Fuel 235 (2019) 1019–1038

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

# An experimental study for carbonate reservoirs on the impact of $CO_2$-EOR on petrophysics and oil recovery

Mohamed Khather[a,*], Ali Saeedi[a], Matthew B. Myers[b], Michael Verrall[c]

[a] *Department of Petroleum Engineering, Curtin University, Curtin Petroleum, 26 Dick Perry Avenue, Kensington, WA 6151, Australia*
[b] *CSIRO Energy, 26 Dick Perry Avenue, Kensington, WA 6151, Australia*
[c] *CSIRO – Mineral Resources, 26 Dick Perry Avenue Kensington, WA 6151, Australia*

ARTICLE INFO

*Keywords:*
$CO_2$-EOR
Carbonate rocks
Fluid-rock interactions
Asphaltene precipitation
Core-flooding

ABSTRACT

The injection of $CO_2$ into deep geological structures for the purpose of $CO_2$ storage and/or enhanced oil recovery ($CO_2$-EOR) may trigger a series of consecutive chemical reactions (e.g. mineral dissolution and asphaltene precipitation) and physical effects (e.g. mechanical compaction and permeability variation). These reactions can significantly impact carbonate reservoirs, due to the presence of highly reactive minerals (e.g. dolomite and calcite), as well as the solvent/precipitation effects of supercritical $CO_2$ on complex crude oil mixtures potentially containing heavy fractions such as wax and asphaltene. A core flooding study has been carried out to evaluate changes in the petrophysical properties of a number of heterogeneous carbonate samples (i.e. limestone and dolostone) after undergoing EOR activities under in situ reservoir conditions. In this study, a number of different measurement techniques are conducted to obtain a comprehensive view of the role that mineral dissolution, mechanical compaction and asphaltene precipitation plays during $CO_2$-EOR in carbonate reservoirs.

The results show that $CO_2$ injection results in higher oil recovery in all the samples evaluated as part of this study. However, early water breakthrough was observed for most samples suggesting a high degree of heterogeneity in the carbonate core samples. In all samples, a decrease in permeability was observed presumably due to asphaltene/resin precipitation and mineral dissolution/precipitation. Chemical analyses of the produced crude oil and scanning electron microscopy images confirmed the precipitation of asphaltene and mineral dissolution that caused permeability reduction. Furthermore, as $CO_2$ concentration in the oil/$CO_2$ mixture increased more asphaltene/resin precipitation was observed. More asphaltene precipitation was observed in higher permeability and more vuggy core samples than in those with intermediate or low permeabilities. This observation can be possibly attributed to relaxation of fluids as they enter the relatively large vugs (with large surface area) from the pore-throats resulting in the flocculation and/or precipitation of asphaltenes. A slight reduction in porosity and pore size was observed in most samples presumably caused by a combination of mineral/asphaltene precipitation and physical compaction.

Overall, the results obtained in this study further highlight the complexities associated with the application of $CO_2$-EOR in underground oil reservoirs where both the crude oil and the rock formation may be expected to interact with the injected fluids. Further research into the underling mechanisms is required.

## 1. Introduction

Carbon dioxide injection or storage in mature or partially depleted oil reservoirs has the major benefit of improved oil recovery providing an offset to the cost of storing $CO_2$. Moreover, it is environmentally beneficial since large amounts of $CO_2$ could be sequestered away safely. Carbonate reservoirs account for about fifty percent of the oil and gas production around the world [26]. However, $CO_2$ storage and EOR in carbonate reservoirs is more challenging due to being typically far more heterogeneous compared to sandstone reservoirs. In addition to the heterogeneous and complex structure of carbonate reservoirs, injected $CO_2$ particularly when it dissolves in brine to create carbonic acid reacts with the calcite and dolomite that comprise carbonate rock formations. Hence, the behaviour of the underground fluids-rock system is expected to be more complex when $CO_2$ is injected into a carbonate formation compared to a predominantly sandstone formation.

---

* Corresponding author.
*E-mail addresses:* m.khather@postgrad.curtin.edu.au (M. Khather), Ali.Saeedi@curtin.edu.au (A. Saeedi), Matt.Myers@csiro.au (M.B. Myers), Michael.Verrall@csiro.au (M. Verrall).

https://doi.org/10.1016/j.fuel.2018.08.094
Received 2 November 2017; Received in revised form 28 March 2018; Accepted 22 August 2018

Furthermore, apart from their macro-scale heterogeneous nature, carbonate rocks tend to also have a more complex pore network system than their sandstone counterparts [20]. Carbonate reservoir rocks, in particular, have a high degree of heterogeneity in terms of their porosity and permeability distributions; tight, vuggy and fractured carbonates are quite common [2]. Limestone reservoirs, in particular, contain a high ratio of calcite ($CaCO_3$). On the other hand, dolomite rocks contain high amounts of dolomite ($CaMg(CO_3)_2$) (greater than50 wt%), calcite ($CaCO_3$) and anhydrite ($CaSO_4$), along with small amounts of non-carbonate phases [50]. Carbonate rocks typically have high surface reaction rates in the presence of $CO_2$ and formation brine which often leads to highly non-uniform dissolution [10].

The injection of carbon dioxide into oil reservoirs is an established EOR method. The process of $CO_2$-EOR can be classified into two major types: $CO_2$ miscible displacement and $CO_2$ immiscible displacement. The performance of the displacement of crude oil by $CO_2$ is influenced by a number of factors including reservoir pressure, temperature, crude oil composition and the phase behaviour of the $CO_2$/oil mixture [12,22]. However, one of the major problems associated with $CO_2$ flooding during EOR processes is asphaltene deposition. Furthermore, during $CO_2$ injection into carbonate rocks (limestone or dolomite), a number of physical and chemical processes will take place. This leads to changes in the petrophysical properties of the host reservoir rock and multiphase behavior in the porous media system. These processes may include the dissolution and/or precipitation of minerals, mechanical compaction due to overburden pressure and asphaltene precipitation. These can alter the pore size distribution and pore network of the rock and in many formations several of these process may be active simultaneously.

### *1.1. Dissolution and precipitation processes during $CO_2$ injection in carbonate rocks*

In general, the main minerals present in carbonate rocks are calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and anhydrite ($CaSO_4$). All of these minerals can readily dissolved by carbonic acid ($H_2CO_3$). The dissolution of $CO_2$ into formation water (or brine) under reservoir pressure/temperature conditions and the subsequent formation of carbonic acid are the main causes of the in situ geochemical reactions. The dissolution of $CO_2$ in the formation brine results in the following reactions [37]:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3,\ \text{and/or} \tag{1}$$

$$H_2O \leftrightarrow OH^- + H^+ \tag{2}$$

The chemical reactions of supercritical $CO_2$ (SC-$CO_2$) with brine and the formation rock could lead to changes in reservoir permeability, pore size distribution and effective porosity. This would influence the storage capacity, injectivity and more generally the multiphase flow characteristics of the formation. The continuous dissolution of $CO_2$ in the formation brine during injection (initially at thermodynamic equilibrium with the rock-forming minerals) leads to a decrease in pH [25]. The main consequence of the decreased pH is the dissolution of carbonate minerals (calcite and dolomite) and an increase in the hydrogencarbonate concentraton [37]. Limestone rocks contain mainly calcium in the form of calcite ($CaCO_3$) and a lower concentration of magnesium (Mg) in the form of magnesium carbonate ($MgCO_3$). Therefore, limestone formations are expected to undergo significant changes to their petrophysical properties due to $CO_2$ injection. Such changes not only occur due to the dissolution of rock minerals, but are also caused by the transportation and possible later precipitation of generated chemicals species in the pore space of the rock [18]. The reactions between calcite, $CO_2$ and formation brine can be defined as follows [37]:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{3}$$

$$H^+ + CaCO_3 \leftrightarrow Ca^{2+} + HCO_3^-\ \text{and/or} \tag{4}$$

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3 \tag{5}$$

Dolostone is another type of carbonate rock which contains high proportions of dolomite or calcium magnesium carbonate ($CaMg(CO_3)_2$). In addition, anhydrite ($CaSO_4$) and calcite ($CaCO_3$) are also present in many dolomite rocks at lower concentrations. The reactions between these minerals, $CO_2$ and formation brine can be defined as follows [37]:

$$2H^+ + CaMg(CO_3)_2 \leftrightarrow Mg^{2+} + Ca^{2+} + 2HCO_3^- \tag{6}$$

$$CaMg(CO_3)_2 + 2H_2CO_3 \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3 \tag{7}$$

$$CaCO_3 + CO_2 + H2O \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{8}$$

$$H^+ + CaCO_3 \leftrightarrow Ca^{2+} + HCO_3^- \tag{9}$$

$$CaCO_3 + H2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3\ \text{and/or} \tag{10}$$

$$CaSO_4 + CO_2 + H_2O \leftrightarrow CaCO_3 + H_2SO_4 \tag{11}$$

The rates of these reaction can strongly impact the degree of alterations to the petrophysical properties of the carbonate rocks. With carbonic acid, the reaction rate constant for calcite is higher than that of dolomite and much higher than the reaction rate constant for quartz [28,43,51]. The reaction of $CO_2$ saturated brine with dolomite and limestone often yields two distinct dissolution fronts. Aside from the differences in the reaction rates, this can be explained by the evolution of a homogeneous dissolution front for low permeability dolomite and an unstable dissolution front for heterogeneous vuggy limestone under the same conditions [40]. Therefore, when a formation contains a combination of calcite (or vuggy limestone) and dolomite, carbonic acid tends to react with calcite at a much faster rate [28]. Consequently, the effect of dissolution and other possible subsequent mechanisms induced by the dissolution (e.g. precipitation, mechanical compaction, etc.) on dolomite rocks is expected to be less than for calcite (or limestone) rocks.

Although the dissolution of rock minerals may be expected to increase the rock permeability, any later precipitation of minerals from solution may actually lead to a reduction in rock permeability and effective porosity [17]. Mineral precipitation and subsequent reduction in permeability have been observed during core-flood experiments by a number of researchers [17,31]. The mineral precipitation that occurred during the core-flood experiments is unsurprisingly correlated with an increase in the pressure drop across the rock samples during the flooding procedure; a larger pressure drop and reduction in permeability is consistent with a higher level of mineral precipitation blocking the pore geometry within the rock [31]. It has been suggested that the attractive forces between transported particles and the pore surfaces within the rock may increase the precipitation rate [18]. Furthermore, it has been suggested in the literature that chemical reactions and subsequent changes in the petrophysical properties of a rock sample strongly depend on the degree of heterogeneity and the distribution of minerals [31]. For laboratory core flooding experiments, flow directions and injection rate can influence the extent of precipitation and how the rock properties might change along the length of the rock sample [18]. Fig. 1 illustrates the process of dissolution and subsequent deposition of carbonate minerals in a carbonate rock subjected to $CO_2$/brine injection. The permeability decline solely to precipitation of dissolved calcite in the pore space can be as high as 90%; temperature, flow rate and the duration of the injection period can also affect the permeability decline [27].

During a core flooding experiment, at the injection point where $CO_2$-saturated brine first comes in contact with the rock, the brine initially establish flow paths through higher permeability channels [48]. This behaviour is more pronounced in highly heterogeneous media such as some of the samples tested here as part of this study. If this is the case, the presence of reactive carbonated brine would begin to react with the rock minerals within these established flow channels.