Carbon dioxide-water-silicate mineral reactions enhance CO₂ storage; evidence from produced fluid measurements and geochemical modeling at the IEA Weyburn-Midale Project

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Abstract

At the International Energy Agency Greenhouse Gas (IEA GHG) Weyburn-Midale Project in Saskatchewan, Canada, CO₂ storage research takes place alongside CO₂ enhanced oil recovery (EOR) in the Weyburn oil field. Over four years of production well monitoring at Weyburn, measured changes in chemical and isotopic data for produced aqueous fluids and gases (i.e., an increase in Ca²⁺, Mg²⁺, K⁺, SO₄²⁻, HCO₃⁻, and CO₂ concentration and a decrease in δ¹³C_HCO₃ and δ¹³C_CO₂ values), confirm the integrity of CO₂ storage, trace CO₂ migration and dissolution in the reservoir fluids, and record a range of water-rock-CO₂ reactions including carbonate mineral dissolution and alteration of K-feldspar. K-feldspar alteration buffers the pH decrease resulting from CO₂ injection, enhances aqueous CO₂ storage as HCO₃⁻ (ionic trapping) and can lead to mineral storage of CO₂ as CaCO₃. Geochemical reaction path simulations of the water-mineral-CO₂ system reproduce the changes in measured data observed over the first few years, confirming proposed reaction pathways and rates. Extension of these history matched reaction path simulations over 100s of years shows that alteration of K-feldspar and other silicate minerals present in the Weyburn reservoir will lead to further storage of injected CO₂ in the aqueous phase and as carbonate minerals.

Keywords: Weyburn, K-feldspar, silicate, monitoring, ionic trapping, pH buffer, CO₂ storage

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1. Introduction

The IEA GHG (International Energy Agency Greenhouse Gas) Weyburn-Midale CO$_2$ Monitoring and Storage Project in Saskatchewan, Canada, involves the injection of around 1.5 million tonnes of CO$_2$ annually into the Weyburn and Midale Fields for the purpose of enhanced oil recovery and geological CO$_2$ storage. The Weyburn and Midale fields in southeast Saskatchewan produce medium gravity H$_2$S-bearing (sour) crude oil from the Midale Beds of the Mississippian (Lower Carboniferous) Charles Formation. The Midale Beds include the Frobisher Evaporite and the Midale Carbonate and are buried at a depth of approximately 1.5km. The Midale Carbonate in the Weyburn and Midale Fields is divided into two flow units: the grainstones and packstones of the depleted calcite-dominated lower ‘Vuggy’ flow unit and the finer grained heterogeneous ‘Marly’ flow unit, with dolomite, anhydrite and a range of silicates. The Marly flow unit is the main target for CO$_2$ injection [e.g. 1,2].

Monitoring of geological storage is essential to evaluate the different storage processes and confirm the integrity of the storage reservoir. In 2000, prior to CO$_2$ injection at Weyburn, produced fluids and gases were sampled from over forty production wells, with a range of chemical and isotopic parameters measured; a further 11 monitoring events followed at four month intervals. Geochemical data from the twelve geochemical monitoring events were used to trace injected CO$_2$, quantify the mass of injected CO$_2$ stored as HCO$_3^-$, estimate molecular CO$_2$ storage in the reservoir fluids and evaluate CO$_2$-aqueous fluid-mineral reactions [1,2,3,4]. Durocher et al. [5] and Perkins et al. [6] suggested that injected CO$_2$ dissolution in the aqueous reservoir fluids at Weyburn would lead to silicate mineral alteration. Alteration of silicate minerals such as Na or K-feldspar (e.g. equation 1), buffers pH and forms Na$^+$ and K$^+$ - HCO$_3^-$ brines, and if there is sufficient Ca$^{2+}$ or Mg$^{2+}$ (or Fe) the reaction can lead to the precipitation of carbonate minerals [e.g.7,8]. The objective of this study was to evaluate whether silicate mineral dissolution occurred in the first phase of the Weyburn-Midale project and to model the potential impact of silicate mineral reactions for future CO$_2$ storage via ionic and mineral trapping.

\[
\begin{align*}
3\text{KAlSi}_3\text{O}_8 \text{(K-feldspar)} + 3\text{H}_2\text{O} + 3\text{CO}_2 & \Rightarrow \\
\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \text{(kaolinite)} + 6\text{SiO}_2 \text{(quartz)} + 2\text{HCO}_3^- + 2\text{K}^+ & \quad (1)
\end{align*}
\]
2. Methods

The procedures used to sample and preserve the produced fluids and gases from wells at Weyburn are based on United States Geological Survey guidelines for geothermal and oilfield fluid analysis [9]. Transient variables (pH, alkalinity) were either measured in the field immediately after sample collection or samples were preserved and then analysed in the laboratory (majority of cations, anions and both fluid and gas carbon and sulfur isotope analyses). Produced fluid and gas samples are the most effective way to monitor CO2-fluid-reservoir interactions in a large active oilfield. Compared with samples from dedicated monitoring wells, fast moving reservoir fluids from producing wells have less time to react with parts of the non-reservoir production environment like the production tubing, well casing, completion materials, and well cements. Physical and chemical changes that take place as fluids move from the reservoir to the surface contribute to uncertainty in the concentration of volatile species and related parameters (e.g. CO2, H2S, HCO3-, pH etc.) and this effect must be evaluated and understood. In the absence of scale formation wellbore transit is not thought to alter the chemical concentration or isotopic composition of the majority of non-volatile species (Ca2+, Mg2+, K+, Cl-, SO42- etc.). For these anions and cations, repeated analysis of Weyburn samples along with analysis of laboratory standards of a known concentration suggests that analytical errors are less than ±10% of the concentration measurements. In contrast, cumulative errors in calculated HCO3- concentration, corrected to reservoir conditions using SOLMINEQ88 [10] are higher at approximately ±20%. This uncertainty in calculated HCO3- concentration results from uncertainties in oil, water, and gas compositions (salinity, oil density, CO2 concentration) and volumes (oilfield separators do not provide high quality volumetric data), surface pH, and alkalinity measurements and physical parameters (pressure, temperature, Henry’s law constants, estimates of CO2 solubility in oil), along with HS- concentration measurements and the resulting contribution of HS- to total alkalinity. Analytical uncertainties for δ13C values of HCO3- and CO2 (i.e. 13C/12C expressed using the δ-notation in ‰ relative to the Vienna Pee Dee Belemnite standard) are approximately ± 0.2 ‰ and ± 0.5 ‰, respectively.

Four wells were selected to provide a sample of the fluid and gas in part of the reservoir volume targeted by CO2 injection. The selected wells have detailed pre-CO2 injection mineralogical and aqueous fluid compositional data [2, 5], while independent monitoring data e.g. 4D seismic, production engineering, gas compositional, and carbon isotope data [4, 11] trace injected CO2 migration into the reservoir volume sampled by the wells. Therefore, the timing of arrival of injected CO2 is indicated by a range of independent data, and the subsequent injected CO2-aqueous fluid-mineral reactions can be evaluated using high quality mineral and aqueous fluid geochemical data.

3. Results

Table 1 summarizes the produced fluid monitoring results from the four selected wells. The initial measurements were taken prior to CO2 injection and the final measurements following approximately three years and three million tonnes of CO2 injection.

Table 1. Changes in the concentration of chemical parameters (mg/L) for aqueous fluid samples from the selected wells during CO2 injection. Concentration uncertainties are approximately ±10%.

<table>
<thead>
<tr>
<th>Well</th>
<th>Ca2+ (mg/L)</th>
<th>Mg2+ (mg/L)</th>
<th>SO42- (mg/L)</th>
<th>K+ (mg/L)</th>
<th>HCO3- (mg/L)</th>
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<tbody>
<tr>
<td>1</td>
<td>initial</td>
<td>1865</td>
<td>433</td>
<td>3411</td>
<td>481</td>
</tr>
<tr>
<td></td>
<td>final</td>
<td>2047</td>
<td>510</td>
<td>3781</td>
<td>728</td>
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<tr>
<td></td>
<td>increase</td>
<td>182</td>
<td>77</td>
<td>370</td>
<td>247</td>
</tr>
<tr>
<td>2</td>
<td>initial</td>
<td>1832</td>
<td>539</td>
<td>3817</td>
<td>670</td>
</tr>
<tr>
<td></td>
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<td>555</td>
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<td>754</td>
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<tr>
<td></td>
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<td>266</td>
<td>16</td>
<td>43</td>
<td>84</td>
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<tr>
<td>3</td>
<td>initial</td>
<td>2011</td>
<td>601</td>
<td>3157</td>
<td>558</td>
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<tr>
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<td>2325</td>
<td>560</td>
<td>3835</td>
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<td></td>
<td>increase</td>
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<td>-42</td>
<td>678</td>
<td>281</td>
</tr>
<tr>
<td>4</td>
<td>initial</td>
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<td>507</td>
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<td>541</td>
<td>3995</td>
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<td></td>
<td>increase</td>
<td>161</td>
<td>34</td>
<td>250</td>
<td>264</td>
</tr>
</tbody>
</table>
4. Discussion

Samples from the selected wells display a range of chemical variability over the monitoring period with significant increases in HCO$_3^-$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, and SO$_4^{2-}$ concentration (i.e. $> 15\%$ of measured initial concentration). As a result of the analytical uncertainties associated with each measured parameter this data only provides an estimate of the magnitude of the reactions taking place during CO$_2$ injection. Increases in SO$_4^{2-}$ concentration for samples from wells 1, 3, and 4 over the defined injection period suggest that anhydrite is dissolving, probably as a result of undersaturation for this mineral due to the changes in pore fluid composition during production operations (e.g. water flooding):

\[ \text{CaSO}_4 \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} \quad (2) \]

The Ca$^{2+}$ contribution from carbonate mineral dissolution can be calculated by subtracting the Ca$^{2+}$ produced via anhydrite dissolution from the total Ca$^{2+}$ concentration increase. The carbonate mineral sourced Ca$^{2+}$ increase together with the Mg$^{2+}$ concentration increase (in milimoles) can then be used to estimate the amount of HCO$_3^-$ produced from dissolution of Ca- and Ca/Mg- carbonates (equations 3 and 4):

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \]
\[ \text{H}_2\text{CO}_3 + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (3) \]
\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \]
\[ 2\text{H}_2\text{CO}_3 + \text{CaMg(CO}_3)_2 \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- \quad (4) \]

This estimate of the amount of HCO$_3^-$ provided by carbonate mineral dissolution is subtracted from the total measured HCO$_3^-$ concentration increase to quantify the HCO$_3^-$ formed via ionic trapping of injected CO$_2$ (equation 5). These chemical data provide an independent evaluation of the relative contributions of HCO$_3^-$ from different sources to compare with the carbon isotope approach used by Raistrick et al. [3].

\[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \quad (5) \]

The measured increase in K$^+$ concentration (Table 1) suggests that the pH decrease caused by CO$_2$ injection led to silicate mineral alteration. The most likely silicate reaction is alteration of K-feldspar (equation 1) to kaolinite, a reaction that buffers pH and leads to enhanced ionic trapping, storing CO$_2$ as K$^+$ - HCO$_3^-$ brines. If sufficient Ca$^{2+}$ is available, the continued alteration of K-feldspar and other silicate minerals has the potential to lead to mineral storage of CO$_2$ as Ca-carbonate [4-8].

Geochemical reaction pathway modeling software GWB (Geochemists Workbench React; [12]) was used to simulate the measured changes in the selected monitoring well chemical data over 750 days following the arrival of injected CO$_2$. This history matching confirms the type and magnitude of CO$_2$-aqueous fluid-mineral reactions recorded in the chemical data (Figure 1). Using measured geochemical, physical, and geological (mineralogical) data to define model conditions, the GWB-React simulations confirm that, following CO$_2$ injection, the dominant source of HCO$_3^-$ is ionic trapping of injected CO$_2$ with carbonate mineral dissolution as a subordinate HCO$_3^-$ source. The simulations also provide an estimation of the amount of injected CO$_2$ required to react with aqueous fluids and minerals to produce the measured chemical changes, and support the hypothesis that K-feldspar alteration is an effective pH buffer during CO$_2$ injection, promoting gradual mineral storage of CO$_2$. 

Figure 1: Well 1, 750 day simulation using Geochemists Workbench React, comparison of simulation results with measured chemical data (dotted black lines and symbols are from measured chemical data). Simulation conditions: temperature 55°C, atmospheric pressure, 0.56g CO₂ added over first 75 days (4).
The modeling timescale was extended to investigate the fate of CO₂ over post injection timescales (i.e. 100s of years). These longer term simulations, matched to the measured data over the first few hundred days, highlight the importance of pH buffering via a range of silicate mineral reactions, including K-feldspar, plagioclase and illite alteration, which lead to mineral storage of the added CO₂. As a result of alteration of these silicate minerals, up to 50% of the HCO₃⁻ generated from CO₂ dissolution over the monitoring interval may be stored as calcite (CaCO₃) over timescales of a few 100 years [4].

5. Conclusions

The produced fluid monitoring data from Weyburn summarized in this study confirm earlier predictions on CO₂-fluid-mineral reactions [5-8] and the interpretation of carbon isotope data [3]. The chemical data, with support from history matched reaction path simulations, suggest that pH buffering and K-HCO₃⁻ brine formation via K-feldspar alteration has enhanced aqueous CO₂ storage (as HCO₃⁻) over the monitoring period. In addition, as indicated by carbon isotope mass balance [3], the chemical data demonstrate that the majority of the increase in the concentration of HCO₃⁻ during CO₂ injection resulted from dissolution and dissociation of injected CO₂, with a minor contribution from carbonate mineral dissolution. Longer term reaction path simulations conducted to simulate 100s of years of CO₂-aqueous fluid-mineral reactions, calibrated via history matching over the first few years, show that reaction of K-feldspar, plagioclase and illite in the Weyburn reservoir has the potential to lead to secure storage of injected CO₂ in the aqueous phase and the precipitation of injected CO₂ as carbonate minerals.

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