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# Pre-, Syn- and Post-CO<sub>2</sub> Injection Geochemical and Isotopic Monitoring at the Pembina Cardium CO<sub>2</sub> Monitoring Pilot, Alberta, Canada

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## Abstract

Geochemical and isotopic data acquired pre-, syn- and post- CO<sub>2</sub> injection at the Pembina Cardium CO<sub>2</sub> Monitoring Pilot in Alberta, Canada is presented. To the author's knowledge this is the first project that has collected and interpreted comprehensive geochemical data over the full life cycle of a CO<sub>2</sub> injection project. Of the 40 parameters measured per sample changes in pH, alkalinity, Ca<sup>2+</sup>, Fe<sup>2+</sup>, δ<sup>13</sup>C of CO<sub>2</sub> and δ<sup>18</sup>O of H<sub>2</sub>O proved to be the most useful parameters as tracers of CO<sub>2</sub> presence and for identifying solubility and mineral trapping in the reservoirs thus demonstrating CO<sub>2</sub> retention mechanisms.

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## 1. Introduction

The injection and subsequent long-term storage of CO<sub>2</sub> in saline aquifers or depleted oil reservoirs is a suitable approach to mitigate anthropogenic CO<sub>2</sub> emissions to the atmosphere and is currently investigated at various sites worldwide. We obtained geochemical and isotopic data from the Pembina Cardium CO<sub>2</sub> Monitoring

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Pilot in Alberta, Canada. The project was an enhanced oil recovery (EOR) operation hosted in the Upper Cretaceous Cardium Formation of the Pembina oil field. The Cardium is a siliciclastic reservoir with minor amounts of carbonate cement (~1.5% siderite and calcite) at approximately 1650 m depth [1]. At this site, CO<sub>2</sub> injection commenced in spring 2005 and ended early in 2010. A total of 46 monitoring events took place between 2005 and 2012 during the 7 years of the CO<sub>2</sub> pilot injection program. To the author's knowledge, this is the first project that has collected and interpreted comprehensive geochemical data over the full life cycle of a CO<sub>2</sub> injection project. The objective of this project was to trace the movement and the fate of the injected reservoir using chemical and isotopic techniques.

### Nomenclature

$\delta^{13}\text{C}$	The ratio of the stable isotopes $^{13}\text{C}:^{12}\text{C}$ in parts per thousand relative to V-PDB
$\delta^{18}\text{O}$	The ratio of the stable isotopes $^{18}\text{O}:^{16}\text{O}$ in parts per thousand relative to V-SMOW
$\delta^2\text{H}$	The ratio of the stable isotopes $^2\text{H}:^1\text{H}$ in parts per thousand relative to V-SMOW
‰	Parts per thousand

## 2. Methods

Geochemical and isotopic monitoring included fluid and gas sampling events pre, during and post CO<sub>2</sub> injection. On each monitoring event, multiple wells were sampled to obtain reservoir fluids and gases and analyses were performed to generate over 40 geochemical parameters for each well and each monitoring event including: major cation and anion concentrations; pH; EC; alkalinity; isotopic composition of water and DIC, and; isotopic and chemical composition of produced gases. Figure 1 shows the timeline of operations at the project.

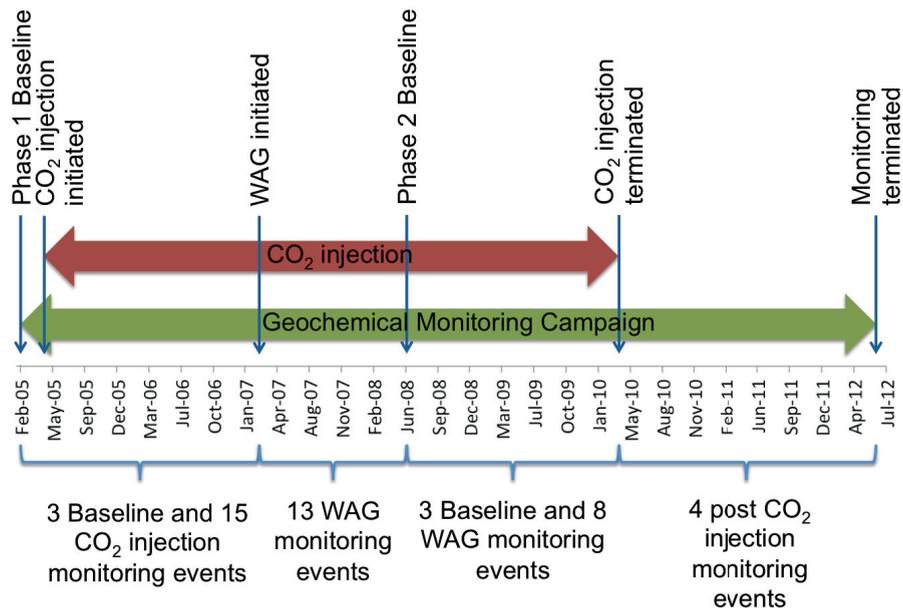


Fig. 1. Timeline of operations and geochemical sampling at the Pembina Cardium CO<sub>2</sub> Monitoring Pilot.

The first phase of the pilot consisted of two side by side inverted five-spot injection patterns; i.e. a central injection well with four producers. Two wells (08-11, 09-11) were shared between the patterns resulting in 6 producers with a further two wells (01-11, 04-12) added to the first phase sampling program (Figure 2). This initial

8 well observation well pattern (Phase 1) was extended to include a further 20 wells (Phase 2) at the site in 2008 (Figure 2). CO<sub>2</sub> injected was delivered via trucks from a local source (<100 km) and had isotopic values of  $\delta^{13}\text{C}$  -4.7 ‰ and  $\delta^{18}\text{O}$  +28.6 ‰.

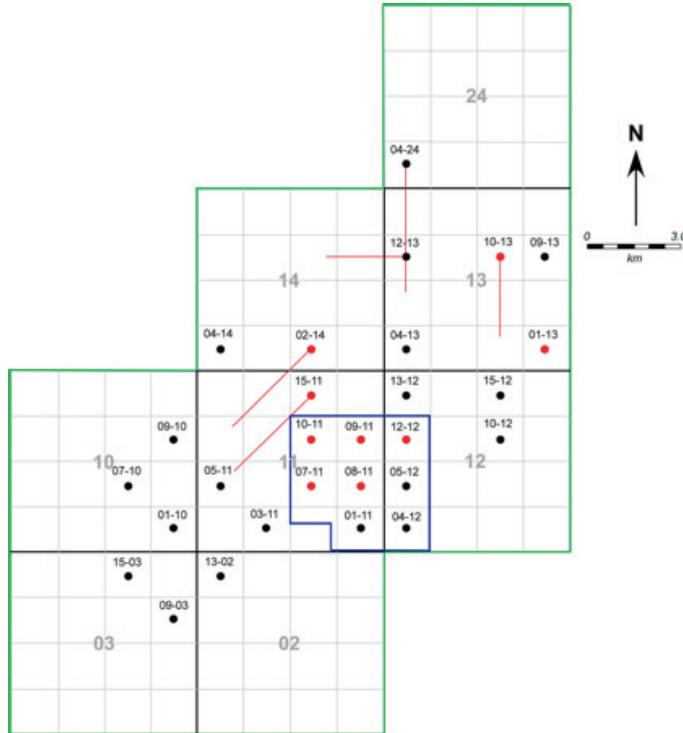


Figure 2. Well locations at the Pembina Cardium CO<sub>2</sub> Monitoring Pilot (locations in Township and Range). The area enclosed by the blue line is the Phase 1 area. The area enclosed by the green line is the Phase 2 area. Wells highlighted in red observed CO<sub>2</sub> breakthrough.

### 3. Results

At 9 out of the 28 observation wells sampled, CO<sub>2</sub> breakthrough (as defined as >10 mol% CO<sub>2</sub> in the gas sampled) was observed (red wells in Figure 2). Areal distribution indicated that CO<sub>2</sub> migrated initially in a NE-SW direction, consistent with regional dip and fracture patterns, with a later migration to the NW. Significant geochemical differences were observed in reservoir fluids between the CO<sub>2</sub> breakthrough wells and the wells where no CO<sub>2</sub> was present. In particular changes in pH (from >7 to 4-6), alkalinity (from 2000 to 6000 mg/l), Ca<sup>2+</sup> (from 10-15 mg/L to ~200 mg/L), Fe<sup>2+</sup> (from <10 mg/L to 100-200 mg/L),  $\delta^{13}\text{C}$  of CO<sub>2</sub> (from baseline values of ~ -15 ‰ to values approaching the injection CO<sub>2</sub> value of -5 ‰) and  $\delta^{18}\text{O}$  of H<sub>2</sub>O (from baseline values of ~ -17 ‰ to a maximum of -5.4 ‰) were observed in samples obtained from the CO<sub>2</sub> breakthrough wells, while baseline values remained unchanged in fluids from wells without CO<sub>2</sub> presence.

### 4. Discussion

The observed changes described in section 3 highlight the potential to use these geochemical and isotopic parameters as tracers of CO<sub>2</sub> presence and for identifying potential mineral reactions in the reservoirs. As an example we discuss changes in the oxygen isotope composition of reservoir water (H<sub>2</sub>O). Although complicated by the introduction of WAG in 2007, the observed changes in  $\delta^{18}\text{O}$  of H<sub>2</sub>O are consistent with the laboratory work of Johnson and Mayer [2] that showed that  $\delta^{18}\text{O}$  values of H<sub>2</sub>O will be altered by isotope exchange with oxygen in CO<sub>2</sub>

at high concentrations, as is the case in CO<sub>2</sub> storage settings. Johnson et al. [3] reported in the earlier phase of the Pembina project (pre water-flood) that water undergoes oxygen isotope exchange with injected CO<sub>2</sub> and that the magnitude of the change in the  $\delta^{18}\text{O}$  values of H<sub>2</sub>O can be used as an indicator for the presence of injected CO<sub>2</sub> and to calculate CO<sub>2</sub> saturation in the reservoir. Johnson et al. [3] also predicted that the largest perturbation in the  $\delta^{18}\text{O}$  values of H<sub>2</sub>O at this site would be to a value of -6.9 ‰ should 100% pore space saturation with CO<sub>2</sub> be approached. In the first phase of the project the largest shift in  $\delta^{18}\text{O}$  values of H<sub>2</sub>O observed was at well 12-12 where a shift of 3.8 ‰ from an average baseline value of -14.1 ‰ resulted in a value of -10.3 ‰ (Figure 3). The results presented here for the post-CO<sub>2</sub> injection phase show a continuation of the trends observed earlier towards the predicted value at many wells and to an even slightly higher  $\delta^{18}\text{O}$  value of -5.4 and -5.6 ‰ at two of the observation wells. In addition, changes in both the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of reservoir fluids at some wells (including the two wells with higher than expected  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values for exchange with CO<sub>2</sub>) indicate mixing with original pore-waters rather than with present-day injection water. This points to the mobilization of water from previously un-swept portions of the reservoir that are being accessed post CO<sub>2</sub> injection at some wells (e.g. Well 12-12, Figure 3).

In general, the chemical parameters highlighted above (pH, alkalinity, Ca<sup>2+</sup>, Fe<sup>2+</sup>,  $\delta^{13}\text{C}$  of CO<sub>2</sub>, and  $\delta^{18}\text{O}$  of H<sub>2</sub>O) showed a continual change throughout the project indicating that chemical reactions with CO<sub>2</sub> in the storage reservoir were progressing not only during the CO<sub>2</sub> injection phase, but also during post-injection monitoring. However, the greatest fluctuations in the parameters were observed during active CO<sub>2</sub> injection with more gradual changes thereafter. This could be a result of the significant amounts of well work-overs during operations or could point towards geochemical reactions approaching equilibrium in the later stages of the observation period. In particular, pH values (recorded at the wellhead) decreased significantly during CO<sub>2</sub> injection in those wells that had CO<sub>2</sub> breakthrough. Changes in pH from baseline values of ~7.5 to ~5 during CO<sub>2</sub> injection before recovering to higher values (~6.5) post CO<sub>2</sub> injection indicate that some amount of pH buffering occurred in the reservoir. This is most likely through mineral reactions as evidenced by the increased concentrations in, for example, alkalinity and Ca<sup>2+</sup> observed in the last stages (post-CO<sub>2</sub> injection) of the project. Lastly, CO<sub>2</sub> concentration in gas samples were observed to decrease post CO<sub>2</sub> injection from maxima of >90% to a mean value of ~60% indicating that either CO<sub>2</sub> is migrating away from the wells or that dissolution of CO<sub>2</sub> into reservoir fluids is increasing over time. The continual changes in both chemical and isotopic parameters in the waters post CO<sub>2</sub> injection would appear to argue, at least in part, for the latter.

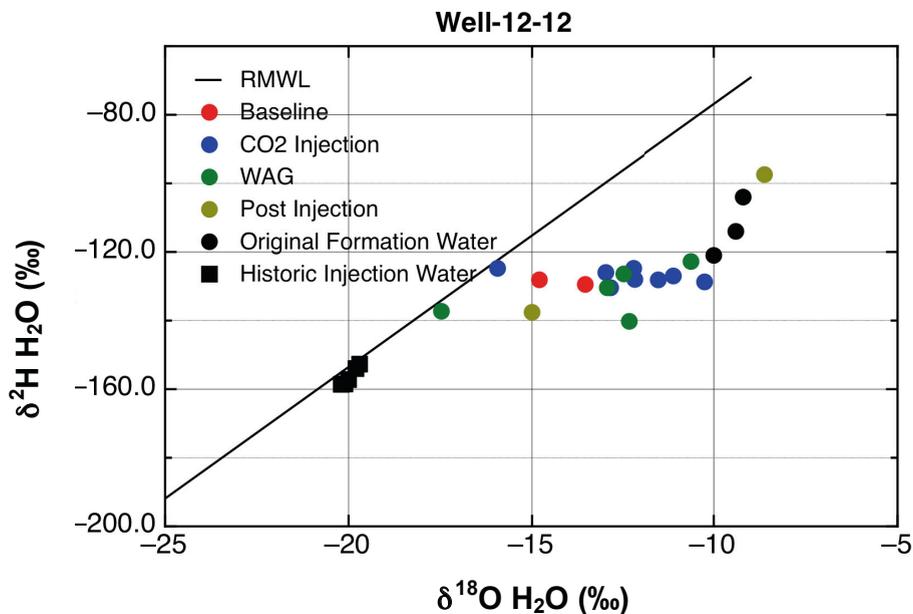


Figure 3. Changes in  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$   $\text{H}_2\text{O}$  for the various phases of the project at one of the observation wells (12-12).

## 5. Conclusion

In conclusion it is demonstrated that continual monitoring of chemical and isotopic parameters in produced fluids and gases can reveal  $\text{CO}_2$  migration and both solubility trapping and mineral reactions taking place in the reservoir thus demonstrating  $\text{CO}_2$  retention mechanisms. The post- $\text{CO}_2$  injection results show that  $\text{CO}_2$  dissolution and mineral reactions continue to progress with time resulting in greater amounts of solubility trapping of injected  $\text{CO}_2$ . In addition the late change in plume migration direction (to the NW) highlighted by the chemical results would not have been identified without the continuous post-injection monitoring program.

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