

Tracing the Fate of Injected CO₂ During Enhanced Oil Recovery using Stable Isotope Techniques

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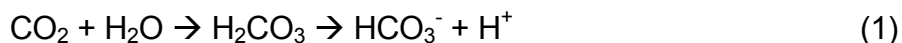
Summary

The use of stable isotope data in detection and quantification of CO₂ is demonstrated as a viable and innovative monitoring technique for the purposes of enhanced oil recovery and geological storage of CO₂. If the injected CO₂ is isotopically distinct from initial CO₂ in the reservoir, predictable variations in the carbon and oxygen isotope ratios of CO₂ and water obtained from the reservoir during geochemical monitoring programs reveal the fate of injected CO₂ in hydrocarbon reservoirs. This is demonstrated using monitoring data obtained for the International Energy Agency Greenhouse Gas Weyburn CO₂ Monitoring and Storage Project, Saskatchewan and for the Penn West Pembina Cardium CO₂-Enhanced Oil Recovery Monitoring Pilot, Alberta. The techniques outlined are applicable to many different storage settings where sufficient isotopic distinction between injected CO₂ and baseline reservoir CO₂ exists.

Introduction

Carbon dioxide (CO₂) storage via injection into geological reservoirs is currently being evaluated as a technology to mitigate atmospheric CO₂ emissions (Gale, 2004). Alberta is situated in a prime location for CO₂ storage being underlain by the Western Canadian Sedimentary Basin (WCSB). The WCSB oil and gas pools have been evaluated to be able to hold 3.7 GT of CO₂, the equivalent of 3 decades worth of CO₂ emissions from the major point sources of CO₂ within the geographical extent of the WCSB (Bachu, 2004). The two study sites are located in the Pembina Oilfield of the WCSB, Alberta, and the Weyburn Oilfield of the Williston Basin in Southern Saskatchewan. The reservoirs are geologically distinct with Penn West being a silicate reservoir and Weyburn a carbonate reservoir.

Detailed monitoring of CO₂ sequestration projects is required to determine the fate of the injected CO₂ and to assess the nature and effectiveness of the storage mechanisms (Raistrick et al., 2006). As CO₂ is injected into a reservoir it will dissolve and dissociate into the reservoir fluids according to equation 1 (Gunter et al., 2004):



Thus the dissolution and dissociation of CO₂ may result in measurable decreases in pH, change in alkalinity as well as other geochemical parameters that can be detected during geochemical

monitoring of produced fluids. In addition, the isotopic composition of produced CO₂ may provide additional clues regarding the fate of injected CO₂ in the reservoir. The objective of this paper is to demonstrate that variations in the isotopic composition of produced fluids and gases combined with geochemical data can be used to effectively trace the fate of CO₂ during enhanced oil recovery in mature oil fields.

Theoretical Background and Methods

At both sites, prior to CO₂ injection an extensive geochemical and isotopic baseline study was conducted recording 38 parameters including alkalinity, pH, gas composition (CO₂, H₂S, C1-C4), major ionic species (Na, K, Cl, Ca, Mg, Fe, etc) and C, O and S isotopic compositions of various compounds. Subsequent monitoring events took place at regular intervals throughout the injection phase recording the same parameters. The use of the stable isotopic composition as a tracer of CO₂ relies on the distinction between baseline reservoir values and those of the injected CO₂. At both study sites, the injected CO₂ is isotopically distinct.

Carbon isotope ratios: If the carbon isotope ratio (typically expressed as $\delta^{13}\text{C}$) of the injected CO₂ is significantly different from that of baseline CO₂ in the reservoir, increasing contributions of injected CO₂ at sampling wells will result in increasing CO₂ contents (usually expressed in mole%) accompanied by $\delta^{13}\text{C}$ values of the CO₂ trending from those of the baseline CO₂ towards those of the injected CO₂. Raistrick et al. (2006) demonstrated the use of $\delta^{13}\text{C}$ values to trace the fate of injected CO₂ in a mature oilfield at Weyburn, Saskatchewan by evaluating $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC) to assess the dissociation and resulting ionic trapping of CO₂ in the reservoir brines. Here, we present $\delta^{13}\text{C}$ values of the free CO₂ gas sampled at the well heads to identify CO₂ breakthrough (or an early warning thereof) at individual wells sampled at both the Weyburn and Penn West sites.

Oxygen isotope ratios: Injection of isotopically distinct CO₂ may not only affect the carbon isotope ratios of CO₂ and DIC in the reservoir, but may also cause changes in the oxygen isotope ratios (usually expressed as $\delta^{18}\text{O}$ values) of the reservoir fluids. Changes in $\delta^{18}\text{O}$ values of water due to CO₂ have rarely been studied in the environmental field due to the minimal amount of CO₂ normally present. However, in a CO₂ storage setting the volume of CO₂-oxygen in the system increases to the point where it may influence the $\delta^{18}\text{O}$ values of the reservoir fluids (Kharaka et al., 2006). Oxygen isotope ratios of produced water may be affected by water injection, but in this case the hydrogen isotope ratios ($\delta^2\text{H}$ values) of the produced water would change concurrently. If no change is observed in the $\delta^2\text{H}$ value of the reservoir fluids, variations in the $\delta^{18}\text{O}$ values may be indicative of the influence of injected CO₂.

It is known that isotopic (equilibrium) exchange proceeds rapidly between the oxygen in CO₂ and oxygen in water of various salinities (e.g. Epstein & Mayeda, 1953). At standard temperatures (25°C) and pressures the isotope enrichment factor between H₂O and CO₂ has been determined to be 40.1 ‰ (Bottinga, 1968). At the temperature of the Penn West (50°C) and Weyburn (56°C) reservoirs this enrichment factor is slightly lower, circa 35 ‰. There are two end member scenarios of isotope exchange between CO₂ and H₂O. In the initial stages of CO₂ injection the majority of the oxygen in the produced water-CO₂ system will come from the produced water. Hence the produced water oxygen isotope ratio will remain constant and will control the $\delta^{18}\text{O}$ value of CO₂ to be 35 ‰ higher than that of the produced water. Conversely, if the majority of the oxygen in the produced water-CO₂ system is sourced from the CO₂ (as may occur towards the end of injection), the CO₂ oxygen isotope ratios will dominate the produced water-CO₂ system. Consequently, the $\delta^{18}\text{O}$ value of the produced water will start to change becoming 35 ‰ lower than that of the injected CO₂.

Examples

Weyburn: Figure 1a-f shows the trends observed for CO₂, $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values throughout 48 months of CO₂ injection for two wells from the Weyburn study site. Well 1 was characterized by increasing mole% CO₂ over time (Fig 1a). At the same time, carbon isotope ratios of CO₂ sampled decreased towards the $\delta^{13}\text{C}$ values of the injected CO₂ (Fig 1b). In addition, the $\delta^{18}\text{O}$ value of the produced water decreased by circa 2 ‰ (Fig 1c), indicating that the injected CO₂ has started to influence the isotopic composition of the produced water. In contrast, Well 2 has not seen significant increases in mole% CO₂ (Fig 1d) and the $\delta^{18}\text{O}$ value of the produced water remained constant (Fig 1f) indicating a negligible influence of injected CO₂. However, the $\delta^{13}\text{C}$ value of CO₂ obtained from Well 2 decreased from its initial value towards that of the injected CO₂ (Fig 1e), suggesting that injected CO₂ is starting to reach this well.

Penn West: Figure 1g-l shows the trends observed in CO₂, $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values throughout 24 months of CO₂ injection for two wells from the Penn West study site. At Well 1, CO₂ increased significantly 6 weeks after injection commenced (Fig 1g). The $\delta^{13}\text{C}$ values of CO₂ increased simultaneously towards that of the injected CO₂ (Fig 1h). In addition, the $\delta^{18}\text{O}$ value of the produced water increased by more than 2 ‰ (Fig 1i), indicating that the injected CO₂ has started to influence the isotopic composition of the produced water. In contrast, changes in CO₂ content and $\delta^{18}\text{O}$ values were insignificant in Well 2 at Penn West (Fig 1j, l). However, the carbon isotope ratios of CO₂ obtained from Well 2 increased towards that of the injected CO₂ indicating that injected CO₂ is starting to reach the well (Fig 1 k).

Conclusions

Carbon isotope ratios are an effective tool to trace the movement and reaction of injected CO₂ in mature oil fields, provided that the injection CO₂ is isotopically distinct. In addition, trends observed in the $\delta^{18}\text{O}$ values of produced water at several wells at Penn West and Weyburn point towards an increasing amount of CO₂ sourced oxygen in the produced waters. The trends in the isotope data are corroborated with independent geochemical data (see companion paper by Shevalier et al.) showing increasing mole% CO₂ at the same wells. Further work to quantify the amount of CO₂ sourced oxygen and thus to quantify the amount of CO₂ dissolved in the produced waters using the $\delta^{18}\text{O}$ values is currently being pursued.

Acknowledgements

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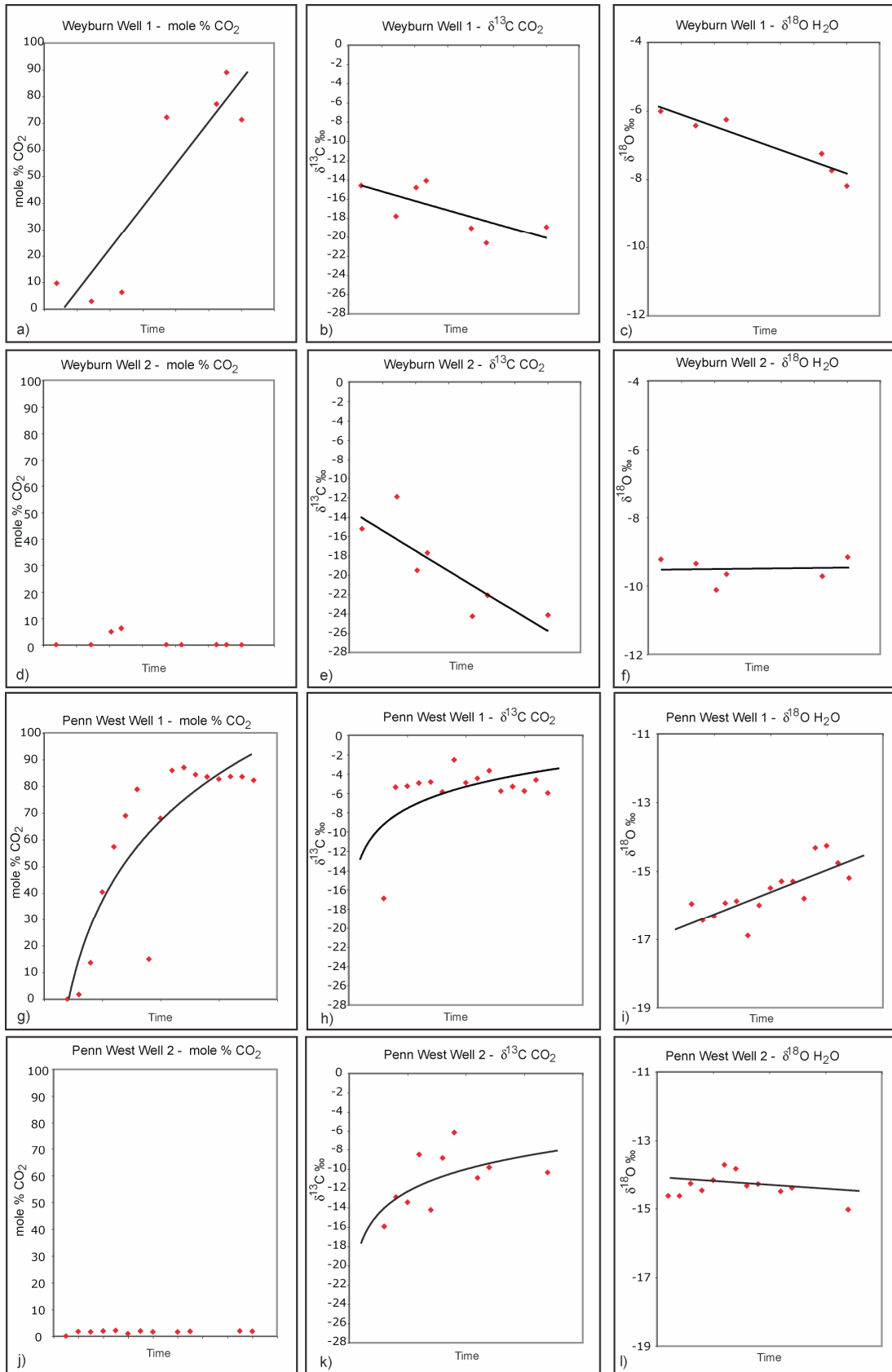


Figure 1: a) mole% CO₂ vs Time, Weyburn Well 1. b) δ¹³C_{CO2} vs Time, Weyburn Well 1. c) δ¹⁸O_{H2O} vs Time, Weyburn Well 1. d) mole% CO₂ vs Time, Weyburn Well 2. e) δ¹³C_{CO2} vs Time, Weyburn Well 2. f) δ¹⁸O_{H2O} vs Time, Weyburn Well 2. g) mole% CO₂ vs Time, Penn West Well 1. h) δ¹³C_{CO2} vs Time, Penn West Well 1. i) δ¹⁸O_{H2O} vs Time, Penn West Well 1. j) mole% CO₂ vs Time, Penn West Well 2. k) δ¹³C_{CO2} vs Time, Penn West Well 2. l) δ¹⁸O_{H2O} vs Time, Penn West Well 2. (Linear & Logarithmic fits shown)