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CO₂ ionic trapping at meta-sedimentary aquifer, following a CO₂ injection push-pull test

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Abstract

In order to study CO₂-water-rock reactions relative to effectiveness of CO₂ geological storage, small-scale CO₂ injection experiments were performed, as single well push-pull tests, at the Lamont Doherty Earth Observatory test well site (New-York, USA).

The injection interval was located at the contact zone between the chilled dolerite and the underlying metamorphosed sedimentary rocks. The variations of post-injection chemical and isotopic characteristics of retrieved water samples (major ions, DIC, $\delta^{13}\text{C}_{\text{DIC}}$) underline the CO₂ reactivity in the aquifer and allow to identify reactions of the dissolved CO₂ with the surrounding rocks, mainly the dissolution of carbonate minerals and complementary cation exchange.

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1. Introduction

Carbon dioxide geological storage in deep aquifers is one of the most promising alternatives to reduce CO₂ emissions to the atmosphere. In this context, CO₂ geological storage, via geochemical trapping, would be achieved according to three mechanisms sequentially ordered: (1) solubility trapping (i.e. the CO_{2(g)} is dissolved into the aquifer fluid), (2) ionic trapping (i.e. the dissolved CO₂ reacts with the host rock minerals to form ionic species (HCO₃⁻ and CO₃²⁻)) and, (3) mineral trapping (i.e. the bicarbonate ions (CO₃²⁻) react with Ca and Mg ions to form stable carbonate minerals). Studies related on CO₂-fluid-rock interactions, within the context of CO₂ geological storage, showed that the chemistry of formation water and rock mineralogy of the reservoir play a determinant role on the efficiency of the CO₂ storage (Gunter et al., 2004 [1]; Rochelle et al., 2004 [2]).

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To investigate the extent of in situ water-rock reactions after a CO₂ injection, single well push-pull tests of the type described by Istok et al. 1997 [3] were performed, in a basaltic and metasedimentary environment. The study was conducted at the Lamont Doherty Earth Observatory campus test well site in Palisades, New York. It includes an instrumental borehole of a total depth of 304 m, which cuts through most of the section of the Palisades sill (chilled dolerite) and into the Newark Basin metamorphosed sediments. In addition, minor calcite occurs in veins and fractures as fracture fillings. Lithological and petrophysical profiles of these formations have been investigated previously (Burgdorff and Goldberg, 2001 [4]; Goldberg and Burgdorff, 2005 [5]). Hydrogeological methods, such as pumping and flow meter tests have been used to identify zones of high permeability and to estimate parameters such as transmissivity, providing us key information about intervals suitable for CO₂ injection experiments (Matter et al., 2006) [6].

The test solution (IS) was prepared in a polyethylene tank by spiking a 1.4m³ volume of background water (BW, extracted from the well) with conservative tracers (NaCl and ¹⁸O). The test solution was then loaded with a CO₂ partial pressure of about 1 bar, the pH of the test solution decreasing to 4.8. The target injection zone was the 10-meter thick permeable dolerite-sediment contact zone, which was hydraulically isolated with a straddle-packer system. The test solution was then injected over a period of 3 hours. After an incubation period of 3 weeks, the test solution/background water mixture (extracted water samples, ES) was continuously pumped back (“pulled”) from the hydraulically isolated zone, until the tracer concentrations were close to pre-test background levels. Physico-chemical parameters were measured ex-situ (pH, temperature, electrical conductivity) and sealed water samples were collected at incremental time intervals for chemical (DIC, major ions) and isotopic ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$ of water) analyses.

2. Results and discussion

The test solution had a $[\text{Cl}]_{\text{IS}}$ concentration of 5.16 mmol.l⁻¹ and a $\delta^{18}\text{O}_{\text{IS}}$ value of 2.1‰, contrasting with those for the background water ($[\text{Cl}]_{\text{BW}} = 1.47$ mmol.l⁻¹ and $\delta^{18}\text{O}_{\text{BW}} = -8.8‰$). During the pull phase, the extracted water samples had intermediate $[\text{Cl}]_{\text{ES}}$ and $\delta^{18}\text{O}_{\text{ES}}$ values decreasing from 2.64 to 1.37 mmol.l⁻¹ and from -5.2 to -9.0‰, respectively. These variations were only due to mixing processes between the background water and the injection solution since conservative tracers remain unchanged by the reactivity of the injected CO₂ saturated water. DIC concentrations varied from 1.2 mmol.l⁻¹ in the background water to 41.4 mmol.l⁻¹ in the injection solution, and $\delta^{13}\text{C}_{\text{DIC}}$ values from -17.8 to -51.1‰, respectively; these variations were due to H₂CO₃-water-rock interactions, in addition to mixing processes.

To retrieve the H₂CO₂ reactivity, we first calculated, for every extracted water sample, the mixing proportions “X” between the injection solution (IS) and the background water (BW), using mass balance equations for the conservative tracers:

$$[\text{Tracer}]_{\text{ES}} = X [\text{Tracer}]_{\text{IS}} + (1-X) [\text{Tracer}]_{\text{BW}} \quad (1)$$

where [Tracer] are the measured $[\text{Cl}]_{\text{ES}}$ concentration or $\delta^{18}\text{O}_{\text{ES}}$ value. X is the fraction of injection solution in the extracted water sample, 1-X being the fraction of the background water. $[\text{Cl}]$ and $\delta^{18}\text{O}$ viewpoints gave coherent mixing proportions, thus attesting the validity of their conservative behavior during this experiment.

For the first six extracted water samples, mixing proportions range from 0.31 to 0.06 while those from the remaining extracted samples yield value near zero (due to the fact that we gradually reach the background level). For the first six extracted water samples, the theoretical effect of the IS-BW mixing on the $\delta^{13}\text{C}_{\text{DIC}}$ and DIC values ($\delta^{13}\text{C}_{\text{DICmix}}$ and DIC_{mix}) was derived by solving the DIC and $\delta^{13}\text{C}_{\text{DIC}}$ mass balance equations:

$$\text{DIC}_{\text{mix}} = X \text{DIC}_{\text{IS}} + (1-X) \text{DIC}_{\text{BW}} \quad (2)$$

$$\delta^{13}\text{C}_{\text{DICmix}} \text{DIC}_{\text{mix}} = X \text{DIC}_{\text{IS}} \delta^{13}\text{C}_{\text{DIC-IS}} + (1-X) \text{DIC}_{\text{BW}} \delta^{13}\text{C}_{\text{DIC-BW}} \quad (3)$$

which yield a mixing hyperbola joining the BW and IS end-member in the $\delta^{13}\text{C}_{\text{DIC}}$ versus DIC diagram (Figure 1).

In this diagram, the data points ($\delta^{13}\text{C}_{\text{DIC-ES}}$ and DIC_{ES}) are located above the mixing hyperbola, indicating the occurrence of additional chemical processes besides pure mixing. Differences in $\delta^{13}\text{C}_{\text{DIC}}$ values and DIC concentrations between the extracted water samples and the theoretical mixing values yield the excesses in ¹³C and DIC:

$$\Delta\delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{DIC-ES}} - \delta^{13}\text{C}_{\text{DICmix}} \quad (4)$$

$$\Delta_{\text{DIC}} = \text{DIC}_{\text{ES}} - \text{DIC}_{\text{mix}} \quad (5)$$

$\Delta\delta^{13}\text{C}_{\text{DIC}}$ and Δ_{DIC} are positive for the first six extracted water samples, ranging from -8 to -5‰ and 5 and 1 mmol.l⁻¹, respectively; indicating that the reactivity of the injection solution increased the DIC concentration and enriched the DIC in ¹³C. This is consistent with carbonate dissolution during the neutralization reaction of H₂CO₃. The amount of added DIC is given by Δ_{DIC} and the $\delta^{13}\text{C}_{\text{DIC-add}}$ of the added DIC by the following mass balance equation:

$$\delta^{13}\text{C}_{\text{DIC-add}} = (\text{DIC}_{\text{ES}} \delta^{13}\text{C}_{\text{DIC-ES}} - \text{DIC}_{\text{mix}} \delta^{13}\text{C}_{\text{DICmix}}) / \Delta_{\text{DIC}} \quad (6)$$

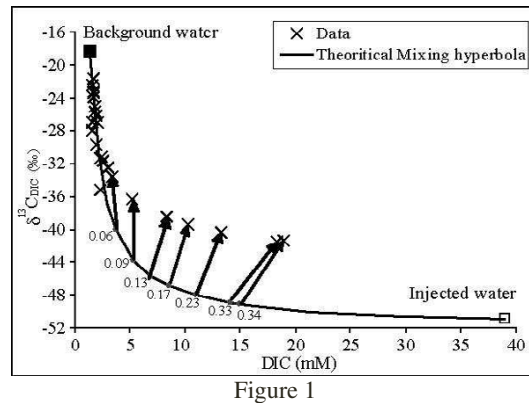


Figure 1

For each extracted water sample, the $\delta^{13}\text{C}_{\text{DIC-add}}$ values range between -21 and -13‰, with uncertainties of about $\pm 10\%$ (calculated from Monte Carlo statistical method). This range marginally agrees with that of the $\delta^{13}\text{C}$ measured for the calcium carbonate measured in the rocks from the target injection interval (ranging from -13 and -8‰) (Assayag et al., 2008).

Besides the dissolution of disseminated calcite, Assayag et al., 2008[8] and Matter et al., 2007[7] showed, from major ions data, the presence of complementary cation exchange of Ca^{2+} and Mg^{2+} ions with Na^+ ion on clay minerals and dissolution of primary rocks, mainly silicates, respectively, during push pull tests performed in the same test site.

The amount of reacted H_2CO_3 is about 28 (± 5) moles. It was calculated by the difference between the amount of injected H_2CO_3 , 53 moles ($= 1320 \text{ l} \cdot 40.2 \text{ mmol.l}^{-1}$), and the amount of the re-pumped (i.e. unreacted) H_2CO_3 , 25 (± 5) moles, (estimated by integrating $[\text{H}_2\text{CO}_3]$ contents over the pumped volumes and correcting for the recovery rate of 25%). The H_2CO_3 consumption (28 moles) is the consequence of several processes.

Mixing between the background water and the injection solution according to $\text{H}_2\text{CO}_3 + \text{CO}_3^{2-} \rightleftharpoons 2\text{HCO}_3^-$. The amount of H_2CO_3 neutralized is evaluated by the difference between the “theoretical” H_2CO_3 content (assuming an ideal mixing) and the “real” H_2CO_3 content (assuming the conservation of alkalinity and of DIC: no degassing, neither dissolution nor precipitation) and is about 0.7 ± 0.5 moles.

Dissolution of carbonate minerals (XCO_3) according to $\text{H}_2\text{CO}_3 + \text{XCO}_3 \rightleftharpoons \text{X}^{2+} + 2 \text{HCO}_3^-$ (where X is Ca or Mg...). Integrating the Δ_{DIC} evaluated above over the pumped volumes, the total amount of added DIC was estimated to range between 16.7 and 12.9 moles. Since the conversion of H_2CO_3 into HCO_3^- does not change the DIC, the mean consumption of H_2CO_3 corresponds to about 14.8 moles.

Cationic exchange according to: $\text{H}_2\text{CO}_3 + \text{Na-Y} \rightleftharpoons \text{HCO}_3^- + \text{Na}^+ + \text{H-Y}$ (Y is a mineral surface). The maximum amount of H_2CO_3 potentially consumed is given by the total amount of released Na^+ ion (i.e. 11.8 moles), the minimum being zero.

Dissolution of minerals such as silicates mostly, according to: $\text{H}_2\text{CO}_3 + \text{XB} \Rightarrow \text{X}^+ + \text{HCO}_3^- + \text{HB}$. Integrating the total dissolved solid cation (TDScat) over the pumped volumes ($\approx 35 \pm 4$ mole), corrected for the Ca^{2+} charge input due to the carbonate dissolution ($\approx -29.6 \pm 2$ mole), the total amount of added DIC is about 5 ± 5 moles. The molar balance of injected and consumed H_2CO_3 by these four processes is zero within the error bars.

3. Conclusions

The main consequence of the CO_2 reactivity was the dissolution of carbonate minerals (fracture fillings) and to a lesser extent the dissolution of primary minerals such as Ca, Mg silicates from the basalt.

Within three weeks of incubation period, approximately 60% of the injected H_2CO_3 has been reacted into HCO_3^- . Less than 2% via acid-base reactions, during the mixing between the background water and the injection solution, about 30% via the dissolution of carbonate minerals (i.e. ionic trapping), and the rest, about 30%, via cationic exchange and dissolution of silicate minerals.

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