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Impact of Injected CO_2 on Reservoir Mineralogy During CO_2-EOR

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Abstract

An investigation of the impact of injected CO_2 on reservoir mineralogy was completed as part of the geochemical monitoring and modelling of the Pembina Cardium CO_2 Monitoring Project southwest of Drayton Valley, Alberta, Canada. Oil production at the pilot is primarily from the upper two of three stacked sandstone units of the Cardium Formation in the Pembina field. Core analyzed included samples from each of the three sandstone units, and encompassed three distinct time periods: pre-water flood (1955), pre-CO_2 flood (2005), and post-CO_2 flood (2007). The results of whole rock analysis (XRF, ICP, and XRD), and microscopy (polarizing and electron microprobe) suggest the three separate sandstone units are both texturally and compositionally similar regardless of when the core was recovered. Framework grains are predominately sub-angular to sub-rounded quartz/chert (up to 90.0 wt%), and include smaller amounts of lithic fragments (shale), feldspar (k-feldspar, and albite), mica (muscovite and chlorite), and fluor-apatite. Authigenic pyrite is found as finely disseminated rhombs throughout the formation. Clay minerals present are predominantly kaolinite and illite. Kaolinite appears as fine discrete pore filling books, and is considered to be authigenic. Illite occurs as a major constituent of shale fragments, as well as fine pore bridging strands. The sandstone's irregular pores are cemented to varying degrees by silica and/or carbonate minerals (calcite and siderite). Dissolution features associated with formation diagenesis, including the degradation of detrital grains (quartz and feldspar), the partial and/or complete removal of carbonate cements, and the presence of residual clays, are found in core from each of the three time periods. Attributing dissolution features in post-CO_2 flood core to the interaction of minerals and carbonic acid is difficult due to the geologic history of the formation.

Keywords: CO_2-EOR; Sandstone; Mineral Dissolution; Microprobe; LPNORM

1. Introduction

Primary crude-oil production typically recovers only 15 to 20% of the oil originally in place. The use of secondary recovery methods such as water-flood can increase oil recovery by as much as 20 to 50% in mature oil fields. However, water is not miscible with oil, and the resulting capillary forces that arise from the oil water interfacial tension can trap the remaining oil in the very small converging and diverging channels that are present in the oil-bearing rock. It is the role of tertiary recovery methods to overcome these capillary forces [1].

The interfacial tension can be overcome by "sweeping" an oil-bearing rock with a miscible fluid such as methane or propane, however the widespread use of these hydrocarbons would be cost prohibitive. Under the right set of conditions, carbon dioxide, an inexpensive alternative is capable of displacing trapped oil. Orr and Taber [1] described in detail the mechanisms by which CO_2 displaces oil. Initially, injected CO_2 dissolves into smaller adjacent droplets of oil, which then swell and coalesce, and are subsequently mobilized by an imposed pressure gradient. As CO_2 pressure increases it behaves as a solvent, extracting light hydrocarbons from the oil, and producing a CO_2-hydrocarbon solution that is fully miscible in oil. This miscible solution is then capable of displacing crude oil without interference from capillary forces.

In addition, the injected carbon dioxide will react with any formation water present to produce a weak acid, i.e. carbonic acid (H_2CO_3).

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
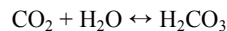
Carbonic acid may then react with reservoir minerals such as carbonates (e.g. calcite, siderite), or silicates (e.g. albite) to produce dissolved ions (Ca^{2+}, Fe^{2+}, HCO_3^- etc.), and secondary minerals such as kaolinite ($Al_2Si_2O_5(OH)_4$):

$$CO_2 + H_2O + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^-$$

$$2CO_2 + 11H_2O + 2NaAlSi_3O_8 \leftrightarrow 2Na^+ + 2HCO_3^- + Al_2Si_2O_5(OH)_4 + 4H_4SiO_4$$
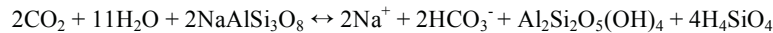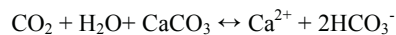
Worden and Smith [2] reviewed geochemical data from eight CO_2-flood experiments, including field and laboratory studies, each of which demonstrated an increase in dissolved ions following the initiation of CO_2 injection. They concluded that in the short term the dissolution of carbonates (calcite, dolomite, and siderite) should be expected, and that silicate dissolution may occur but at a much slower rate than carbonate dissolution.

Of particular interest to the current study is the work of Sayegh et al. [3] who reported the results of laboratory CO_2-flood experiments in which carbonated and non-carbonated brines were circulated through core recovered from Cardium sandstone. The concentration of calcium in the circulating brine increased in those cores flooded with CO_2. In addition, the results of XRD and SEM analysis of pre and post-CO_2 flood core indicated that both calcite and siderite cements had been dissolved.

An investigation of the impact of injected CO_2 on reservoir mineralogy was completed as part of the geochemical monitoring and modeling of the Pembina Cardium CO_2 Monitoring Project southwest of Drayton Valley, Alberta, Canada. The access to core recovered before and after the initiation of CO_2 injection at the site provided a unique opportunity to study the impact of CO_2 injection on reservoir mineralogy at the pilot scale.

2. Site Description

The Pembina oilfield of south central Alberta covers approximately 4000 km^2. The most prolific unit in the field is the Cardium Formation with daily oil production of approximately 10,000 m^3 per day. Primary production began in 1953 with the discovery of the Socony Seaboard Pembina No.1 well located at 100/04-16-048-08W5; water flooding in the field was initiated in late 1950's. Total production from both primary and secondary methods is near the maximum recoverable for the pool (approximately 1.4 billion barrels), and tertiary recovery by CO_2 flood is now being evaluated.

The Pembina Cardium CO_2 Monitoring Project is located approximately fifteen kilometres south west of Drayton Valley, Alberta, and is centred on Penn West's battery located at 09-11-048-09W5 (Fig 1).
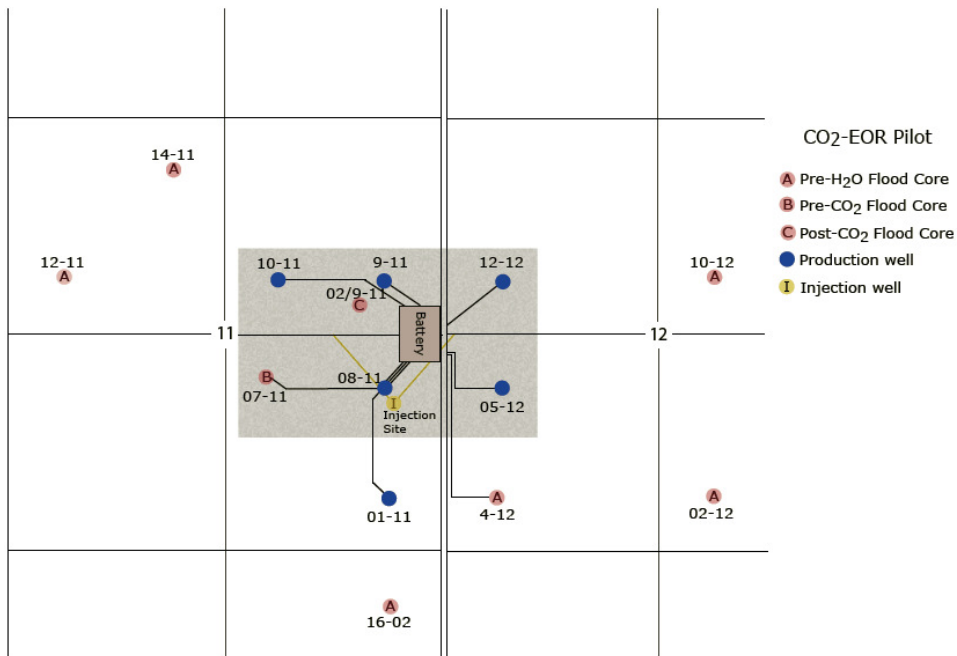
Figure 1: The Pembina Cardium CO$_2$ Monitoring Project located at 09-11-048-09W5.

The pilot consists of two, five-spot injection patterns; i.e. central injection well with four producers. Two of the producing wells (08-11-048-09W5 and 09-11-048-09W5) are shared by each pattern, resulting in two injection wells and six producers in the pilot. Oil production at the site is primarily from the upper two of three stacked sandstone units of the Pembina Cardium Formation [4]. Carbon dioxide injection at the site was initiated in March of 2005 at a rate of approximately 50m^3 per day.

3. Samples

Samples for analysis were collected from archived and fresh core recovered at three distinct time periods: pre-water flood (1955), pre-CO$_2$ flood (2005), and post-CO$_2$ flood (2007). Pre-water flood samples were collected from each of the three sandstone units from wells located at 16-2-048-09W5, 12-11-048-09W5, 14-11-048-09W5, 2-12-048-09W5, and 4-12-048-09W5, and 10-12-048-09W5, pre-CO$_2$ flood samples were collected from the well located at 02/07-11-048-09W5, and post-CO$_2$ flood samples were collected form the well located at 02/09-11-048-09W5.

4. Methods

Samples collected were subdivided at the University of Calgary, i.e. approximately one third of the sample was archived, one-third was used for thin-section preparation, and one third was ground for whole rock geochemistry.

Thin-sections, including: one small format (1" x 2") for standard petrography, and one large format (2" x 3") for electron micro-probe analysis, were prepared by Calgary Rock and Material Services (Calgary, Alberta). Thin-

sections analysis was completed at the University of Calgary using a Nikon Optiphot polarizing microscope, and a Jeol JXA-8200 electron microprobe in both energy dispersion (EDS) and wavelength dispersion (WDS) modes.

Whole rock geochemistry, including: X-Ray Fluorescence (XRF), Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES), X-Ray Diffraction (XRD), total carbonate, and total sulfide analysis, was completed by SGS Laboratories (Lakefield, Ontario).

Linear programming normative analysis (LPNORM, [5]) was completed at the University of Calgary in consultation with Dr. John Bloch of the University of New Mexico, Albuquerque.

5. Results and Discussion

Changes in produced water chemistry following the initiation of CO_2 injection at the site suggest that dissolution of formation minerals in particular carbonates, is occurring [6]. For those wells where CO_2 "breakthrough" has occurred there has been a concomitant increase in dissolved inorganic ions [6]. For example, the results of produced water analysis for the well at 09-11-048-09W5 show a significant increase in Ca^{2+} and Sr^{2+} concentrations above baseline levels (Fig. 2), most likely the result of calcite cement dissolution.

Ca vs Sr Concentration
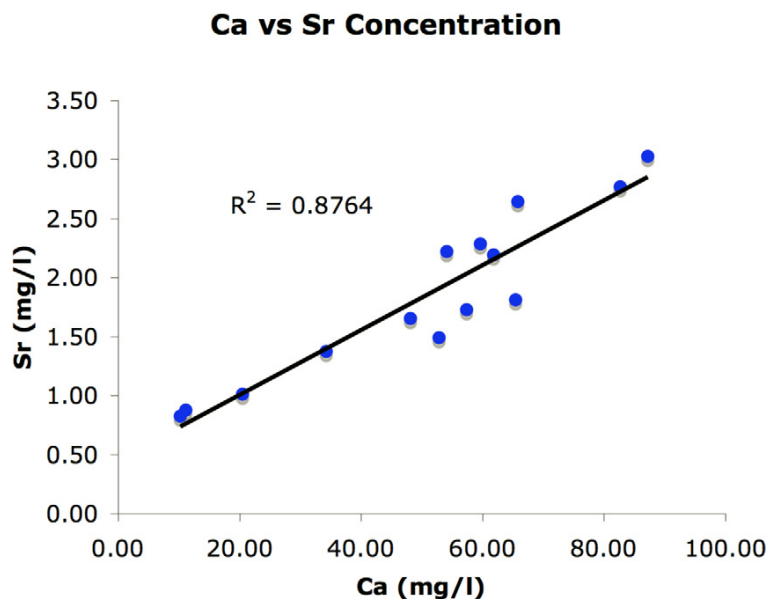
$R^2 = 0.8764$

Figure 2: Changes in produced water chemistry (09-11-048-09W5) following 18 months of CO_2 injection.

In spite of the observed changes in formation water chemistry the results of quantitative mineralogy suggest that samples recovered from each of the three time periods were compositionally similar (Table 1).

Table 1: Mean and Standard Deviation (brackets) of Mineral Composition (wt%) of recovered core.

	Pre-H_2O	Pre-CO_2	Post-CO_2
Quartz	86.5 (1.2)	85.5 (2.1)	89.0 (2.5)
K-spar	0.9 (0.4)	1.5 (0.6)	0.6 (0.6)
Albite	0.7 (0.8)	1.6 (1.1)	2.0 (0.5)
Mus/Ill	3.9 (1.1)	2.6 (1.8)	2.8 (0.8)
Chlorite	0.9 (0.3)	0.9 (0.7)	0.3 (0.3)
Kaolinite	2.2 (0.4)	2.8 (0.7)	2.2 (0.5)
Calcite	0.1 (0.2)	0.1 (0.1)	0.4 (0.6)
Siderite	0.8 (0.9)	1.1 (1.1)	0.5 (0.6)
Pyrite	0.4 (0.5)	0.6 (0.7)	0.3 (0.3)

The sandstone samples analyzed are composed primarily of quartz (up to 90%), with smaller amounts of feldspar (k-feldspar, and albite), muscovite, chlorite, pyrite, and clay (illite and kaolinite) present. Carbonate minerals present include both calcite and siderite.

Since carbonate mineral dissolution occurs more rapidly than silicate mineral dissolution [2], the initial changes in formation water chemistry should reflect the composition of carbonates present. The carbonates were examined in more detail by electron microprobe and the average composition of calcite is presented in Table 2.

Table 2: Average Oxide Composition (wt%) of Carbonate Cements

Oxide	Calcite
CaO	54.3
MgO	0.3
FeO	1.3
SrO	1.6
CO_2	42.3

As expected, the calcite was composed predominantly of calcium carbonate with smaller amounts of strontium, iron and magnesium present. The dissolution of calcite of this composition would account for the near linear increase in both calcium and strontium described in Figure 2.

The lack of any significant mineralogical differences between pre and post-CO_2 core may have more to do with the limitations of sampling than the absence of any water/rock interaction at the site. The well from which the post-CO_2 core was recovered may have been too far from the injector to have been affected. Worden and Smith [2] concluded that dissolution reactions would be more pronounced near the site of CO_2 injection, where the decrease in pH would be the greatest. In addition, the degree to which the three sandstone units are cemented varies considerably with depth. For the current study, samples for both pre and post-CO_2 core analysis were chosen from sections of core most likely to be, or to have been, swept by CO_2 rich fluids, i.e. exhibited significant porosity/permeability and a

minimum amount of cementation. A more complete analysis of the variability of cementation at the site is needed to determine the vertical extent of carbonate cement removal.

In addition to being compositionally similar, an analysis of the images generated by the electron microprobe (BSE) suggests that the sandstone units are "texturally" similar as well (Figures 3 and 4). Framework grains are predominantly sub-angular to sub-rounded quartz and chert, and include smaller amounts of lithic fragments (shale), feldspar (k-feldspar, and albite), mica (muscovite and chlorite), and fluor-apatite. Authigenic pyrite is found as finely disseminated rhombs throughout the formation. Kaolinite appears as fine discrete pore filling books, and is considered to be authigenic. Illite occurs as a major constituent of shale fragments, as well as fine pore bridging strands. Irregular pores are cemented to varying degrees by silica and/or carbonate minerals (calcite and siderite).
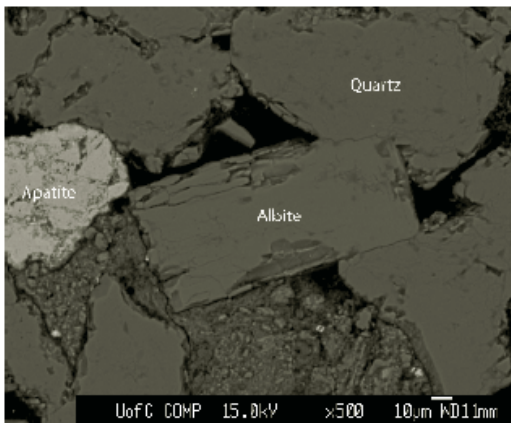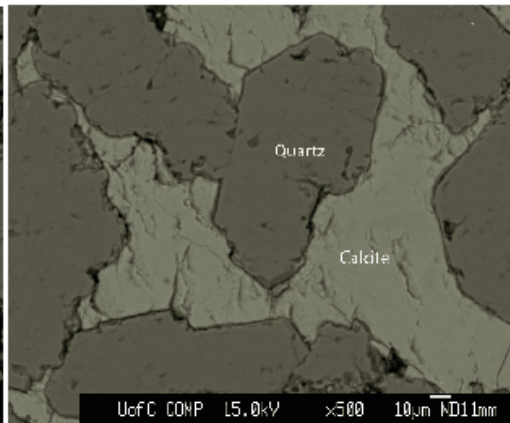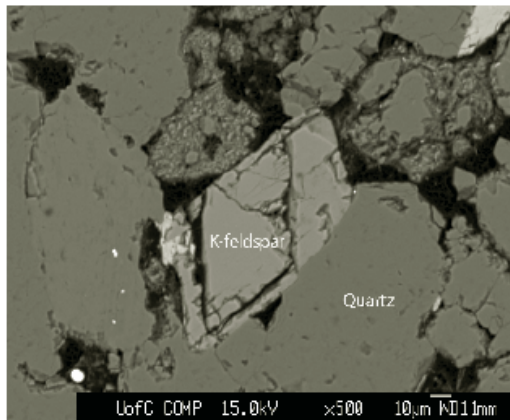

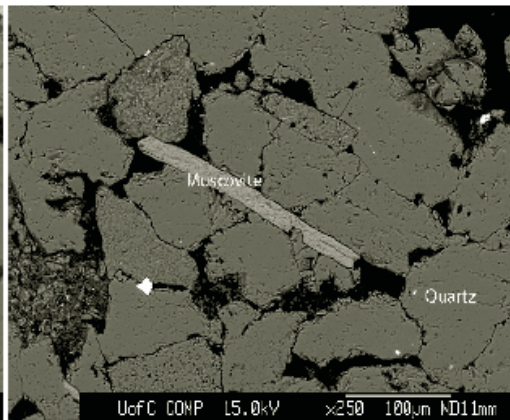*Figure 3. Photomicrographs of Sandstone (BSE). Figures 3a and b Pre-H_2O Flood (14-11-048-09W5); Figures 3c Pre-H_2O Flood (12-11-048-09W5); and Figure 3d Post-CO_2 Flood (02/09-11-048-09W5).*

Dissolution features, including the degradation of detrital grains (quartz and feldspar), the partial and/or complete removal of carbonate cements, and the presence of residual clays, are found in samples from each of the three time periods (Fig. 4). The dissolution of quartz and feldspar (albite and k-feldspar) may have initiated much earlier in the formation's diagenetic history, possibly during an episode of carbonate cementation [7]. The subsequent removal or partial removal of carbonate cements appears to predate both water-flood and CO_2 injection at the site and may be related to the "charging" of the Cardium with meteoric water, again much earlier in its diagenetic history. Machemer and Hutcheon [8] suggested at least two separate dissolution events occurred during formation diagenesis, one prior to and one subsequent to carbonate precipitation.
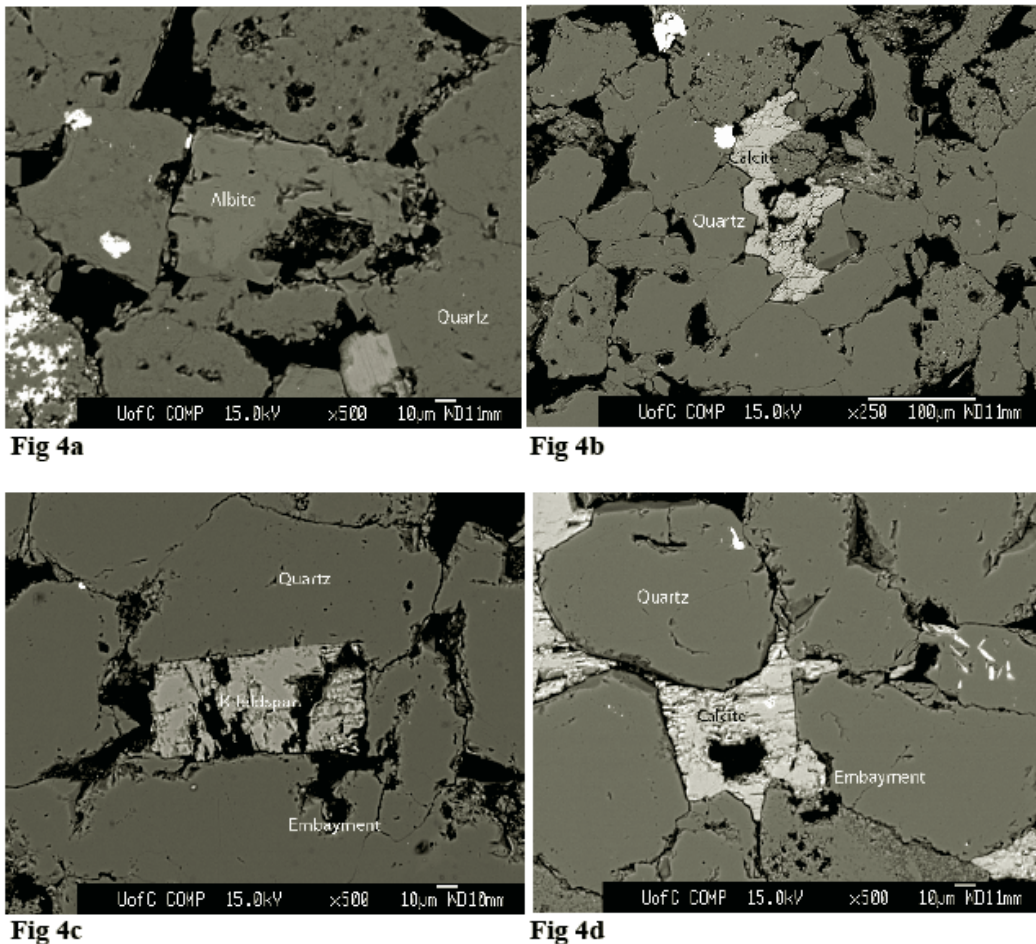

Figure 4. Photomicrographs of Cardium Sandstone (BSE) showing dissolution of feldspars and calcite. Figures 4a Pre-H_2O Flood (14-11-048-09W5); Figure 4b Pre-CO_2 Flood (02/07-11-048-09W5); Figures 4c and d Post-CO_2 Flood (02/09-11-048-09W5).

Mineral trapping (i.e. the interaction of carbonic acid, dissolved ions, basic aluminosilicate minerals, and the precipitation of new solid mineral phases that incorporate carbonate in their structure) has been described as a possible means of sequestering anthropogenic CO_2 in saline aquifers and mature oil fields, although these types of reactions could take 100s of years to complete [9]. In the current study, no new carbonate mineral phases were found in samples from the post-CO_2 flood core.

6. Conclusions

Changes in formation water chemistry following the initiation of CO_2 injection suggests mineral dissolution by carbonic acid is occurring at the site. The absence of a significant difference in quantitative mineralogy between pre and post-CO_2 samples may be more indicative of the difficulty of obtaining a representative sample set and/or sample location, than of a lack of water/rock interaction. Attributing dissolution features in the post-CO_2 flood core to the interaction of minerals and carbonic acid appears to be complicated by the Cardium geologic history.

7. Acknowledgements

8. References

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