



Johnson, Gareth and Mayer, Bernhard and Shevalier, Maurice and Nightingale, Michael and Hutcheon, Ian (2011) Quantifying CO2 pore-space saturation at the Pembina Cardium CO2 monitoring pilot (Alberta, Canada) using oxygen isotopes of reservoir fluids and gases. Energy Procedia, 4. pp. 3942-3948. ISSN 1876-6102 , <http://dx.doi.org/10.1016/j.egypro.2011.02.333>

This version is available at <https://strathprints.strath.ac.uk/66711/>

Strathprints is designed to allow users to access the research output of the University of Strathclyde. Unless otherwise explicitly stated on the manuscript, Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. Please check the manuscript for details of any other licences that may have been applied. You may not engage in further distribution of the material for any profitmaking activities or any commercial gain. You may freely distribute both the url (<https://strathprints.strath.ac.uk/>) and the content of this paper for research or private study, educational, or not-for-profit purposes without prior permission or charge.

Any correspondence concerning this service should be sent to the Strathprints administrator: strathprints@strath.ac.uk



ELSEVIER

Available online at www.sciencedirect.com

 ScienceDirect

Energy Procedia 4 (2011) 3942–3948

**Energy
Procedia**

www.elsevier.com/locate/procedia

GHGT-10

Quantifying CO₂ pore-space saturation at the Pembina Cardium CO₂ Monitoring Pilot (Alberta, Canada) using oxygen isotopes of reservoir fluids and gases

Gareth Johnson^{a*}, Bernhard Mayer^a, Maurice Shevalier^a, Michael Nightingale^a, and Ian Hutcheon^a.

Applied Geochemistry Group, Department of Geoscience, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada, T2N1N4.

Abstract

Geochemical and isotopic monitoring allows determination of CO₂ presence in the subsurface through the sampling of produced fluids and gases at production and/or monitoring wells. This is demonstrated by data from 22 months of monitoring at the Pembina Cardium CO₂ Monitoring Pilot in central Alberta, Canada. Eight wells centered around two CO₂ injectors were sampled monthly between February 2005 and February 2007. Stable isotope analyses of the samples revealed that changes in the $\delta^{13}\text{C}_{\text{CO}_2}$ values in produced gas as well as changes in the $\delta^{18}\text{O}$ values of the produced fluids indicate CO₂ presence and identify trapping mechanisms at select production wells. Using equilibrium isotope exchange relationships and CO₂ solubility calculations, fluid and gas saturations in the pore space in excess of that occupied by oil were calculated. We demonstrate that stable isotope measurements on produced fluids and gases at the Pembina Cardium CO₂ storage site can be used to determine both qualitatively and quantitatively the presence of CO₂ around the observation well, given that the injected CO₂ is isotopically distinct.

© 2011 Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: CCS; oxygen isotope ratios; pore-space saturation; Pembina, Cardium.

1. Introduction

Monitoring of injected CO₂ is necessary to prove both the safety and validation of geologic CO₂ storage [1]. Monitoring is also required under the emerging regulatory regimes being developed for Carbon Capture and Storage (CCS) in the USA [2], Europe [3] and Australia [4] amongst others. A highly desirable component of verification of CO₂ storage within the reservoir is an assessment of the saturation of the pore-space that is occupied by CO₂. Geochemical and isotopic monitoring approaches are suitable for tracing the movement and fate of CO₂ in the subsurface through the sampling of produced fluids and gases at production and/or monitoring wells [5, 6]. The objective of this study was to further develop geochemical and isotopic monitoring techniques capable of quantifying CO₂ storage in the subsurface.

2. Site Description

The Pembina Cardium CO₂ Monitoring Pilot site (Fig. 1) is located near the town of Drayton Valley, west of Edmonton (Alberta, Canada) in the Pembina Field which is the largest individual [7], and one of the oldest onshore oilfields in Canada. The Cardium is a siliciclastic reservoir at approximately 1650 m depth and reservoir temperature and pressure of 50°C and 19MPa respectively [8].

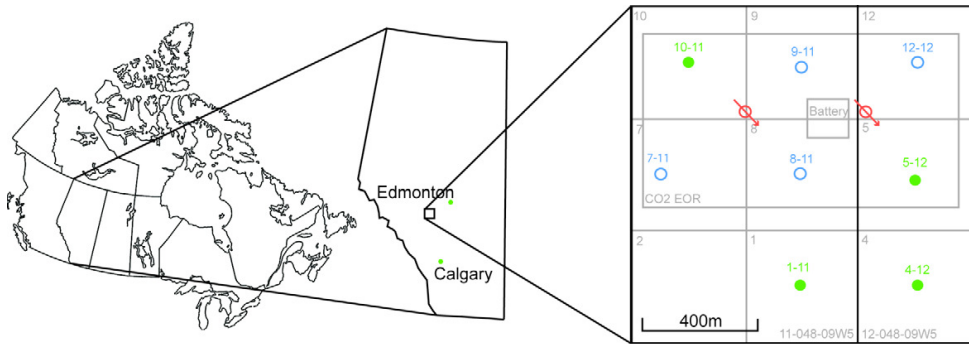


Figure 1. Location map of the Pembina Cardium CO₂ Storage Monitoring Pilot in west-central Alberta. Well bottom-hole locations shown as: Blue open circles = Group 1 wells; Green solid circles = Group 2 wells, and; Red open circles with arrow = CO₂ injectors. Grey outlined area shows CO₂-EOR area containing 6 of the production wells and both CO₂ injectors.

The pilot is an enhanced oil recovery (EOR) operation hosted in the Upper Cretaceous Cardium Formation of the Pembina oil field. Dashtgard et al. [9] provided a detailed description of the geology of the reservoir. Primary production began in the Pembina Oilfield in 1953. Decreasing pressure, increasing gas-oil ratios and production declines led to water-flood pilots as early as 1956 [10]. As production peaked in the early 1970's [11] and total production from primary and secondary methods was near the maximum recoverable, tertiary recovery by CO₂ flood was considered [9] and begun in 2005.

Approximately 75,000 tons of liquid CO₂ were delivered by truck and injected between 2005 and 2008 by two injector wells over two 5-spot patterns (1 injector, 4 producers) where 2 production wells are shared between the patterns [8] (Fig. 1). Casing gas and fluid samples were obtained from eight production wells sampled approximately monthly between February 2005 and March 2008. Baseline data were collected between February and April 2005 allowing an assessment of the natural variability of various geochemical parameters. Following baseline sampling and the commencement of CO₂ injection, 15 monitoring events took place between May 2005 and January 2007. In February 2007, the EOR operation switched to a water alternating gas (WAG) regime and a further 13 monitoring events took place until March 2008.

3. Methods

Fluid samples were collected at the 8 individual well locations in 8L carboys. The carboys were sealed immediately after water was collected to minimize further degassing from the fluids. After a couple of minutes to allow oil and water legs to separate, a fluid sample was taken from the bottom of the carboy and transferred to a 125ml flint glass bottle and filled without headspace. From this sample, alkalinity and pH values were determined in the field. Separate samples were filtered and transferred into 125ml Nalgene bottles for cation and anion analyses in the laboratory by ion chromatography and atomic absorption spectroscopy, respectively and a sub-sample was transferred to 10 mL glass vacu-tainers for subsequent isotopic analysis. Casing gas samples were collected in sealed containers and the chemical composition was analyzed in the field using a Varian CP4900 Micro GC. CO₂ fluxes were calculated by multiplying the total volume of gas produced by the mole fraction of CO₂ measured at the well head during the sampling events.

In addition to chemical analyses, the isotopic compositions of water, CO₂, and dissolved inorganic carbon (DIC) were determined. Carbon isotope ratios of CO₂ ($\delta^{13}\text{C}_{\text{CO}_2}$) were determined from the casing gas samples using a GC coupled to an isotope ratio mass spectrometer (IRMS) and reported relative to V-PDB. Oxygen isotope ratios of CO₂ ($\delta^{18}\text{O}_{\text{CO}_2}$) were determined by comparison against oxygen isotope ratios of CO₂ generated from internationally accepted reference materials (NBS 19 was reacted with phosphoric acid at 25°C and the appropriate isotope fractionation corrections were applied) and certified calibration gases (Messer Griesheim) and are reported versus V-SMOW with an uncertainty of $\pm 0.2\text{‰}$. Water $\delta^{18}\text{O}$ values were determined by using standard CO₂ equilibration techniques followed by dual inlet IRMS [12]. Hydrogen isotope ratios of water samples were determined using the chromium reduction technique [13]. Oxygen and hydrogen isotope ratios are recorded using the usual delta (δ) notation ($\delta^{18}\text{O}$, $\delta^2\text{H}$) in per mil (‰) deviation relative to V-SMOW with an analytical uncertainty of $\pm 0.2\text{‰}$ and $\pm 2.0\text{‰}$ respectively, according to the equation:

$$R_{\text{sample}} [\text{‰}] = \left[\frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right] \cdot 1000 \quad [1]$$

where R represents the $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios of samples and reference materials, respectively.

4. Results and Discussion

Chemical and isotopic data are presented for 22 months of monitoring at the Pembina Cardium CO₂ Monitoring Pilot in the Pembina oilfield in central Alberta, Canada. Stable isotope analyses revealed changes in the $\delta^{18}\text{O}$ values of the produced fluids (Fig. 2) as well as changes in the $\delta^{13}\text{C}_{\text{CO}_2}$ values in produced gas (Fig. 3) indicating CO₂ presence and identifying trapping mechanisms at various production wells.

The eight production/observation wells were divided into two groups based on different chemical and isotopic responses. Group 1 wells were characterized by marked increases in the $\delta^{18}\text{O}$ values of the produced fluids (Fig. 2, Table 1) and the $\delta^{13}\text{C}$ values of produced CO₂ (Fig. 3, Table 1) with a concurrent increase in the CO₂ content of the gas (Fig. 4). Group 2 wells showed no increase in the $\delta^{18}\text{O}$ values of the fluids (Fig. 2, Table 1), smaller increases in $\delta^{13}\text{C}$ values of CO₂ (Fig. 3, Table 1) and only marginal increases in CO₂ content (Fig. 4). In addition, total CO₂ fluxes at group 1 wells ($>100,000\text{ m}^3$) far exceeded those at group 2 wells ($<1500\text{ m}^3$) (Table 1).

Table 1. CO₂ flux, changes in $\delta^{18}\text{O}$ values of produced fluids and changes in $\delta^{13}\text{C}$ values of produced CO₂ at each well over 22 months of CO₂ injection.

Group	Well	CO ₂ flux [m ³]	$\Delta \delta^{18}\text{O H}_2\text{O} [\text{‰}]$	$\Delta \delta^{13}\text{C CO}_2 [\text{‰}]$
1	7-11	157000	+1.1	+11.4
	8-11	123000	+0.7	+10.2
	9-11	297000	+2.4	+17.4
	12-12	461000	+3.9	+14.9
2	1-11	400	+0.6	+9.1
	10-11	200	-0.1	+5.6
	4-12	1200	-0.3	+6.2
	5-12	750	-0.6	+7.9

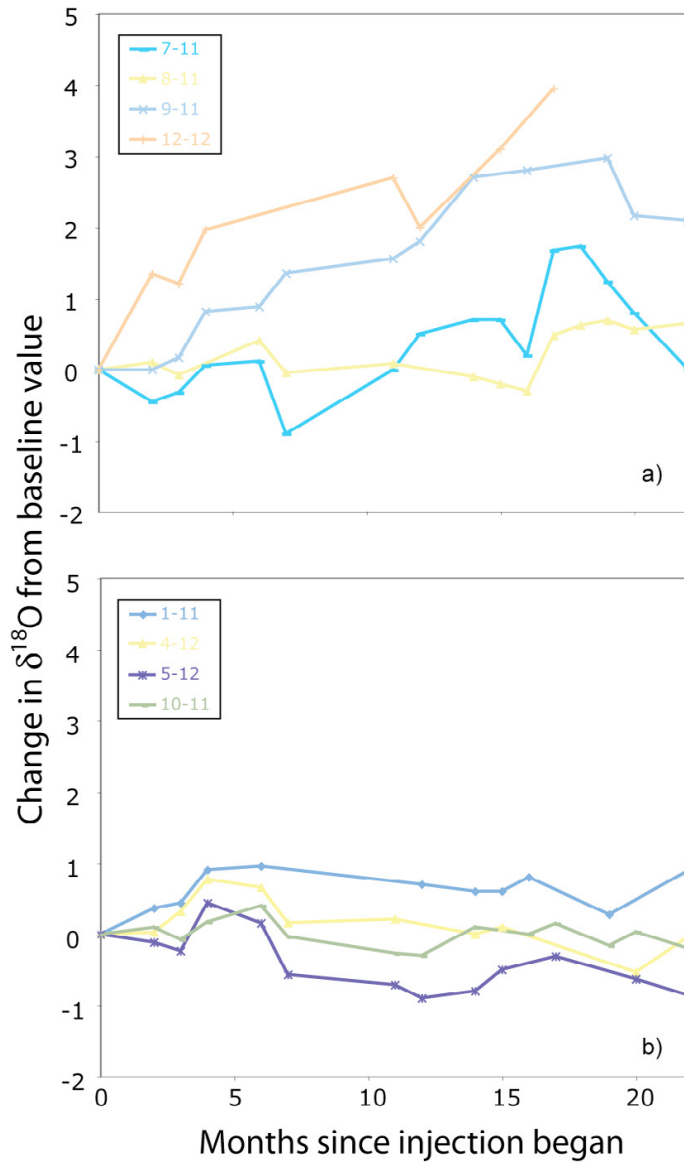


Figure 2. Change of $\delta^{18}\text{O}$ of produced fluids from baseline values (0) at group 1 (a) and 2 (b) wells over 22 months of CO_2 injection.

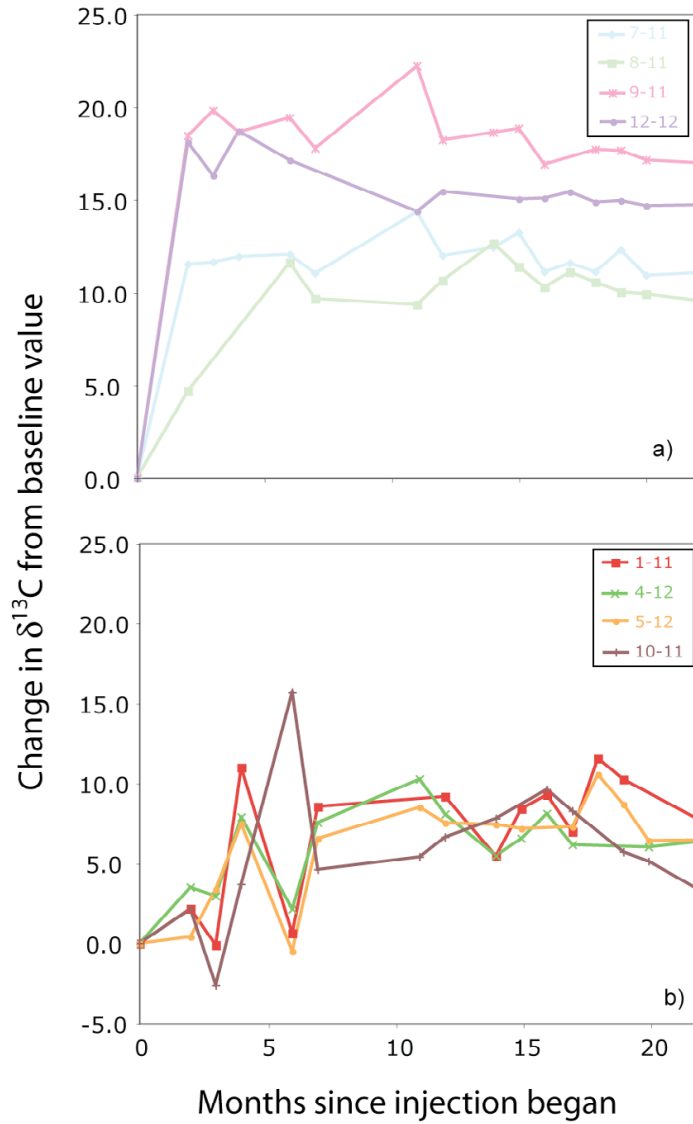


Figure 3. Change of $\delta^{13}\text{C}$ of CO_2 in produced gas from baseline values (0) at group 1 (a) and 2 (b) wells over 22 months of CO_2 injection.

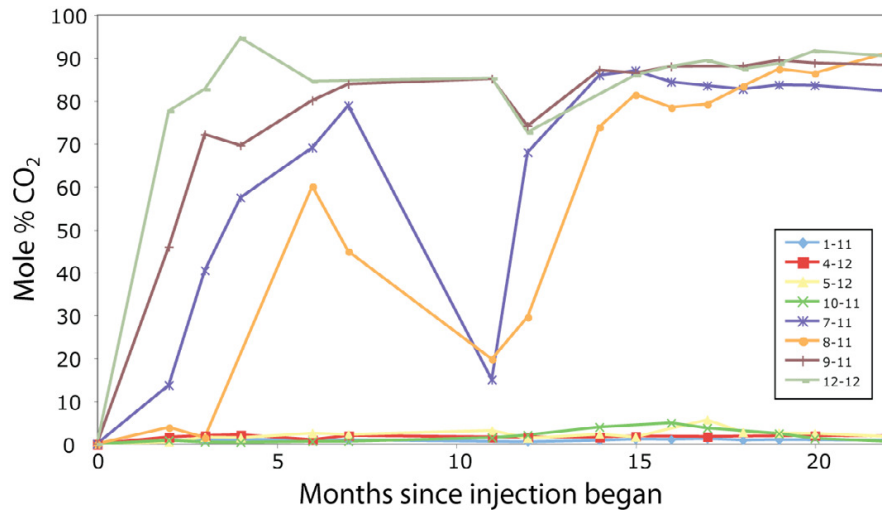


Figure 4. CO₂ contents (mole % CO₂) of produced gas at all wells over 22 months of CO₂ injection.

Oxygen isotope exchange between CO₂ and water has been studied intensively for more than five decades [12, 14, 15]. At isotopic equilibrium under the reservoir conditions of the Pembina project, oxygen in CO₂ is expected to have a $\delta^{18}\text{O}$ value that is 35 ‰ higher than that of water [14], with the $\delta^{18}\text{O}$ value of CO₂ typically being controlled by the latter. However, Kharaka et al. [5] showed that $\delta^{18}\text{O}$ values of water were altered under CO₂ storage scenarios at the Frio project in Texas, USA, due to the presence of high quantities of CO₂. At the Pembina project, injection CO₂ had a $\delta^{18}\text{O}$ value of +29 ‰ and baseline water had $\delta^{18}\text{O}$ values near -15 ‰. This difference of circa 44 ‰ is larger than the oxygen isotope enrichment factor between H₂O and CO₂. Therefore, high amounts of CO₂ in isotopic equilibrium with water have the potential to increase the $\delta^{18}\text{O}$ values of water by up to 9 ‰. The extent of increase of the $\delta^{18}\text{O}$ values of the water is directly related to the fraction of oxygen in the system that is sourced by the CO₂ [16]. The observed changes in the $\delta^{18}\text{O}$ values of water (Table 1, Figure 2) are larger than can be caused by dissolved CO₂ and thus must result from exposure of the water to free phase CO₂. Thus by assessing the magnitude of the change in the $\delta^{18}\text{O}$ value of the water, pore-space saturations of CO₂ in the system can be calculated [16].

Using equilibrium oxygen isotope exchange relationships between water and CO₂ and CO₂ solubility calculations [17], fluid and gas saturations in the pore space in excess of that occupied by oil were calculated. For group 1 wells, fluids were saturated with CO₂ (solubility trapping) and had free-phase CO₂ pore-space saturations in excess of oil in the range 0.05-0.60 (structural/stratigraphic trapping). Fluids obtained from group 2 wells were either subsaturated with respect to CO₂ and hence had no free phase CO₂ (3 wells) or were saturated but with very little free-phase CO₂ with pore-space saturations <0.1 (1 well). These saturation values are consistent with the changes in both CO₂ content and $\delta^{13}\text{C}$ values observed in the casing gas collected at the same wells (Figs. 3, 4) as well as other geochemical proxies [18].

5. Conclusions

We conclude that chemical and stable isotope measurements of produced fluids and gases at CO₂ storage sites can be used to determine both qualitatively and quantitatively the presence of CO₂ around observation wells, provided that the injected CO₂ is isotopically distinct. If a sufficient number of observation/production wells exist, this method can be used to determine the fate of CO₂ in the reservoir near observation wells, but lacks the ability to assess CO₂ saturations away from these sampling points. Geophysical methods have been demonstrated to give spatial resolution [19, 20] for CO₂ presence, but cannot satisfactorily quantify CO₂ saturation over the entire range of expected saturation values. Therefore, we suggest that geochemical and isotopic monitoring in combination with

geophysical monitoring is highly desirable to assess CO₂ pore-space saturation throughout the reservoir. This approach is considered a critical step in determining more accurate 'CO₂ budgets' for CO₂ storage sites.

6. Acknowledgements

Funding for the Pembina Cardium CO₂ 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.

References

- [1] IPCC, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., Davidson, O., de Coninck, H.C., Loos, M., and Meyer, L.A., (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, p.442.
- [2] USEPA, 2008. United States Environmental Protection Agency. Federal Requirements Under the Underground Injection Control (UIC) Program for Carbon Dioxide (CO₂) Geologic Sequestration (GS) Wells: Proposed Rule. July 15 2008, Federal Register, Vol. 73, No. 144, pp 43534-43541. Available online at: <http://www.epa.gov/fedrgstr/EPA-WATER/2008/July/Day-25/w16626.pdf>
- [3] EC, 2009. Directive 2009/31/EC of the European Parliament and of the Council on the geological storage of carbon dioxide and amending Council Directive 85/337/EEC, European Parliament and Council Directives 2000/60/EC, 2001/80/EC, 2004/35/EC, 2006/12/EC, 2008/1/EC and Regulation (EC) No 1013/2006. Available online at: <http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0114:0135:EN:PDF>
- [4] Australian Government, 2008. Offshore Petroleum Amendment (Greenhouse Gas Storage) Bill, 2008. A Bill for an Act to amend the Offshore Petroleum Act 2006, and for other purposes.
- [5] Kharaka, Y.K., Cole, D.R., Hovorka, S.D., Gunter, W.D., Knauss, K.G., and Freifeld, B.M., 2006. Gas-water-rock interactions in Frio Formation following CO₂ injection: Implications for the storage of greenhouse gases in sedimentary basins. *Geology*, v.34, no.7, pp.577-580.
- [6] Raistrick, M., Mayer, B., Perez, R., Shevalier, M. Hutcheon, I., Perkins, E. & Gunter, B. (2006): Using chemical and isotopic data to trace injected carbon dioxide and quantify ionic trapping in oilfield brines at Weyburn, Saskatchewan, Canada. –*Environmental Science & Technology*, 40(21): 6744-6749.
- [7] Owen, E.W., 1975. Trek of the oil finders: a history of exploration for petroleum. AAPG Memoir 6, 1647 p.
- [8] Hitchon, B., (ed.) 2009. Pembina Cardium CO₂ Monitoring Pilot: A CO₂ EOR Project, Alberta Canada. Geoscience Publishing. ISBN 978-0-9680844-5-8.
- [9] Dashtgard, S.E., Buschkuehle, M.B.E., Fairgrieve, B., and Berhane, H., 2008. Geological characterization and potential for carbon dioxide (CO₂) enhanced oil recovery in the Cardium Formation, central Pembina Field, Alberta. *Bulletin of Canadian Petroleum Geology*, v. 56, n.2, pp.147-164.
- [10] Justen, J.J., 1957. Canada's Pembina Field. *Journal of Petroleum Technology*, v.9, n.9, pp.21-26.
- [11] Krause, F.F., Collins, H.N., Nelson, D.A., Machemer, S.D., and French, P.R., 1987. Multiscale anatomy of a reservoir: geological characterization of Pembina-Cardium pool, west-central Alberta, Canada. *AAPG Bulletin*, v.71, pp.1233-1260.
- [12] Epstein, S., and Mayeda, T.K., 1953. Variations of the ¹⁸O/¹⁶O ratio in natural waters: *Geochimica et Cosmochimica Acta*, v.4, pp.213.
- [13] Gehre M., Hoefling, R., Kowski, P., and Strauch, G., 1996. Sample Preparation device for quantitative hydrogen isotope analysis using chromium metal. *Anal. Chem.*, v.68, n.24, pp. 4414-4417.
- [14] Bottinga, Y., 1968. Calculation of fractionation factors for carbon and oxygen in the system calcite – carbon dioxide – water: *Journal of Physical Chemistry*, v.72, pp.800-808.
- [15] Mills, G.A., and Urey, H.C., 1940. The kinetics of isotopic exchange between carbon dioxide, bicarbonate ion, carbonate ion and water. *Journal of American Chemical Society*, v.62, pp.1019-1026.
- [16] Johnson, G., Mayer, B., Nightingale, M., Shevalier, M., and Hutcheon, I., (in review). Using Oxygen Isotope Ratios to Quantitatively Assess Trapping Mechanisms during CO₂ Injection into Geological Reservoirs: the Pembina Case Study. *Chemical Geology*.
- [17] Duan, Z., and Sun, R., 2003. An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chemical Geology*, v.193 p. 257– 271.
- [18] Shevalier, M., Nightingale, M., Johnson, G., Mayer, B., Perkins, E., and Hutcheon, I., (2009): Monitoring the reservoir geochemistry of the Pembina Cardium CO₂ monitoring project, Drayton Valley, Alberta. *Energy Procedia*, Volume 1, Issue 1, Pages 2095-2102.
- [19] Chadwick, A., Arts, R., Eiken, O., Williamson, P., and Williams, G., 2006. Geophysical monitoring of the CO₂ plume at Sleipner, North Sea: An outline review. *In* S. Lombardi et al. (eds.), *Advances in the Geological Storage of Carbon Dioxide*, pp.303–314.
- [20] White, D.J., Hirsche, K., Davis, T., Hutcheon, I., Adair, R., Burrows, G., Graham, S., Bencini, R., Majer, E., and Maxwell, S.C., 2004. Theme 2: Prediction, Monitoring, and Verification of CO₂ Movements. *In* Wilson, M., and Monea, M., (eds.) 2004. IEA GHG Weyburn CO₂ Monitoring & Storage Project Summary Report 2000-2004. Regina: Petroleum Technology Research Centre, pp.73-148.