

## Reservoir Geochemical Monitoring of the PennWest CO<sub>2</sub>-EOR Site

Maurice Shevalier\*  
University of Calgary, Calgary, AB  
maurice@earth.geo.ucalgary.ca

Michael Nightingale, Gareth Johnson, Bernhard Mayer and Ian Hutcheon  
University of Calgary, Calgary, AB, Canada

and

Ernie Perkins  
Alberta Research Council, Edmonton, AB, Canada

### Summary

A regular monthly geochemical monitoring program involving the collection and chemical and isotopic analysis of fluids and gases was conducted since February 2005 at the PennWest CO<sub>2</sub>-EOR pilot, near Drayton Valley in Central Alberta. Six producing wells were sampled along with two control wells located outside of the pilot area. Chemical and isotopic data revealed that injected CO<sub>2</sub> is retained in the water by both solubility trapping and ionic trapping mechanisms in four of six producing wells. These reactions are evidenced by decreases in the wellhead pH over time and increases in the concentrations of calcium and iron. Also, the  $\delta^{13}\text{C}$  values and the concentration of CO<sub>2</sub> measured over time in these four wells show CO<sub>2</sub> break through. In October 2007 the four remaining wells showed signs of solubility trapping, as indicated by the rapid decrease in wellhead pH values.

### Introduction

Produced water, gas and oil samples from the PennWest CO<sub>2</sub>-EOR pilot, near Drayton Valley in Central Alberta, have been collected on a near monthly basis since February 2005. The objectives of the geochemical monitoring program are as follows:

1. to regularly monitor fluids and gases for changes in chemical and isotopic composition;
2. to regularly monitor injection water and CO<sub>2</sub> for chemical and isotopic composition changes;
3. using the monitoring and mineralogy data to assist in determining possible geochemical reactions occurring within the oil/brine/rock system;
4. using the geochemical data to determine the effectiveness of this type of reservoir for CO<sub>2</sub> storage during and after injection.

To date, a total of three baseline (prior to CO<sub>2</sub> injection) and 26 monitoring sampling events have been carried out. Each sample was analyzed for 38 chemical and isotopic parameters. In addition,

regular sampling and measurements of the isotopic composition of the injection CO<sub>2</sub> have also occurred. Samples were taken from six producing wells from within the CO<sub>2</sub>-EOR pilot site and two monitoring wells, 01-11 and 04-12, located outside of the EOR Pilot site.

## Geochemical Monitoring and Results

Samples of gases and fluids were obtained at the wellheads. The fluid samples were collected in a carboy and then sealed. The water samples from the carboys were filtered and preserved for anion, cation and isotope analyses. Also casing gas samples from the wellheads were collected. On-site gas chromatographic compositional analyses were performed and samples for isotopic analysis were collected. On-site analyses for pH and total alkalinity were also performed on raw, unfiltered water samples (Emberly et al., 2005).

Some analytical results from the baseline and monitoring trips are summarized in Figures 1-7. Figure 1 shows the measured wellhead pH as a function of sampling date. Half of the wells sampled (07-11, 08-11, 09-11, 12-12) show a decrease in pH to ~6.5 while the remaining wells (01-11, 10-11, 04-12, 05-12) have a fairly constant pH of ~7.5. After July 2007, the pH of all the produced waters began to significantly drop, over 3.5 pH units for 01-11. Figure 2 shows the total alkalinity of the sample as a function of sampling date. The total alkalinity for all samples remained constant until May 2006. During this sampling event, four wells (07-12, 09-11, 10-11, 12-12) showed a spike in the total alkalinity then returned to previous levels. Also, in June 2006 the total alkalinity dropped from ~3500 mg/L to ~1450 mg/L and then increased to ~2650 mg/L in October 2007. Figure 3 shows the calcium concentration as a function of the sampling date. As with pH, the same four wells (07-11, 08-11, 09-11, 12-12) showed a general increase over time while the remaining wells remained constant. Wells 12-12 and 8-11 show a dramatic increase in calcium (2038 mg/L and 181 mg/L respectively) in July 2007. The log of the iron concentration as a function of sampling date is shown in Figure 4. All four wells (07-11, 08-11, 09-11, 12-12) that show increases in concentrations over time for total alkalinity and calcium show an increase in iron concentration while the remaining wells have relatively constant iron concentrations.

The CO<sub>2</sub> concentrations in the casing gas as a function of sampling dates are shown in Figure 5. Initially the CO<sub>2</sub> concentrations were less than 2% for all wells. As with total alkalinity, four wells (07-11, 08-11, 09-11, 12-12) showed an increase in CO<sub>2</sub> typically to more than 80% while the remaining four wells showed only a very minor increase in the CO<sub>2</sub> concentration. There was a drop in CO<sub>2</sub> concentration in two wells, 07-11 and 08-11 in Feb 2006. Initial  $\delta^{13}\text{C-CO}_{2(g)}$  values were below -15‰. As with nearly all the other monitoring parameters, the  $\delta^{13}\text{C-CO}_{2(g)}$  values as a function of sampling dates (Figure 6) the same four wells (07-11, 08-11, 09-11, 12-12) show a quick initial change in the  $\delta^{13}\text{C}$  value while the remaining four change slowly. Also shown on this plot are the measured  $\delta^{13}\text{C}$  values of the injection CO<sub>2</sub> as a function of sampling date, which ranged between -1 and -5‰ throughout the observation period.

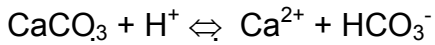
Figure 7 shows the carbon isotopic ratio of bicarbonate versus the sampling date. The measured  $\delta^{13}\text{C}$  values for bicarbonate are very similar to those of the injected CO<sub>2</sub> except for sampling events in January and February 2007, when a significant decrease in the  $\delta^{13}\text{C}$  values from ~-10‰ to ~-20‰ was observed. Thereafter,  $\delta^{13}\text{C}$  values return to values between ~0‰ and ~-5‰.

## Discussion

The dissolution of CO<sub>2</sub> into water forms carbonic acid via reaction 1, solubility trapping, resulting in acidification of the water (Gunter et al., 2004). If there are any reactant minerals present, e.g. calcite, then mineral dissolution may occur (reaction 2) resulting in a free cation, e.g. Ca<sup>2+</sup>, and a bicarbonate ion, ionic trapping (Gunter et al., 2004).



*solubility trapping* (1)



*ionic trapping* (2)

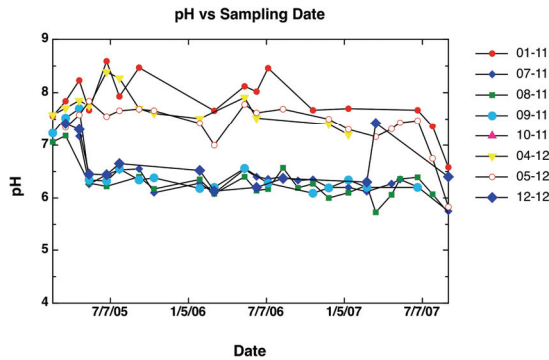


Figure 1: Wellhead pH versus sampling date

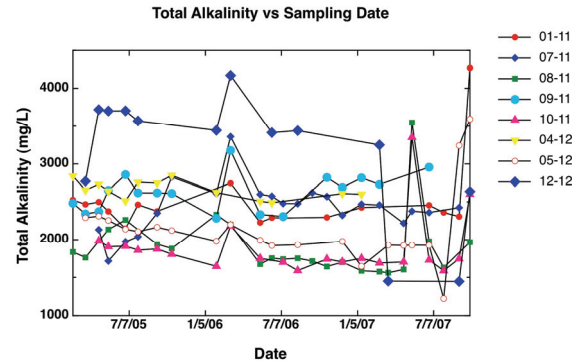


Figure 2: Total alkalinity versus sampling date. The alkalinity is measured in the field.

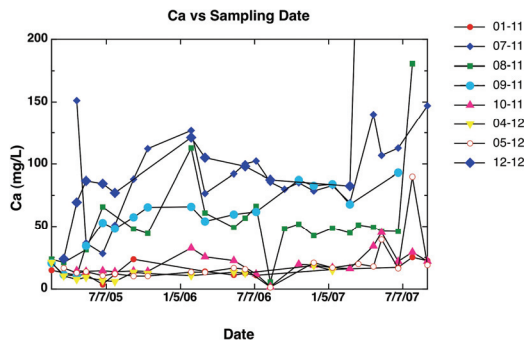


Figure 3: Calcium concentration versus sampling date

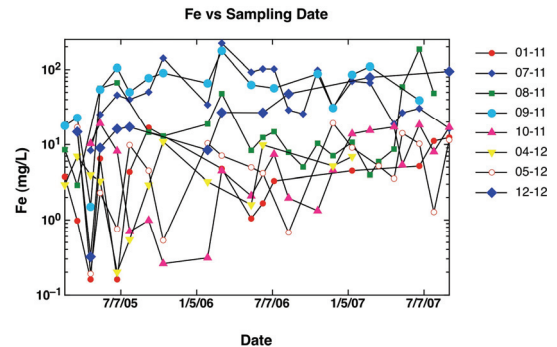


Figure 4: Log iron concentration versus sampling date.

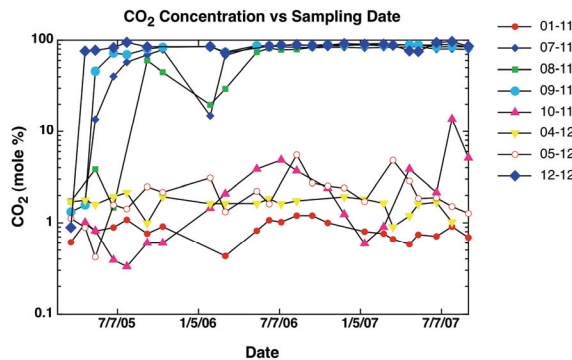


Figure 5: Log CO<sub>2</sub> concentration versus sampling date.

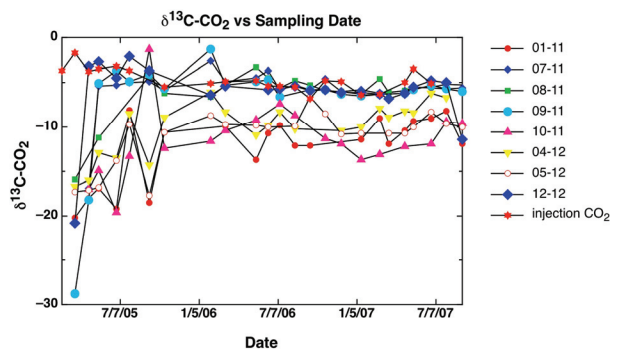


Figure 6: δ<sup>13</sup>C of CO<sub>2</sub> versus sampling date.

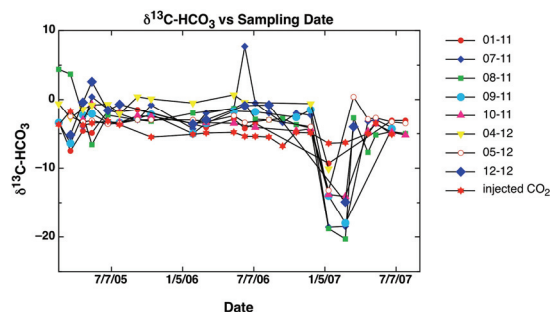


Figure 7:  $\delta^{13}\text{C}$  of  $\text{HCO}_3^-$  versus sampling date.

Figure 1 shows a marked decrease in the pH in four wells, 07-11, 08-11, 09-11 and 12-12, occurring in May 2005. Break-through of  $\text{CO}_2$  at these four wells, indicated by the increase in  $\text{CO}_2$  concentration in the casing gas (Fig. 5), also occurred in May 2005, indicating that the decrease in pH is due to solubility trapping of  $\text{CO}_2$  in water (reaction 1). Simultaneously, an increase in calcium and iron concentrations was observed in the fluids obtained from the same four wells (Fig. 3, 4), suggesting that dissolution of carbonate minerals and/or cements commenced (reaction 2). The remaining four wells showed a pH decrease in July 2007, indicating solubility trapping occurred more than 2 years later. With the exception of well 12-12, total alkalinity remained relatively constant over time. Even though there is calcite and siderite dissolution occurring the amount of calcite and siderite dissolved and thus the amount of extra bicarbonate added to the system, is relatively small. Thus there is little change in the total alkalinity.

Carbon isotope ratios are a suitable tracer for the fate of the injected  $\text{CO}_2$  (see also companion paper by Johnson et al.) The carbon isotopic composition of the injected  $\text{CO}_2$  is significantly higher than that of the initial  $\text{CO}_2$  in the reservoir (Figure 6). As  $\text{CO}_2$  injection progressed, wells 07-11, 08-11, 09-11 and 12-12 displayed a rapid increase in the  $\delta^{13}\text{C}\text{-CO}_{2(g)}$  values towards those of the injected  $\text{CO}_2$ ,  $\sim 5\text{‰}$  (figure 7), providing evidence that the  $\text{CO}_2$  is derived from the injected  $\text{CO}_2$ . In contrast,  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  in the other wells remained low around  $-10\text{‰}$ , indicating that this gas is a mixture of injected and reservoir  $\text{CO}_2$ .

Figure 7 shows the carbon isotopic ratio of bicarbonate versus sampling date and all follow a similar trend i.e. the  $\delta^{13}\text{C}$  of the bicarbonate is  $\sim 3\text{‰}$ , except for the January 2007 and February 2007 which drops to a range of  $\sim 10\text{‰}$  to  $-20\text{‰}$ . This significant drop does follow the expected trend of decreasing isotopic ratios if calcite or siderite dissolution is occurring since the range of  $\delta^{13}\text{C}\text{-HCO}_3^-$  from this process can be as low as  $-25\text{‰}$  to  $-30\text{‰}$  (Machemer and Hutcheon, 1988).

## Conclusions

Four of the six producing wells, 07-11, 08-11, 09-11 and 12-12, show results consistent with both solubility and ionic trapping as well as  $\text{CO}_2$  break through which occurs as early as May 2005, 66 days after  $\text{CO}_2$  injection began. The remaining two wells, 10-11 and 05-12, and the two monitoring wells, 01-11 and 04-12, show that solubility trapping commences much later (July 2007), but do not show signs of  $\text{CO}_2$  break through. Hence, this project demonstrates that a combination of chemical and isotopic measurements on fluids and gases regularly sampled from monitoring wells is an effective method to assess reactions in mature fields undergoing enhanced oil recovery. These methods will also help to verify  $\text{CO}_2$  storage.

## Acknowledgements

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## References

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