current model, it is assumed that ferrihydrite [as $Fe(OH)_3(s)$], is the adsorbent. The reaction constants for surface protonation are taken from Dzombak and Morel (1990), and surface complexation reactions of carbonate from Appelo et al. (2002). The model considered quartz, K-feldspar and muscovite as the major aquifer minerals, with a small amount of calcite, magnesite and $Fe(OH)_3(s)$), based on QXRD results, with a full list of mineralogical composition listed in Table 3. Calcite and magnesite were not detected using QXRD for sample CNG 60; the calcite volume fraction was calibrated based on the measured breakthrough curve of Ca and pH, and that for magnesite was calibrated from the measured breakthrough curve of Mg and pH. In the current model, $Fe(OH)_3(s)$ was used as the proxy of all possible adsorbents and its amount was calibrated based on the measured breakthrough curve of pH and As. Equilibrium constants for these minerals and other secondary

phases allowed to form are given in Table 3. These data were taken from Data0.dat.YMPv4.0, a EQ3/6 (Wolery, 1993) database qualified by the U.S. Department of Energy for the Yucca Mountain.

As SGW initially displaces the pore water residing in the column, the measured concentrations for the first effluent water sample actually represents the initial water composition in the column. The model therefore uses first measured concentration of the effluent as the initial concentrations. The concentrations of major cations and anions in the SGW were calculated from the recipe found in Lawter et al. (2014) and those for the trace elements are assigned small values of 10^{-15}. The SGW was pH adjusted to a value of 7.5 prior to the start of the experiment and the concentration of dissolved CO_2 is calculated by assuming equilibrium with atmosphere (CO_2 partial pressure of $10^{-3.4}$ bar), which yields a total concentration of dissolved CO_2 of 2.35×10^{-4} M. After the SGW is purged with CO_2, the pH decreases to 4 and the concentration of dissolved CO_2 is calculated by equilibrating with CO_2 partial pressure of 0.14 bar (2 PSI, see Table 2) which leads to a total dissolved CO_2 concentration of 5.1×10^{-3} M.

The simulations were conducted with TOUGHREACT Version 2 (Xu et al., 2011), which implements a general form of rate law for the dissolution and precipitation of solid phases (Lasaga et al., 1994; Steefel and Lasaga, 1994):

$$r = kA\left|1-\left(\frac{K}{Q}\right)^{\theta}\right|^{\eta} \quad (1)$$

where r is the kinetic rate, k is the rate constant (mol/m^2/s) which is temperature dependent, A is the reactive surface area per kg water, K is the equilibrium constant for the mineral–water

reaction written for the destruction of one mole of mineral, and Q is the reaction quotient. Here, for simplicity, the exponents θ and η are assumed equal to 1. The reactive surface area, A, is a function of the mineral specific surface area (e.g., cm^2/g mineral) and the volume fraction of the mineral in the sediment.

The rate constant for calcite dissolution is given as a combination of neutral, acid and carbonate mechanisms (Palandri et al., 2005; Plummer et al., 1979):

$$k_{\square} = 1.5\times10^{-6} e^{-E_a^{nu}/RT} + 0.5\, e^{-E_a^{H}/RT} a_H + 9.6\times10^{-5} e^{-E_a^{CO2}/RT} a_{CO2} \quad (2)$$

where E_a^{nu}, E_a^{H} and E_a^{CO2} are activation energies with values of 23.5, 14.4 and 35.4 (kJ/mol), respectively. The rate constant for the neutral, acid and carbonate mechanisms, are respectively 1.5×10^{-6} (mol/m^2/s), 0.5 (mol/m^2/s/M) and 9.6×10^{-5} (mol/m^2/s/M). a_H is the H^+ activity and a_{CO2} is the activity of dissolved CO_2. In the model, the specific surface area of calcite (60 cm^2/g) was calibrated, together with the initial calcite volume fraction, to match the breakthrough of alkaline earth metals observed for the column test on sample CNG 60. The same specific surface area of calcite is also used in the base model for sample CNG 110.

The rate constant for magnesite dissolution is also given as a combination of neutral, acid and carbonate mechanisms (Palandri et al., 2005):

$$k_{\square} = 4.75\times10^{-10} e^{-E_a^{nu}/RT} + 4.16\times10^{-7} e^{-E_a^{H}/RT} a_H + 1.74\times10^{-6} e^{-E_a^{CO2}/RT} a_{CO2} \quad (3)$$

where E_a^{nu}, E_a^H and E_a^{CO2} are activation energies with values of 23.5, 14.4 and 62.8 (kJ/mol), respectively. The rate constant for the neutral, acid and carbonate mechanisms, are respectively 4.75×10^{-10} (mol/m^2/s), 1.46×10^{-7} (mol/m^2/s/M) and 1.74×10^{-6} (mol/m^2/s/M). In the model, the specific surface area of magnesite (200 cm^2/g) was calibrated, together with the initial magnesite volume fraction, to match the breakthrough of Mg and pH observed for the column test on sample CNG 60. We use the same specific surface area of magnesite in the base model for sample CNG 110.

Because minerals other than calcite and magnesite have negligible effects on the chemical changes in the column due to the short duration of the experiment, their surface areas and rate constant are taken from Xu et al. (2006) and Zheng et al. (2012) without further calibration. Note that $Fe(OH)_3(s)$ has intangible dissolution over the course of the experiment, which means its dissolution has little effect on the chemical change in the experiment, and as the adsorbent it is important.

3.2. Modeling results

The focus of this paper is the interpretation of concentration changes observed in the CNG 60 column, which shows systematical and well correlated changes in concentration of various elements. The model interpretation of pH, and some alkali and alkaline earth metals including Ca, Mg, Ba, Sr and Cs whose changes have been widely observed in the laboratory and field tests, and As and Pb which are of great environmental concern and less commonly observed in the field and lab tests are specifically targeted. A model for the column test on sample CNG 110 was also developed based on that for CNG 60.

3.2.1. Models for the CNG 60 column: The base case

The pH drops immediately following flowing CO_2 saturated SGW through the column, although the extent of drop varies depending on the pH buffering processes. Figure 1 shows the comparison of the measured and simulated pH for the CNG 60 column experiment. In the current model, dissolution of calcite and magnesite are the major reactions that buffer pH, with less pH buffering effect from the surface protonation. The pH buffering by the dissolution of calcite has been well understood and demonstrated (Birkholzer et al., 2008; Carroll et al., 2009; Wang and Jaffe, 2004); the pH buffering by the surface protonation is also well known and has been demonstrated recently in the context of the impact of CO_2 leakage on groundwater (Zheng et al., 2009; Zheng et al., 2012). However, the effect of magnesite dissolution on pH is not widely reported. As demonstrated in Figure 3, removal of magnesite leads to underestimation of pH after around 400 hours. As the CO_2 saturated SGW flushes through the column, calcite dissolution is the primary pH buffer process. After about 400-500 hours, calcite is most likely depleted. Because surface protonation has limited pH buffer capacity, pH keeps decreasing and eventually reaches a level close to the pH of the injected SGW (pH = 4), if additional pH buffering from magnesite dissolution is not considered (Figure 3, "model no magnesite"). This motivates the consideration of magnesite in the base model. Also motivating the inclusion of magnesite in the model is the concentration level of Mg, which will be discussed later (Figure 2).

Measured breakthrough curves for Ca, Ba, Sr and Cs show a similar trend — a sharp increase in concentration upon the arrival of CO_2 saturated SGW and then a quick drop. A similar trend has also been observed in a field test conducted in Mississippi (Trautz et al., 2013b), which was interpreted with a model concept that considered the dissolution of minute amount of calcite and the concurrent cation exchange reactions (Trautz et al., 2013b; Zheng et

al., 2012). Here we apply the same concept but recalibrate the quantity of calcite and surface area (which affect the dissolution rate of calcite). A volume fraction of 0.045% and a specific surface area of 60 cm^2/g are used for calcite, which leads to a decent fit of the measured breakthrough curve of Ca as shown in Figure 1. Calcite is not observed by XRD because the volume fraction is well below the detection limit of 1%, but Ca bearing coating was detected in CNG 60 by SEM/EDS analysis. It is also noteworthy that a volume fraction of calcite below the XRD detection limit is also used in the model for the field test described in Trautz et al. (2013a), where the presence of calcite in the sediments was later confirmed by micro-X ray spectroscopy. The specific surface area of 60 cm^2/g for calcite is also higher than that used in Trautz et al. (2013a) (9.8 cm^2/g), which is justified considering the difference between the column test with <2 mm sample in this paper and the field test in Trautz et al. (2013b). Because the dissolution rate of calcite is a function of pH and dissolved CO_2 (or CO_2 partial pressure) as shown in Equation (2), the dissolution of calcite is significantly accelerated upon the arrival of CO_2 saturated SGW which is low in pH and high in dissolved CO_2. Such an acceleration of calcite dissolution is the key for a sharp increase in Ca concentration, but the concentration decrease after the peak (Figure 1) is due to the depletion of calcite.

The increase in Ca concentration due to calcite dissolution triggers a series of cation exchange reactions. As a result, the concentrations of most alkali and alkaline earth metals show a similar pulse-like shape in the breakthrough curves, e.g., Sr, Ba (Figure 1) and Cs (Figure 2). The model reasonably follows the measured breakthrough curves of Sr and Cs, but underestimates the measured data of Ba although qualitatively the model results and data for Ba match. The quantitative mismatch between model results and data for Ba could be eased if

279 another Ba release mechanism is considered, which will be discussed later in this paper. In the
280 current model, Mn is controlled only by cation exchange reaction. Model results match the first
281 peak in the Mn breakthrough curve but fail to catch the stepwise increase in the Mn
282 concentration in the effluent (Figure 2). The fact that Mn concentration keeps increasing
283 indicates there is dissolution of Mn bearing minerals. However, no Mn bearing minerals were
284 detected in mineral characterization; they might be of too small quantity to be identified.
285 Interestingly the breakthrough curve of Si shows a pattern (Figure 2) similar to Ca, Cs, Sr and
286 Ba, except Si has a more pronounced peak after the second and third stop-flow events. The
287 similarity between Si and and Ca breakthrough had also been observed in a field test in
288 Mississippi (Pugh et al., 2013). Because Si bearing minerals are unlikely to dissolve as quickly
289 as calcite, and based on findings previously presented in the literature (Pugh et al., 2013), we
290 included adsorption/desorption reactions for Si in the model (see Table 4) and, as a result, a
291 qualitative match between model and experimental data was achieved for Si (Figure 2).

292 The SGW contains a fairly high concentration of Na which largely determines the
293 concentration of Na in the effluent. However, cation exchange with Ca can also cause small
294 pulses in the breakthrough curve of Na, as shown in Figure 2. In addition, the SGW contains
295 about 1.57×10^4 mg/L Mg. Without an additional source of Mg from magnesite, as shown by the
296 "model no magnesite" in Figure 3, cation exchange makes the simulated Mg concentration after
297 the first peak fairly lower than that of measured data. The dissolution of magnesite in the base
298 model improves the fit between measured and simulated Mg concentration. Increasing the
299 dissolution rate of magnesite could raise the concentration level of Mg after the first peak and
300 improve the fit. However, this will drive the pH higher and decrease the fit between measured

301 and simulated pH. If dolomite instead of magnesite is used, model results for Mg are similar, but
302 the fit between measured and simulated pH and Ca become slightly worse.

303 Generic modeling works (Apps et al., 2010; Zheng et al., 2009) and models for the field
304 test (Zheng et al., 2012) have shown that desorption due to pH drop could be the main process
305 that controls the release of trace elements such as As and Pb in response to the CO_2 leakage in
306 groundwater. The close match between the measured and simulated breakthrough curve of As
307 (Figure 1) in this paper seems to support this concept. The surface complexation reactions for As
308 are listed in Table 2; the amount of the adsorbent, which is assumed to be $Fe(OH)_3(s)$ is
309 calibrated. Note that here we use the adsorption/desorption of As from $Fe(OH)_3(s)$ as a proxy of
310 all possible adsorption/desorption reactions including those that could occur on the surface of
311 clay minerals. The fit of measured Pb concentration with model results (Figure 1) is less
312 desirable, but the model catches the concentration changes fairly well after the third stop-flow
313 event.

314 ***3.2.2. An alternative model with Ba impurity in calcite***

315 Because most sediments contain some clay and subsequently cation exchange reaction is
316 ubiquitous, the dissolution of calcite and the concurrent Ca-driven cation exchange have been
317 used so far to explain the change of Ba concentration. Another possibility that could not be ruled
318 out is that Ba could be present in calcite as an impurity so that Ba is released concomitantly with
319 Ca as calcite dissolves. This concept has been used by Lu et al. (2010) to interpret the release of
320 metals upon CO_2 intrusion in groundwater in their laboratory experiment. This concept was also
321 tested here by modeling the dissolution of calcite containing 2.5 mol % Ba impurity as shown by
322 the following reaction.

$$\text{Ba-Calcite} + CO_2(g) + H_2O = 0.975Ca^{+2} + 0.025Ba^{+2} + 2HCO_3^- \quad (4)$$

323

324 The equilibrium constant for reaction (4) was calculated by assuming an ideal solid solution
325 between calcite and witherite. This seems to result in a better fit for Ba concentration compared
326 to the base case (Figure 4), suggesting that this is a plausible process for the release of Ba.

327 ***3.2.3. Models for the CNG 110 column: The base model***

328 Based on the model for sample CNG 60 and correcting the amount of minerals according
329 to the experimental measurement, a model was created to describe the data collected from the
330 column test conducted with sample CNG 110. CNG 110 differs significantly in the content of
331 calcite with CNG 60. Differences in other major minerals such as quartz and feldspar in sample
332 CNG 110 in comparison with CNG 60 most likely have only negligible effects on elemental
333 concentration changes considering the short duration of the test.

334 Like the model for sediment CNG 60 model, the model for sediment CNG 110 catches
335 the measured breakthrough curve of pH, but the modeling curve starts to deviate after 400 hours
336 of experimental time (Figure 1). The fact that simulated pH remains at the same level before and
337 after 400 hours indicates that calcite has not been depleted. Model results for CNG 60 shows it
338 takes 400-500 hours to run out of calcite at a volume fraction of 0.045%, so it is not possible to
339 deplete 1% calcite in 400 hours.

340 Upon the arrival of CO_2 saturated SGW, the dissolution of calcite leads to a quick
341 increase of Ca concentration and maintains a relatively high level thereafter. On the contrary,
342 measured data shows a slow increase and does not reach the high concentration level shown by
343 model results (Figure 1).

In the current model concept, because cation exchange occurs concurrently with calcite dissolution, Sr typically follows the change of Ca, as illustrated by the model and data for the column test of CNG 60. However, in contrast with the slow rising and then somewhat stabilized concentration of Ca, the Sr in the CNG 110 column shows a pulse-like trend. Model results for Sr show a slow rising in concentration and a slow decrease due to the depletion of exchangeable Sr, failing to match the column breakthrough curve for Sr (Figure 1). Similar phenomenon is observed for Ba (Figure 1). The measured Ba breakthrough curve shows sharp pulse-like behavior, in contrast to the slow rising and falling shown by model results.

The concept of calcite dissolution and accompanied cation exchange has been used successfully to interpret field tests in Montana (Zheng et al., 2012) and Mississippi (Trautz et al., 2013b). It has also been proved a valid concept for modeling the column test conducted with sediment CNG 60. By varying the amount and dissolution rate of calcite, and CEC, reasonable fit between measured data and model results can be achieved. However, such concept failed to explain the observation in the column test with CNG110. Looking at Figure 1, the dilemma is the mismatch between the Ca breakthrough curve and those for Ba and Sr. Lowering the dissolution rate of calcite could improve the match between measured and simulated Ca concentrations, but would further deteriorate the match between measured and simulated Ba. To match the pulse-like behavior in the breakthrough curve of Ba and Sr, calcite needs to be depleted shortly after the arrival of CO_2-charged SGW, but with 1% calcite present in the sediment, depletion is implausible.

The CNG 60 model explains the concentration changes in As and Pb by desorption caused by the drop of pH, but the CNG110 model fails to match the observed data for As and Pb.

As the pH in the CNG 110 column test decreases less than that in the test on CNG 60, there is less desorption and therefore As and Pb are lower as shown by the model for CNG 110, although it departs from measured data (Figure 1).

3.2.4. An alternative model for CNG 110 with higher CEC

The CEC is a key parameter that affects the Ba and Sr solid and liquid phase concentrations. In the base model for CNG 110, a CEC of 1.55 meq/100 g was used which was also used for the model for CNG 60. However, as the clay content in CNG 110 is different, the CEC varies as well. In a sensitivity run, the CEC was increased to 8 meq/100 g, hoping to improve the match between model and measured data. Higher CEC leads to higher concentration after the initial rising, but still fails to make the simulated initial peak closer to the measured data for Ba and Sr (Figure 5).

The model for CNG 60 shows that inclusion of Ba impurity in calcite leads to a better fit of measured data of Ba. This was also applied to the model for CNG 110, with 1 mol% Ba included in calcite. The continuous dissolution of calcite results in a sustainable increase in Ba concentration, which deviates significantly from the measured experimental data.

4. DISCUSSION

4.1. About the initial amount of calcite

In the column test, pH decreases upon the arrival of CO_2-saturated SGW at the outlet, and the Ca concentration soars up quickly and then decreases after reaching a peak concentration. The temporal profiles for the concentration of other alkali and alkaline earth metals such as Sr and Ba in the effluent follow almost precisely the pattern of Ca. Similar patterns of temporal

387 concentration changes have also been observed in a field test conducted in Mississippi (Trautz et
388 al., 2013b). In this test, groundwater from a confined hydrostratigraphic interval was pumped and
389 carbonated above ground, then re-injected into the same interval (in a dipole, closed loop system)
390 of an aquifer at approximately 50 m deep. Injection of carbonated groundwater at this site lasted
391 for around 5 months, preceded by an extensive monitoring period of background conditions and
392 followed by a post-injection monitoring period of around 10 months. Four monitoring wells were
393 emplaced downstream of the injection well. The concentration changes of alkali and alkaline
394 earth metals in the nearest monitoring well shows exactly the same pulse-like shape as we
395 observed in the column tests presented in this paper. To mimic the Ca concentration profile at the
396 Mississippi field test with reactive transport model, a small amount of calcite (~0.006–0.009%),
397 an amount that is enough to create the concentration peak but lead to depletion of calcite after the
398 arrival of CO_2-charged water, has to be used in the model. The concentration change of the rest
399 of the alkali and alkaline earth metals then can be interpreted as Ca-driven cation exchange
400 reaction. However, because calcite were not detected using XRD, doubt on such model
401 interpretation had been raised when the model was first published (Trautz et al., 2013b), despite
402 the amount of calcite used in the model being much lower than the detection limit of XRD. A
403 later laboratory study with the same sediment (Varadharajan et al., 2013) found calcite using
404 micro-X ray spectroscopy, which confirmed the validity of considering a small amount of calcite
405 in the model. Intuitively, we applied the same model concept to interpret the breakthrough curve
406 of Ca, Sr, Cs and Ba for the column test conducted with sample CNG 60, and found a good
407 match between model and experimental data. We therefore conclude that a small amount of
408 calcite does exist in sample CNG 60 as indicated by the SEM/EDS results and despite not being
409 detected by XRD.

4.2. About the impurity of trace metals in calcite

It is not uncommon for calcite to contain metal impurities. Some researchers (Kirsch et al., 2014; Lu et al., 2010; Wunsch et al., 2014) thus proposed the dissolution of calcite with impurities to explain the concurrent rise in concentrations of Ca and other metals. In this paper, we first used the dissolution of calcite and Ca-driven cation exchange to explain the breakthrough curve of Ba, and then tried to use the dissolution of calcite with Ba impurity (Section 3.2.2) to match the data. The former model catches the initial and final concentration of Ba and the latter model catches the peak better. In another study Zheng et al. (2014), we tested both these concepts (or models), and the concept of calcite dissolution with Ba impurity did a less desirable job to match the Ba release from a batch experiment (Varadharajan et al., 2013). These two concepts have the same the reaction kinetics that is controlled by the calcite dissolution rate. The difference between these two concepts is that in the first concept, cations interfere with each other due to competition on exchangeable sites and are constrained by CEC, whereas in the second concept, cations are more independent of each other and are only constrained by the fraction of impurity in the calcite. The conclusion is that both concepts are plausible and a model for a column (or batch) test cannot delineate which one is at play.

4.3. Constraining relevant chemical parameters for large scale model

In the context of assessing the risk of CO_2 leakage on groundwater, reactive transport models are indispensible tools. The predictability of a reactive transport model is dictated by the chemical reactions considered in the model and key parameters for these reactions. Column tests with the sediment from the target aquifer and the interpretive reactive transport model for the column will play a key role in raising our confidence for the large scale reactive transport

models. First, a column test is a screening tool to determine which elements could be released by the leakage of CO_2. Batch experiments can be used for such purpose as well, but tend to be too aggressive because of the large water-to-solid ratio and long residence time for water-rock interaction. For example, batch experiments (Varadharajan et al., 2013) were conducted for the sediments from an aquifer where a field test was conducted (Trautz et al., 2013); some elements in the EPA primary groundwater regulation list, such as As, Pb, showed significant increases in the batch experiment, but were not even detected in the field test(Pugh et al., 2013). Because column tests are typically conducted at water-to-solid ratio close to field conditions and take into account the interaction between transport processes and chemical reactions, it is a better proxy to the field condition and therefore a better tool than batch experiments to determine which elements are going to be released. Second, interpretation of column tests with reactive transport models helps to delineate the controlling chemical reactions and calibrate the key parameters. For example, in this paper, a close match between the model and column data for Sr clearly indicates that Ca-driven cation exchange is the reaction that controls the release of Sr, and the reactive surface area of calcite and CEC are the key parameters which can be well constrained from the Ca and Sr breakthrough curves. Matching the As and Pb data with model results confirms the control of adsorption/desorption on the release of As and Pb and can be used to calibrate the amount and surface area of adsorbents.

5. CONCLUSIONS

To assess the long term risk of CO_2 geological sequestration, numerical models have to be employed to evaluate the potential impact of the CO_2 leakage on shallow groundwater overlying the sequestration site. The understanding of the key chemical processes and parameters

454 are critical for the predictablity of numerical models. Model interpretation of laboratory and field
455 tests was an effective way to enhance such understanding. Column experiments in which CO_2
456 saturated SGW flows through a column packed with material from High Plains aquifer were
457 conducted and concentrations of several chemical constituents in the effluent water were
458 determined. In this paper, reactive transport model was developed to interpret the observed
459 concentration changes, attempting to shed light on the chemical reactions and key parameters
460 that control the concentration changes of these constituents.

461 The column test conducted with sediment CNG 60 shows systematical and well
462 correlated changes in concentration of various elements. A reactive transport model can match
463 the concentration changes of pH, Ca, Mg, Ba, Sr, Cs, As and Pb fairly well. Calcite dissolution
464 and Ca-driven cation exchange reactions are the major drivers for the concentration changes of
465 Ca, Ba, Sr, and Cs, which is consistent with the findings revealed by models developed with data
466 generated from other sites (Trautz et al., 2013b; Zheng et al., 2012). The pH-driven
467 adsorption/desorption reactions are the reason for concentration increases of As and Pb. The
468 volume fraction and reactive surface area of calcite, CEC and sorption capacity are key
469 parameters in determining the magnitude of concentration increase. Model results also show that
470 the dissolution of calcite with Ba impurity could be an alternative explanation of the increase in
471 Ba concentration. The model interpretation of column test clearly showed that understanding the
472 metal-sediment association and key parameters are critical for the predictability of numerical
473 models.

474 The model for sample CNG 60 was corrected for the amount of minerals (mainly calcite)
475 based on the measurement for sample CNG 110, to interpret the column test results for the

476 sample CNG 110. Although the model follows well the experimental pH data, it fails to explain
477 the concentration changes of the rest of the constituents. The poor correlation between the
478 concentration of Ca, Ba and Sr, and the erratic concentration of Ca are probably the reasons for
479 the mismatch between data and model. Pb and As data are also quite scattered so that it is hard
480 to draw a clear trend and subsequently to interpret them with a model. While re-examination of
481 the column test for sample CNG 110 and the conceptual geochemical modeling might be helpful
482 for better understanding of the observations from column test for sample CNG 110, it illustrates
483 the challenge we are facing when modeling the intriguing interactions between transport and
484 chemical reactions involved in the test.

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FIGURE CAPTIONS

Table 1. Cation exchange reactions and selectivity coefficients, using the Gaines-Thomas convention (Appelo and Postma, 1994).

Table 2. Surface complexation reactions and surface complexation constants (logK) on ferrihydrite (Dzomback and Morel, 1990; Appelo et al., 2002; Jordan et al., 2007).

Table 3. Equilibrium constants (logK) and initial volume fraction of minerals in the sediment (on a dry basis). LogK are for reactions that are written with the primary species listed in the first column of Table 2.

FIGURE CAPTIONS

Figure 1. Simulated and observed breakthrough curves of pH, Ca, Sr, Ba, As, Pb, Na and Cs for the column test of sample CNG60 (red) and CNG 110 (black). Cs and Na are not included for CNG 110.

Figure 2. Simulated and observed breakthrough curves of Si, Mn, Na and Cs for the column test of sample CNG60.

Figure 3. Simulated and observed breakthrough curves of pH and Mg with and without magnesite included in the model for the column test of sample CNG60.

Figure 4. Observed breakthrough curves of Ba for the column test of sample CNG 60 (both graphs) and CNG 110 (right graph), and simulated results in the base model and a model with Ba impurity in calcite.

Figure 5. Observed breakthrough curves of Ba and Sr for the column test of sample CNG110 and simulated results in the base model and a model with higher CEC value.

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