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):

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+ \]  \hspace{1cm} (1)

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 δ13C) 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 δ13C 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 δ13C values to trace the fate of injected CO2 in a mature oilfield at Weyburn, Saskatchewan by evaluating δ13C values of dissolved inorganic carbon (DIC) to assess the dissociation and resulting ionic trapping of CO2 in the reservoir brines. Here, we present δ13C 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 δ18O values) of the reservoir fluids. Changes in δ18O 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 δ18O 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 (δ2H values) of the produced water would change concurrently. If no change is observed in the δ2H value of the reservoir fluids, variations in the δ18O 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 δ18O 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 δ18O 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, δ¹³C_CO₂ and δ¹⁸O_H₂O 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 δ¹³C values of the injected CO₂ (Fig 1b). In addition, the δ¹⁸O 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 δ¹⁸O value of the produced water remained constant (Fig 1f) indicating a negligible influence of injected CO₂. However, the δ¹³C 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, δ¹³C_CO₂ and δ¹⁸O_H₂O 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 δ¹³C values of CO₂ increased simultaneously towards that of the injected CO₂ (Fig 1h). In addition, the δ¹⁸O 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 δ¹⁸O 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 1k).

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 δ¹⁸O 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 δ¹⁸O values is currently being pursued.
Acknowledgements

Funding for the Penn West Pembina Cardium CO₂-Enhanced Oil Recovery Monitoring Pilot is from Penn West Energy Trust, Alberta Energy Research Institute, Western Economic Diversification Canada and Natural Resources Canada. Funding for the IEA GHG Weyburn CO₂ Monitoring and Storage Project is provided by the Petroleum Technology Research Centre in collaboration with EnCana Corporation (the operator of the Weyburn oil field).

References


Figure 1: a) mole% CO₂ vs Time, Weyburn Well 1. b) $\delta^{13}$C CO₂ vs Time, Weyburn Well 1. c) $\delta^{18}$O H₂O vs Time, Weyburn Well 1. d) mole% CO₂ vs Time, Weyburn Well 2. e) $\delta^{13}$C CO₂ vs Time, Weyburn Well 2. f) $\delta^{18}$O H₂O vs Time, Weyburn Well 2. g) mole% CO₂ vs Time, Penn West Well 1. h) $\delta^{13}$C CO₂ vs Time, Penn West Well 1. i) $\delta^{18}$O H₂O vs Time, Penn West Well 1. j) mole% CO₂ vs Time, Penn West Well 2. k) $\delta^{13}$C CO₂ vs Time, Penn West Well 2. l) $\delta^{18}$O H₂O vs Time, Penn West Well 2. (Linear & Logarithmic fits shown)