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Carbon dioxide-water-silicate mineral reactions enhance CO_2 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, CO_2 storage research takes place alongside CO_2 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 Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-}, HCO_3^-, and CO_2 concentration and a decrease in $\delta^{13}C_{HCO3-}$ and $\delta^{13}C_{CO2}$ values), confirm the integrity of CO_2 storage, trace CO_2 migration and dissolution in the reservoir fluids, and record a range of water-rock-CO_2 reactions including carbonate mineral dissolution and alteration of K-feldspar. K-feldspar alteration buffers the pH decrease resulting from CO_2 injection, enhances aqueous CO_2 storage as HCO_3^- (ionic trapping) and can lead to mineral storage of CO_2 as $CaCO_3$. Geochemical reaction path simulations of the water-mineral-CO_2 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 CO_2 in the aqueous phase and as carbonate minerals.

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_2S-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.

$$3KAlSi_3O_8 \text{ (K-feldspar)} + 3H_2O + 3CO_2 \Rightarrow$$
$$Al_4Si_4O_{10}(OH)_8 \text{ (kaolinite)} + 6SiO_2 \text{ (quartz)} + 2HCO_3^- + 2K^+ \tag{1}$$

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. CO_2, H_2S, HCO_3^-, 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 (Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-} 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 HCO_3^- concentration, corrected to reservoir conditions using SOLMINEQ88 [10] are higher at approximately ±20%. This uncertainty in calculated HCO_3^- concentration results from uncertainties in oil, water, and gas compositions (salinity, oil density, CO_2 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 CO_2 solubility in oil), along with H_2S concentration measurements and the resulting contribution of HS^- to total alkalinity. Analytical uncertainties for $\delta^{13}C$ values of HCO_3^- and CO_2 (i.e. $^{13}C/^{12}C$ 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 CO_2 injection. The selected wells have detailed pre-CO_2 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 CO_2 migration into the reservoir volume sampled by the wells. Therefore, the timing of arrival of injected CO_2 is indicated by a range of independent data, and the subsequent injected CO_2-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 CO_2 injection and the final measurements following approximately three years and three million tonnes of CO_2 injection.

Table 1. Changes in the concentration of chemical parameters (mg/L) for aqueous fluid samples from the selected wells during CO_2 injection. Concentration uncertainties are approximately ±10%.

Well		Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	SO_4^{2-} (mg/L)	K^+ (mg/L)	HCO_3^- (mg/L)
1	*initial*	1865	433	3411	481	118
	final	2047	510	3781	728	920
	increase	182	77	370	247	802
2	*initial*	1832	539	3817	670	205
	final	2099	555	3774	754	1637
	increase	266	16	-43	84	1432
3	*initial*	2011	601	3157	558	318
	final	2325	560	3835	839	1678
	increase	314	-42	678	281	1360
4	*initial*	2018	507	3744	627	433
	final	2179	541	3995	892	1456
	increase	161	34	250	264	1022

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):

$$CaSO_4 \Rightarrow Ca^{2+} + SO_4^{2-} \tag{2}$$

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):

$$CO_2 + H_2O \Rightarrow H_2CO_3$$
$$H_2CO_3 + CaCO_3 \Rightarrow Ca^{2+} + 2HCO_3^- \tag{3}$$

$$CO_2 + H_2O \Rightarrow H_2CO_3$$
$$2H_2CO_3 + CaMg(CO_3)_2 \Rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \tag{4}$$

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].

$$CO_{2(aq)} + H_2O \Rightarrow H_2CO_3 \Rightarrow H^+ + HCO_3^- \tag{5}$$

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.
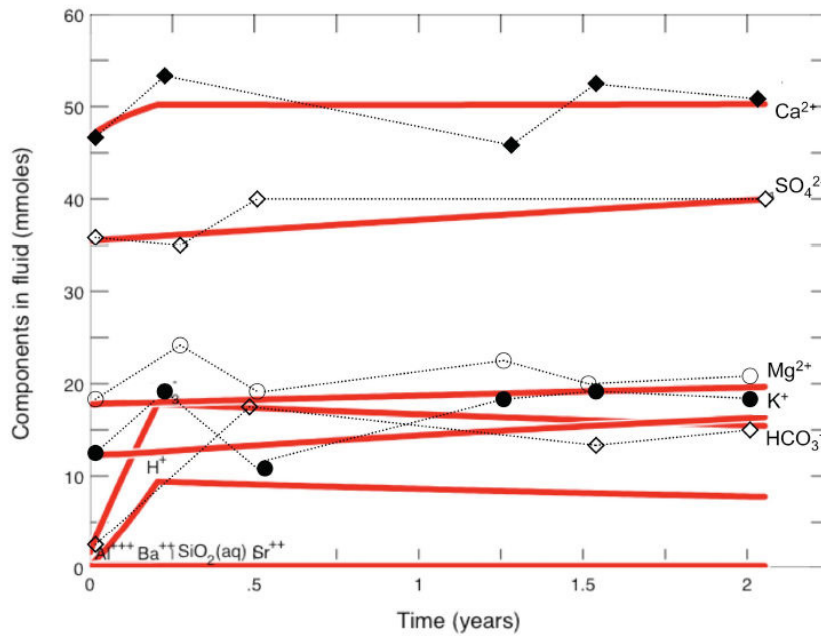
Figure1: Well 1, 750 day simulation using Geochemists Workbench React, comparison of simulation results with measured chemical data (dotted black lines and symbols are from measured chemical data). Simulation conditions: temperature 55°C, atmospheric pressure, 0.56g CO_2 added over first 75 days (4).

The modeling timescale was extended to investigate the fate of CO_2 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 CO_2. As a result of alteration of these silicate minerals, up to 50% of the HCO_3^- generated from CO_2 dissolution over the monitoring interval may be stored as calcite ($CaCO_3$) 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 $K-HCO_3^-$ brine formation via K-feldspar alteration has enhanced aqueous CO_2 storage (as HCO_3^-) 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 HCO_3^- during CO_2 injection resulted from dissolution and dissociation of injected CO_2, with a minor contribution from carbonate mineral dissolution. Longer term reaction path simulations conducted to simulate 100s of years of CO_2-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 CO_2 in the aqueous phase and the precipitation of injected CO_2 as carbonate minerals.

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