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Energy Procedia 1 (2009) 2095–2102

**Energy
Procedia**www.elsevier.com/locate/procedia

GHGT-9

Monitoring the reservoir geochemistry of the Pembina Cardium CO₂ Monitoring Project, Drayton Valley, Alberta

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Abstract

The Pembina Cardium CO₂ Monitoring Project in central Alberta was built to assess the Cardium formation's storage potential for CO₂ and stimulate oil production. Three baseline trips and 28 monitoring trips were undertaken over a three year period from February 2005 to March 2008 to collect fluids and gas from eight producing wells. Chemical and isotope analyses were conducted on the fluid and gas samples to determine the changes in the geochemistry of the pilot area and to assess the fate of the injected CO₂. It was found that within 67 days after commencement of CO₂ injection, injection CO₂ break-through occurred in four of the eight monitoring wells. Further, CO₂ dissolution was observed in three of the four monitoring wells in this time frame and in one well, 12-12, both CO₂ dissolution and calcite mineral dissolution were observed within 67 days of the onset of CO₂ injection. Within 18 months siderite dissolution and calcite dissolution were observed in all four of these wells. In the remaining four wells, CO₂ dissolution was observed, indicated by a slow decreased in pH from 7.5 to 7.2 with no significant change in total alkalinity or calcium concentration in the water. Inter-well communications were observed between wells 08-11 and 12-12 by means of residual "kill fluid" migration occurring from well 12-12 to well 08-11.

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Keywords: CO₂ storage; geochemistry; fluid-rock interaction; CO₂ dissolution; mineral dissolution; CO₂-EOR;

1. Introduction

The Pembina Cardium CO₂ Monitoring Project was undertaken to examine the possibility of stimulating oil production using a CO₂ flood under the Royalty Credit Program of the Alberta Department of Energy in 2003. In conjunction with this program, a CO₂-EOR monitoring Pilot Project was developed to assess the Cardium Formation's storage potential for CO₂. The Applied Geochemistry Group at the University of Calgary participation included examining the chemical reactions that occur in the gas-oil-water-rock within the reservoir prior to, during and following CO₂ injection by means of a geochemical sampling and analysis program. Produced gases and fluids

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were analyzed for a broad range of chemical and isotopic parameters to determine the chemical processes within the reservoir and to track the path and fate of the injected CO₂.

The Pembina Cardium CO₂ Monitoring Project is operated by PennWest Energy Trust and is located approximately 15 km WSW of the town of Drayton Valley in Central Alberta, Canada (Fig. 1) where a light gravity crude oil is produced from the Pembina Field of the Upper Cretaceous Cardium Formation [1]. The Cardium has been described as stacked marine sandstone sheets with interstitial shale beds. The Cardium Formation overlies black shale from the Blackstone Formation. Shale of the Wapiabi Formation serves as a reservoir cap rock [Fig. 1]. The reservoir is, on average, at 50°C and 19 MPa pressure [2,3].

The Pembina Field is a giant oil field covering approximately 4,000 km² with over 11,700 oil and gas wells. The Cardium formation is the most prolific oil producing horizon which began primary production in 1953 and waterflooding started in 1960. The original oil in place for the Pembina Cardium is estimated at 1,237 x 10⁶ m³ with the total production from primary and secondary production techniques near the maximum recovery for the pool resulting in tertiary oil recovery using CO₂ now being evaluated [1].

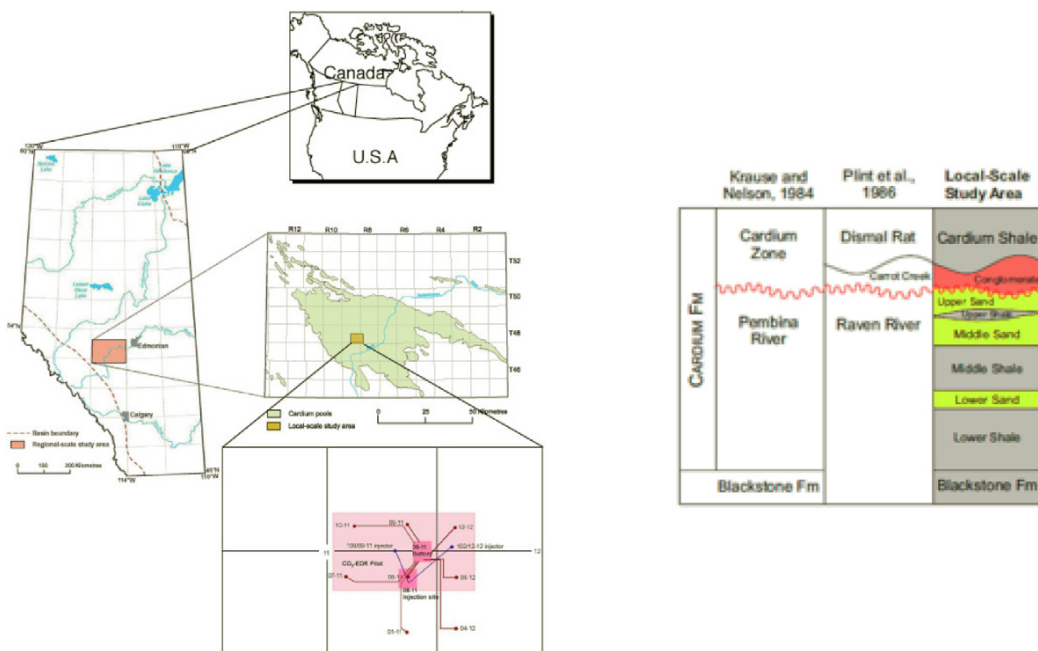


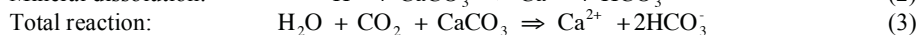
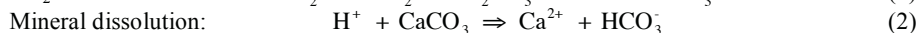
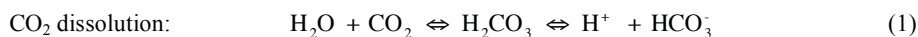
Fig. 1. Location and local scale stratigraphy of the PennWest Pilot site. The map on the left shows the location of the study area. The section on the right shows the local scale study area along with the naming schemes presented by Krause et al. [4] and Plint et al. [5].

1.1. Miscible CO₂ flooding

Under the correct pressure, temperature and oil composition conditions, liquid CO₂ at the surface becomes a super critical fluid at depth (i.e. it has the density of a fluid but the viscosity of a gas). Under these conditions the CO₂ becomes miscible with the oil and causes the residual oil to swell, lowering the viscosity (Fig. 2). Another factor, which may increase oil recovery during CO₂ injection is an increase in the permeability due to the acid nature of the CO₂-water mixture. The acid gases may dissolve carbonate cements or minerals in the formation matrix resulting in an increase in permeability [6].

1.2. Geochemical reactions during CO₂ storage

Reservoirs with Fe-, Mg- and Ca- bearing carbonates are able to trap CO₂ via the following reactions:



Reaction (1) represents CO₂ dissolution resulting in a pH decrease. The bicarbonate alkalinity as a result of CO₂ dissolution does not increase due to the presence of the proton from carbonic acid dissociation, i.e. the bicarbonate will not react with the acid titrante. Reservoir mineral dissolution, e.g. calcite, is represented by reaction (2). This reaction results in increased pH and increased cation concentrations and a higher bicarbonate alkalinity. If both reactions occur, shown in reaction (3), then for each mole of CO₂ injected and reacted one mole of cation and two moles of HCO₃⁻ are dissolved in the *in situ* fluid.

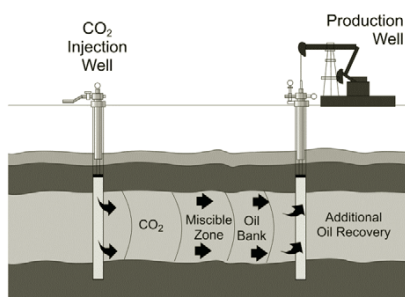


Fig. 2. A cartoon depicting CO₂ injection and enhanced oil recovery (modified from IEA web site).

The objective of this project was to use geochemical and isotopic techniques to assess the fate of injected CO₂ in the Cardium formation and identify CO₂-fluid-mineral reactions in the reservoir.

2. Methods

The Penn West CO₂-EOR project consists of two injection wells with six producing wells surrounding the injection wells. Two of the producing wells are shared by the two patterns. Two monitoring wells to the south of the producing wells were also included in the monitoring program (Fig. 1). Three baseline trips were completed along with 28 near monthly sampling trips beginning in February 2005 and finishing off in March 2008.

2.1. Sampling and Analyses

Fluid and gas samples were collected from the wellhead. The fluid sample was separated into oil and water fractions in a carboy. From the fluid fraction a raw water sample was taken for total alkalinity and pH measurements. The remaining water was filtered onsite and separated into acidified and un-acidified fractions. The following analyses were performed on the water samples: electrical conductivity, anion and cation concentrations (Ca, Mg, K, Na, Fe, Li, Mn, Si, Ba, Sr, Cl, Br, SO₄, F, NO₃), and stable isotope ratios of water and dissolved inorganic carbon ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}_{\text{DIC}}$). Parameters measured for each production well gas samples included mole % of He, N₂, CO₂, CH₄, C₂H₆, C₃H₈, C₄H₁₀ and C₅H₁₂. Also $\delta^{13}\text{C}$ values of CO₂, CH₄, C₂H₆, C₃H₈, C₄H₁₀ and C₅H₁₂ in the gas were determined [7].

2.2. Mineralogy

The mineralogy of core samples obtained from the study area was also determined using a variety of different techniques and is described in detail in a companion paper [8].

3. Results

3.1. Mineralogy

A summary of the average mineralogical composition for each stratigraphic unit is shown in Table 1. It is evident that there are reactive carbonate minerals, calcite and siderite, present in the stratigraphic units.

3.2. Geochemical Monitoring

Fig. 3a shows the measured wellhead pH as a function of sampling date for all baseline and monitoring trips. Fluids from four wells show a significant decrease in the pH to ~6.4 early on in the sampling program (07-11, 08-11, 09-11 and 12-12). The pH for fluids in the other wells (01-11, 10-11, 04-12, 05-12) remained relatively unchanged at ~7.5 until very late in the sampling program when pH values did begin to decrease. Beginning in July 2007 the pH for fluids from all wells began to decrease, most notably in 01-11. The minimum pH for fluids from all wells was observed in October 2007 and followed by an increase to previously observed levels.

Table 1: Average mineralogical composition of each stratigraphic unit.

Mineral Phases	Cardium Shale wt%	Conglomerate wt%	Upper Sandstone wt%	Middle Sandstone wt%	Lower Sandstone wt%	Cemented Sandstone wt%	Interstitial Shale wt%	Siderite Nodule wt%
Quartz	46.0	85.6	86.4	86.2	86.8	45.3	43.5	4.7
Kaolinite	6.3	1.9	2.3	2.6	2.1	1.5	4.4	0.9
Chlorite	3.3	1.0	0.8	1.0	1.0	0.0	2.2	0.1
Albite	2.7	0.3	0.5	0.6	1.3	0.8	2.3	1.5
Smectite	0.9	0.0	0.0	0.0	0.0	0.0	2.2	0.0
Calcite	0.2	1.7	0.2	0.2	0.1	12.5	0.2	4.0
Muscovite	15.6	1.8	2.6	2.1	2.3	1.6	17.1	4.1
Illite	14.0	2.1	1.7	1.4	1.5	1.1	14.1	3.3
Anatase	0.7	0.1	0.1	0.1	0.2	0.1	0.7	0.2
Apatite	0.4	0.5	0.3	0.3	0.3	0.0	0.7	1.2
Pyrolusite	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.2
Siderite	0.5	0.5	1.1	0.7	0.4	32.3	1.1	75.5
Pyrite	1.6	0.2	0.5	0.4	0.2	0.4	1.4	0.1
K-feldspar	3.7	1.1	0.9	1.2	1.1	1.0	3.1	0.7

Fig. 3b displays total alkalinity as a function of sampling date. Total alkalinity remained constant until March 2006 when there was a spike in total alkalinity for wells 10-11 and 08-11 in May 2007 Well 05-12 showed a spike in the alkalinity in Nov 2007. Well 12-12 showed an immediate increase in the total alkalinity and followed the same trend as the rest of the wells until March 2007 followed by significant variability thereafter.

Fig. 4a shows calcium concentrations versus sampling date displaying similar trends as pH, i.e. the same four wells showed a significant increase in calcium concentrations (07-11, 08-11, 09-11, 12-12) displaying significant variability towards the end of the observation period. Fluids from the other four wells were characterized by a fairly constant calcium concentration (01-11, 10-11, 04-12, 05-12).

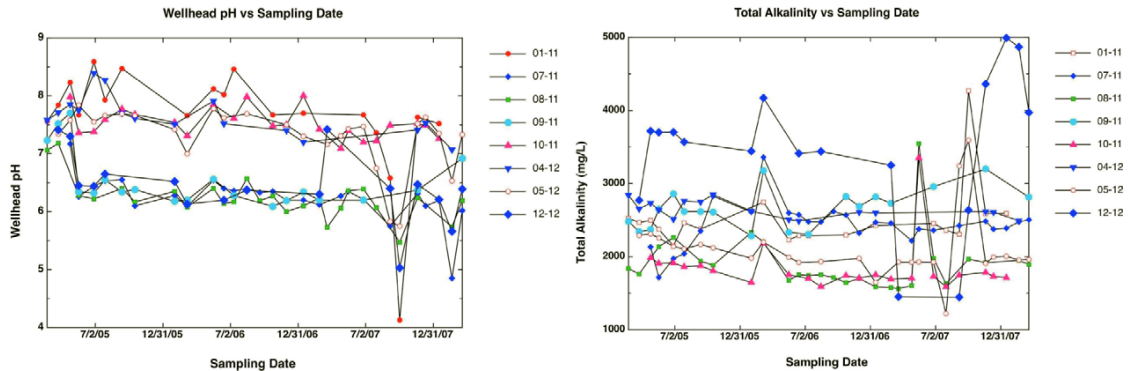


Fig. 3. Wellhead pH versus sampling date (left) and total alkalinity versus sampling date (right) measured in produced fluids. Both these parameters are measured in the field immediately after fluid sampling.

Iron concentrations versus sampling date are shown in Fig. 4b. Two of the wells, 07-11 and 09-11 showed an early significant increase in the concentration of iron followed by high but variable concentrations for two thirds of the sampling period followed by a decrease in iron concentration. Fluids from well 12-12 showed a slow increase in the concentration of iron for three quarters of the study period followed by lower but variable concentrations. Well 08-11 showed an initial increase in iron concentration followed by lower but variable concentrations. The remaining wells were characterized by very low iron concentrations of iron with no significant increase over the observation period of the study.

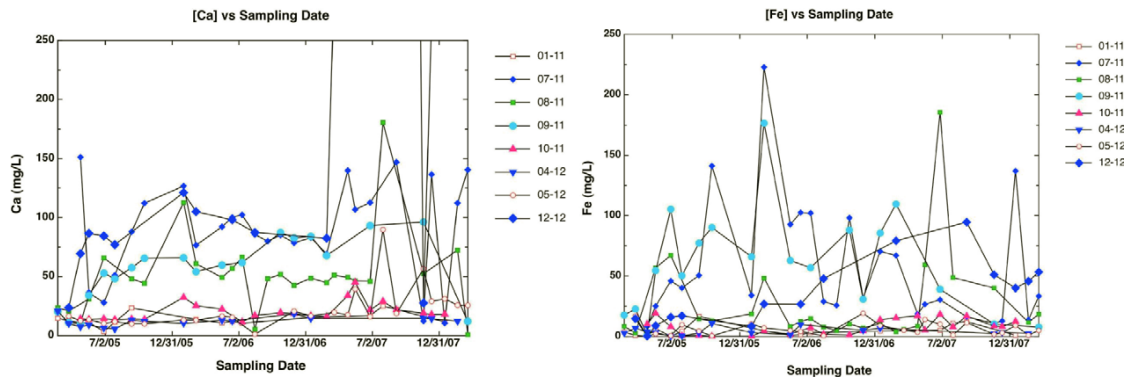


Fig. 4 Concentration of calcium versus sampling date (left) and concentration of iron versus sampling date (right).

The concentration of CO_2 present in the casing gas as a function of sampling date is shown in Fig. 5a. Four wells (07-11, 08-11, 09-11 and 12-12) showed a significant increase in CO_2 concentration shortly after commencement of CO_2 injection. There was a decrease in CO_2 concentration in late 2005 to early 2006 for all four wells but then the concentration returned to high values and continued to increase. The remaining four wells all displayed very low concentrations of CO_2 with a slight increase for 10-11 at the end of the study.

Initial $\delta^{13}\text{C-CO}_{2(g)}$ values were below -15% during baseline sampling. In contrast, the injection gas had $\delta^{13}\text{C-CO}_{2(g)}$ values ranging from -1 to -7% . A plot of $\delta^{13}\text{C-CO}_{2(g)}$ values versus sampling date (Fig. 5b) shows a rapid

increase in the $\delta^{13}\text{C-CO}_{2(\text{g})}$ values for wells 07-11, 08-11, 09-11 and 12-12 towards those of the injection CO_2 . The remaining four wells were also characterized by increasing $\delta^{13}\text{C}$ values towards values around -10 ‰.

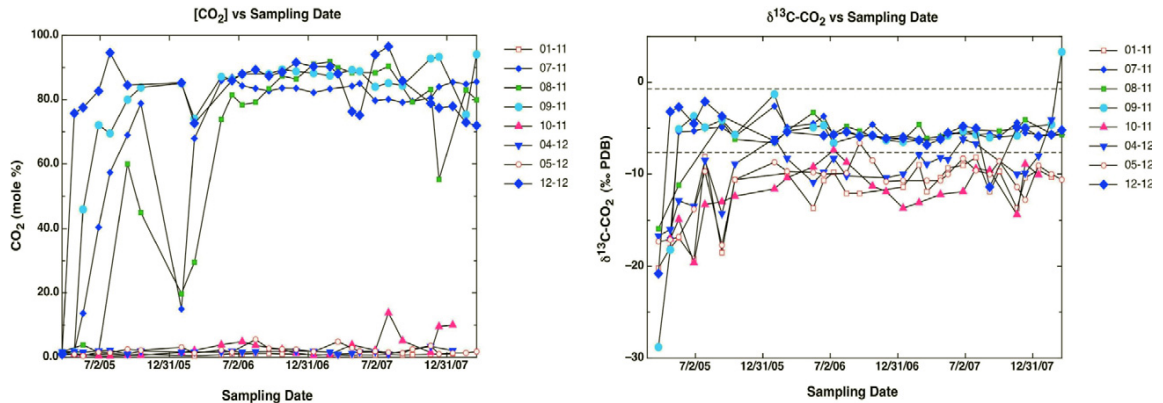


Fig. 5 Concentration of CO_2 in casing gas versus sampling date (left) and $\delta^{13}\text{C-CO}_{2(\text{g})}$ values versus sampling date (right). The concentration of CO_2 is measured in the field.

4. Discussion

The source of the CO_2 observed at the wellheads was determined by using carbon isotopes as a tracer. Fig. 6a shows the $\delta^{13}\text{C-CO}_{2(\text{g})}$ values as a function of concentration of CO_2 in the casing gas. For the four wells with high concentration of CO_2 , nearly all of the measured isotopic ratios fell within the range of the injection CO_2 isotopic ratio. This indicates that the CO_2 observed at these four wells, (07-11, 08-11, 09-11 and 12-12), was injection CO_2 , indicating that CO_2 break-through has occurred in these for wells. For the four wells with low CO_2 gas concentrations, the measured isotopic ratios did not fall within the range of the isotopic composition of the injection gas, but trended towards the $\delta^{13}\text{C}$ value of injection gas with slightly increasing CO_2 concentrations.

Comparing the trends in the other data reveals that the decrease in pH for the four wells (07-11, 08-11, 09-11 and 12-12) displayed in Fig. 3 correlates well with the increase in the concentration of CO_2 in the produced gas. Further the CO_2 observed at the producing wells was injection CO_2 , since the $\delta^{13}\text{C-CO}_{2(\text{g})}$ values of the produced CO_2 fall within the range of the $\delta^{13}\text{C-CO}_{2(\text{g})}$ values of the injected CO_2 (Fig. 5). When CO_2 dissolution occurs in water, as shown in reaction (1), there was a decrease in pH but no change in bicarbonate concentration. During the time period when pH was decreasing and CO_2 increases in the casing gas, there was no significant change in total alkalinity for three of the wells (Fig. 3), which is a measure of bicarbonate present in the water. CO_2 injection commenced on March 13, 2005 and within 67 days a significant decrease in pH, on the order of 1.0 pH units, was observed. This indicates that CO_2 dissolution has occurred in these three wells.

The exception to this trend is well 12-12 where the total alkalinity increased significantly during this time period. In addition to the pH decrease and the total alkalinity increase, Fig. 4 shows that there is an increase in the concentration of calcium, from 23.8 mg/L at baseline 2 monitoring event to 86.6 mg/L during monitor 1, an increase of over 3.5 times in only 67 days. Based on these observations, both reactions (1) and (2), CO_2 dissolution and calcite mineral dissolution, were occurring in the vicinity of well 12-12. While there is siderite present in the study area, significant dissolution was not observed in the first 67 days due the slower kinetics of this reaction when compared to calcite. The concentration of iron increased however marginally from 14.8 mg/L at baseline 2 to 17.1 mg/L for monitor 3.

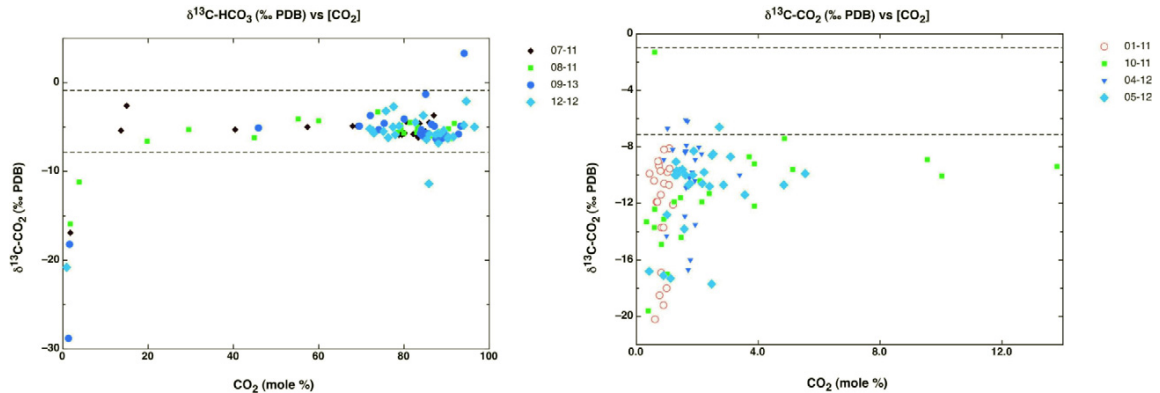


Fig 6. $\delta^{13}\text{C-CO}_{2(\text{g})}$ values versus concentration of CO_2 for wells with high CO_2 concentrations (left) and $\delta^{13}\text{C-CO}_{2(\text{g})}$ values versus concentration of CO_2 for wells with low CO_2 concentrations (right). The dashed lines on each plot indicate the range of $\delta^{13}\text{C-CO}_{2(\text{g})}$ values for the injection CO_2 .

After the initial changes in pH, the pattern of decreasing pH for the four wells (07-11, 08-11, 09-11 and 12-12) does not continue. Fluids from these wells have a fairly constant pH of ~ 6.4 while total alkalinity slowly increases (Fig.3) indicating that reaction (2), mineral dissolution, has started to occur. This is supported by the calcium concentrations which slowly increased circa 5-fold over an 18 month observation period (Fig. 4). During this time period the iron concentration also increased slowly on average by a factor of 2 to 3 (Fig. 4). This indicates that both calcite and siderite dissolution have occurred.

The remaining four wells, (01-11, 10-11, 04-12, 05-12), show a slight decrease in pH throughout the observation period from ~ 7.5 to 7.2 (Fig. 3). There does not appear to be an increase in total alkalinity or calcium concentration during this time frame. Wells 01-11 and 05-12 show a significant decrease in pH in October 2007, when the pH decreased from the average of ~ 7.5 to 4.13 and 5.75 respectively before recovering to the average pH of ~ 7.2 . This may be due to a well work over that was occurring on a neighboring well, 04-12.

Well 12-12 shows a significant increase in calcium, from an initial concentration of 82.5 mg/L in February 2007 to 2038 mg/L in September 2007 (Fig. 4). An increase in nitrate was also observed in the water, from 0 mg/L to 8953 mg/L in September 2007. Significant increases in calcium were observed in well 08-11, increasing from 45.9 mg/L in June 2007 to 180.6 mg/L in July 2007. Nitrate concentrations increased from 0 mg/L in June to 575.5 mg/L in July 2007. Well 12-12 underwent a pump replacement where a different “kill fluid”, a very dense fluid pumped into the well bore to prevent the flow of reservoir fluids to the surface without the use of pressure control equipment, was used by the service company. The “kill fluid” was calcium nitrate based and was used because it is denser than the standard KCl “kill fluids”. The operator recorded in their logs that the volume of fluid that was removed from the well after the service work was the same as the volume that was pumped down the well bore. However, since the fluid was much denser than reservoir fluids, it is likely that density driven flow had occurred, leaving a significant amount of “kill fluid” in the reservoir. This “kill fluid” then mixed with the reservoir fluids and migrated to well 08-11 due to draw down of the reservoir fluids by pumping occurring at well 08-11 when well 12-12 was not operating. This observation is important because it shows that there is inter-well communication occurring between two wells, 08-11 and 12-12 which are located on either side of the injector well. At the time that this inter-well communication was observed, CO_2 injection was not occurring in this part of the pilot site.

5. Conclusions

Determining the fate of injected CO_2 is important for assessing the success of carbon storage projects. For this pilot study, the trends in the chemical and isotopic compositions of the waters and gases suggest that in four of the

eight producing wells injection CO₂ is reacting with formation water, lowering the pH of the fluids resulting in dissolution of carbonate minerals. This mineral reaction with calcite occurred in one well, 12-12, only 67 days after CO₂ injection commenced. After 18 months, fluids obtained from all four wells showed both calcite and siderite mineral dissolution. These reactions result in the storage of injected CO₂ as bicarbonate ions within the formation water. For the four other wells there was also evidence for increasing proportions of injected CO₂ and CO₂ storage via CO₂ dissolution, i.e. the formation of carbonic acid. Hence it was demonstrated that chemical and isotopic techniques can be successfully used to monitor the fate of injected CO₂ in the reservoir. It was also shown that the use of “kill fluids” during well workovers can affect the geochemical composition of the produced fluids and that it is important to distinguish these effects from those caused by CO₂ injection.

Acknowledgments

This work was carried out with the strategic guidance and financial support of the Alberta Energy Research Institute, the Alberta Government, Western Economic Diversification Canada, Natural Resources Canada and Penn West Energy Trust. The authors appreciate the efforts of many individuals who aided in the collection and interpretation of the geochemical data presented here, including: Fred Keith and Pierre Schaub, Dwayne Sparks and Tarun Kashib of Penn West Energy Trust, and Steve Taylor, Yan Gao and the technicians from the Isotope Science Laboratory at the University of Calgary.

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