

Available online at www.sciencedirect.com**ScienceDirect**

Energy Procedia 63 (2014) 4150 – 4154

Energy

Procedia

GHGT-12

Pre-, Syn- and Post-CO₂ Injection Geochemical and Isotopic Monitoring at the Pembina Cardium CO₂ Monitoring Pilot, Alberta, Canada

Gareth Johnson^{a*}, Chantsalmaa Dalkhaa^b, Maurice Shevalier^b, Michael Nightingale^b
Bernhard Mayer^b and Stuart Haszeldine^a

^a*School of GeoSciences, University of Edinburgh, West Mains Road, Edinburgh, Scotland, EH9 3JW*

^b*Applied Geochemistry Group, Department of Geoscience, University of Calgary, Calgary, Alberta, Canada, T2N 1N4*

Abstract

Geochemical and isotopic data acquired pre-, syn- and post- CO₂ injection at the Pembina Cardium CO₂ 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 CO₂ injection project. Of the 40 parameters measured per sample changes in pH, alkalinity, Ca²⁺, Fe²⁺, δ¹³C of CO₂ and δ¹⁸O of H₂O proved to be the most useful parameters as tracers of CO₂ presence and for identifying solubility and mineral trapping in the reservoirs thus demonstrating CO₂ retention mechanisms.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: Geochemical Monitoring; Stable Isotopes; MMV; CO₂ Storage; CCS;

1. Introduction

The injection and subsequent long-term storage of CO₂ in saline aquifers or depleted oil reservoirs is a suitable approach to mitigate anthropogenic CO₂ emissions to the atmosphere and is currently investigated at various sites worldwide. We obtained geochemical and isotopic data from the Pembina Cardium CO₂ Monitoring

* Corresponding author. Tel.: +44 131 650 7010; fax: +44 131 650 7340.

E-mail address: g.johnson@ed.ac.uk

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, CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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.

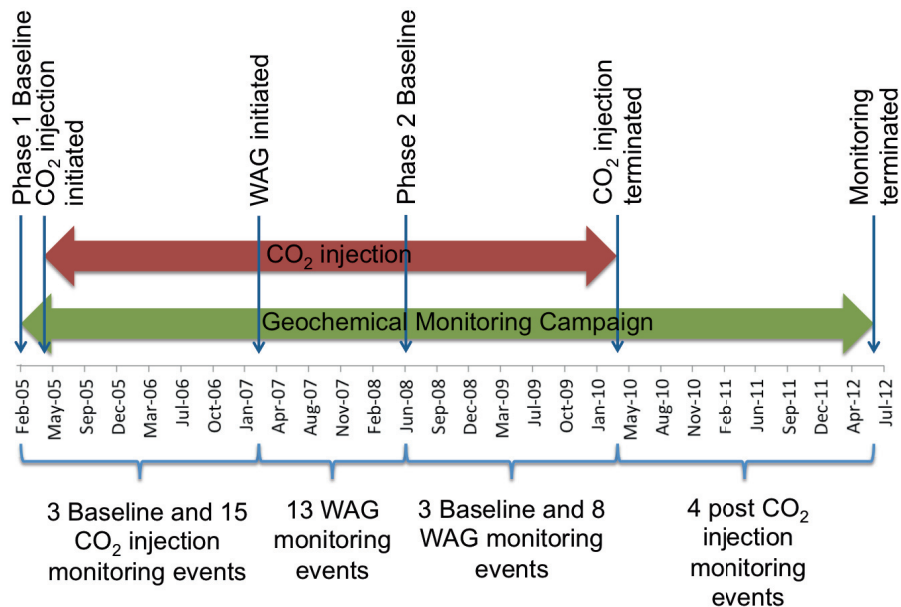


Fig. 1. Timeline of operations and geochemical sampling at the Pembina Cardium CO₂ Monitoring Pilot.

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). CO₂ 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 ‰.

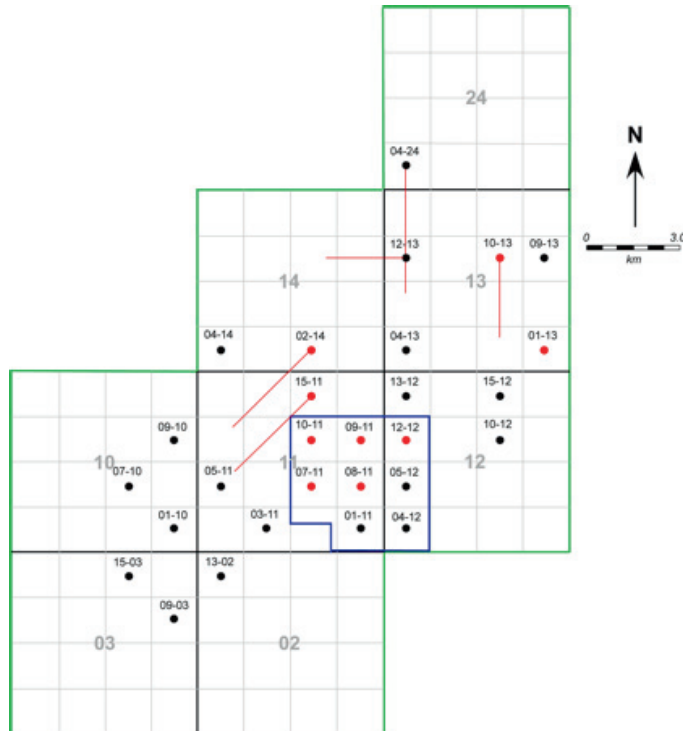


Figure 2. Well locations at the Pembina Cardium CO₂ Monitoring Pilot (locations in Township and Range). The area enclosed by the blue line is the Phase 1 area. The area enclosed by the green line is the Phase 2 area. Wells highlighted in red observed CO₂ breakthrough.

3. Results

At 9 out of the 28 observation wells sampled, CO₂ breakthrough (as defined as >10 mol% CO₂ in the gas sampled) was observed (red wells in Figure 2). Areal distribution indicated that CO₂ 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 CO₂ breakthrough wells and the wells where no CO₂ was present. In particular changes in pH (from >7 to 4-6), alkalinity (from 2000 to 6000 mg/l), Ca²⁺ (from 10-15 mg/L to ~200 mg/L), Fe²⁺ (from <10 mg/L to 100-200 mg/L), $\delta^{13}\text{C}$ of CO₂ (from baseline values of ~ -15 ‰ to values approaching the injection CO₂ value of -5 ‰) and $\delta^{18}\text{O}$ of H₂O (from baseline values of ~ -17 ‰ to a maximum of -5.4 ‰) were observed in samples obtained from the CO₂ breakthrough wells, while baseline values remained unchanged in fluids from wells without CO₂ presence.

4. Discussion

The observed changes described in section 3 highlight the potential to use these geochemical and isotopic parameters as tracers of CO₂ presence and for identifying potential mineral reactions in the reservoirs. As an example we discuss changes in the oxygen isotope composition of reservoir water (H₂O). Although complicated by the introduction of WAG in 2007, the observed changes in $\delta^{18}\text{O}$ of H₂O are consistent with the laboratory work of Johnson and Mayer [2] that showed that $\delta^{18}\text{O}$ values of H₂O will be altered by isotope exchange with oxygen in CO₂

at high concentrations, as is the case in CO₂ 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 CO₂ and that the magnitude of the change in the $\delta^{18}\text{O}$ values of H₂O can be used as an indicator for the presence of injected CO₂ and to calculate CO₂ saturation in the reservoir. Johnson et al. [3] also predicted that the largest perturbation in the $\delta^{18}\text{O}$ values of H₂O at this site would be to a value of -6.9 ‰ should 100% pore space saturation with CO₂ be approached. In the first phase of the project the largest shift in $\delta^{18}\text{O}$ values of H₂O 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-CO₂ 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 CO₂) 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 CO₂ injection at some wells (e.g. Well 12-12, Figure 3).

In general, the chemical parameters highlighted above (pH, alkalinity, Ca²⁺, Fe²⁺, $\delta^{13}\text{C}$ of CO₂, and $\delta^{18}\text{O}$ of H₂O) showed a continual change throughout the project indicating that chemical reactions with CO₂ in the storage reservoir were progressing not only during the CO₂ injection phase, but also during post-injection monitoring. However, the greatest fluctuations in the parameters were observed during active CO₂ 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 CO₂ injection in those wells that had CO₂ breakthrough. Changes in pH from baseline values of ~7.5 to ~5 during CO₂ injection before recovering to higher values (~6.5) post CO₂ 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 Ca²⁺ observed in the last stages (post-CO₂ injection) of the project. Lastly, CO₂ concentration in gas samples were observed to decrease post CO₂ injection from maxima of >90% to a mean value of ~60% indicating that either CO₂ is migrating away from the wells or that dissolution of CO₂ into reservoir fluids is increasing over time. The continual changes in both chemical and isotopic parameters in the waters post CO₂ injection would appear to argue, at least in part, for the latter.

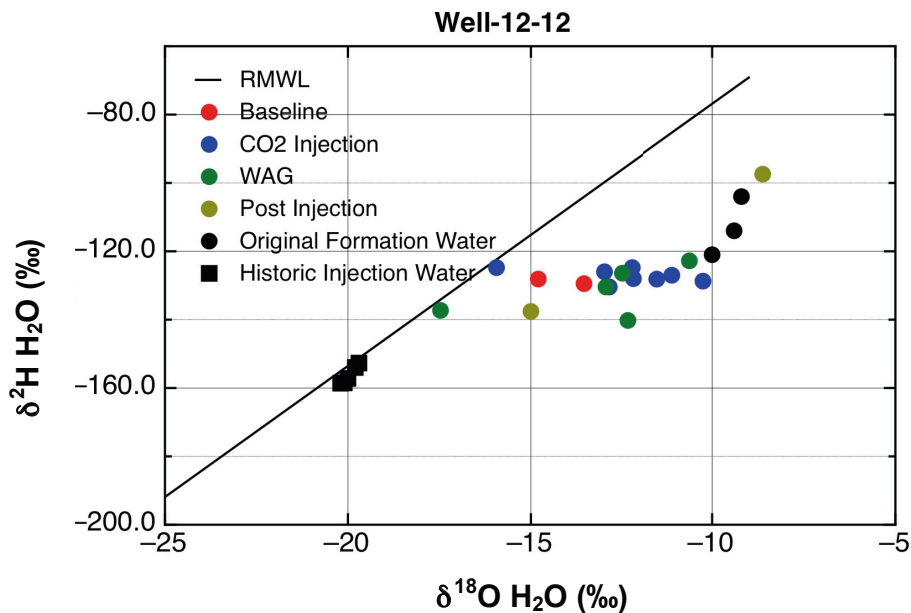


Figure 3. Changes in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ H_2O for the various phases of the project at one of the observation wells (12-12).

5. Conclusion

In conclusion it is demonstrated that continual monitoring of chemical and isotopic parameters in produced fluids and gases can reveal CO_2 migration and both solubility trapping and mineral reactions taking place in the reservoir thus demonstrating CO_2 retention mechanisms. The post- CO_2 injection results show that CO_2 dissolution and mineral reactions continue to progress with time resulting in greater amounts of solubility trapping of injected 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.

Acknowledgements

Funding for the Pembina Cardium CO_2 Monitoring Project was provided by Penn West Energy Trust, Alberta Energy Research Institute, Western Economic Diversification Canada, Natural Resources Canada and the Alberta Government. Analytical services provided by staff of the Isotope Science Laboratory and the Applied Geochemistry Laboratory at the University of Calgary are also gratefully acknowledged. Dwayne Sparks at Penn West Energy Trust is also greatly thanked for his input and data provision regarding field operations.

References

- [1] Hitchon, B. (Ed.), 2009. Pembina Cardium CO_2 Monitoring Pilot: A CO_2 EOR Project, Alberta Canada. Geoscience Publishing. ISBN: 978-0-9680844-5-8.
- [2] Johnson, G., & Mayer, B. (2011): Oxygen isotope exchange between H_2O and CO_2 at elevated CO_2 pressures: implications for monitoring of geological CO_2 storage. – *Applied Geochemistry*, v.26, pp.1184-1191.
- [3] Johnson, G., Mayer, B., Nightingale, M., Shevalier, M. & Hutcheon, I. (2011): Using oxygen isotope ratios to quantitatively assess trapping mechanisms during CO_2 injection into geological reservoirs: The Pembina case study. – *Chemical Geology*, v.283, n.3-4, p185-193.