Yen Adams Sokama-Neuyam*, Jann Rune Ursin*

EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF CO$_2$ INJECTIVITY

1. INTRODUCTION

Climate change could become the single biggest environmental and humanitarian crisis unless drastic measures are put in place to halt the increasing concentrations of greenhouse gases in the atmosphere. Carbon Capture and Storage (CCS) is seen as a promising technique that could reduce net carbon emission to the environment. The feasibility of CCS depends on the presence of adequate storage capacity and availability of a threshold well injectivity.

Desaturation of the reservoir rock and salt precipitation near the wellbore have been identified as permeability and injectivity impairment mechanisms [1]. During injection of dry supercritical CO$_2$ into brine-saturated formation, water is removed through advection or evaporation [2]. Advection of the aqueous phase decreases as brine saturation approaches immobility. At immobile brine saturation, evaporation becomes the dominant mechanism for brine desaturation. When the brine concentration exceed supercritical concentration, salt is precipitated into the porous medium. Salt precipitation is high around the injection well vicinity because fluxes, concentrations and saturation gradients are highest [3]. Even minimal salt deposition near the injection zone could impose significant CO$_2$ injectivity impairment [4].

Researchers have reported overwhelming evidence of permeability and injectivity impairment induced by salt precipitation. Bacci, et al. [5] reported 3–5% porosity reduction and permeability impairment between 13% and 75% from laboratory experiments. Results from analytical and numerical modeling studies reveals various levels of impairment of petrophysical properties of the reservoir rocks [6, 7].

Some mitigation measures to reduce the impact of salt precipitation on CO$_2$ injectivity have been suggested. Numerical studies predict that horizontal wells and hydraulic fracturing in the near well region could reduce the impact of precipitated minerals [8].
Jasinski, et al. [9] reported that halite scaling in production wells could be reduced by dilution of the produced water with low salinity water both downhole and in the production system. They used treated sea water as the diluent. Other numerical modeling experiments suggest that injecting a slug of fresh water prior to CO2 injection could reduce salt precipitation and permeability loss near the injection well [10]. The detrimental environmental impact of hydraulic fracturing coupled with the high cost of drilling horizontal wells means fresh water or low salinity water injection could be a viable alternative for reducing the impact of salt precipitation on permeability and therefore CO2 injectivity in the wellbore vicinity.

The challenge imposed by low salinity water (LSW) injection into sandstone rocks is fines migration [11]. Below certain critical salinity, LSW could interact chemically with loosely attached fine particles on the pore walls. It has also been reported that, at relatively high injection rates, turbulence from the injected fluid could detach formation fines from the pore walls of sandstone rocks [12]. Transport of the detached colloidal particles by the injected fluid could clog pore channels and obstruct fluid flow, reducing injectivity as a result [13]. Therefore, brine salinity and CO2 injection rate could be optimized for efficient mitigation of salt precipitation.

Our goal is to identify and study the parameters that govern injectivity improvement induced by alternate injection of CO2 and low salinity brine. We describe the experimental process and link the observations with theoretical modeling. The results are then presented and discussed.

2. EXPERIMENTS

Materials

Liquefied CO2, purity percentage of 99.7 and synthetic formation water (FW) with brine salinity of about 105.51 g/l are the main fluids in most of the experiments (Tab. 1). The diluent LSW were prepared by diluting specific portions of FW with deionized water (Tab. 2). The porous media is outcrop sandstone core samples, 20 cm long and 3.81 cm in diameter. Table 3 summarizes the characteristics of the sandstone core samples.

<table>
<thead>
<tr>
<th>Mineral composition in formation water [14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral</td>
</tr>
<tr>
<td>NaCl</td>
</tr>
<tr>
<td>Na2SO4</td>
</tr>
<tr>
<td>KCl</td>
</tr>
<tr>
<td>MgCl2·6H2O</td>
</tr>
<tr>
<td>CaCl2·2H2O</td>
</tr>
<tr>
<td>SrCl2·6H2O</td>
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</table>
Table 2
Diluent brine salinity

<table>
<thead>
<tr>
<th>LSW</th>
<th>% FW</th>
<th>Salinity (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSW1</td>
<td>80</td>
<td>84.408</td>
</tr>
<tr>
<td>LSW2</td>
<td>50</td>
<td>52.755</td>
</tr>
<tr>
<td>LSW3</td>
<td>20</td>
<td>21.102</td>
</tr>
<tr>
<td>LSW4</td>
<td>10</td>
<td>10.551</td>
</tr>
</tbody>
</table>

Table 3
Characteristics of sandstone core samples

<table>
<thead>
<tr>
<th>Rock Mineral</th>
<th>CO₂ (l) Perm (mD)</th>
<th>Porosity (%)</th>
<th>Pore Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berea</td>
<td>1484 ± 6.5</td>
<td>20.48</td>
<td>46.71</td>
</tr>
<tr>
<td>Kirby</td>
<td>372 ± 3.4</td>
<td>20.96</td>
<td>47.80</td>
</tr>
<tr>
<td>Bandera</td>
<td>139 ± 5.6</td>
<td>16.97</td>
<td>38.80</td>
</tr>
</tbody>
</table>

Experimental setup

Laboratory core flooding experiments were performed in a CO₂ flow rig (Fig. 1).

![Fig. 1. Schematic of the experimental setup that was used in the study](image)

The Quizix pump deliver brine through the connected piston cell into the core. The regulator enables the ISCO CO₂ pump to receive liquid CO₂ at the set pressure. The 36 cm long core holder is positioned in the oven at constant temperature. A long coiled tubing at the injection end of the core holder delays fluid flow in order for injected fluid to attain thermal equilibrium in the oven. A sensitive differential pressure transducer...
measures pressure drop across the core. At the outlet, two backpressure regulators regulate the injection pressure of brine and CO₂. Piston cells, connected to the backpressure gauges collect effluent CO₂ and brine.

**Experimental procedure**

**The impact of salt precipitation:** A dry core sample was prepared and mounted into the core holder. The core was flooded with liquid CO₂ (26°C, 80 bar) at constant rate of 1ml/min to complete saturation. Initial liquid CO₂ pressure drop across the core sample was measured. The core was then dried and vacuum saturated with brine, prepared and flooded with about 20 Pore Volumes (PV) of the same brine at 1ml/min to attain complete brine saturation. The saturated core was vaporized with supercritical CO₂ at constant injection to complete dryness which is indicated by a constant pressure drop across the core. The impaired core sample was further dried in an oven at 60°C for about 12 hours so that the properties of the core can be compared to its initial characteristics. Liquid CO₂ pressure drop across the core was then measured to evaluate the change in CO₂ injectivity induced by mineral precipitation. Injectivity impairment induced by mineral deposition can be estimated from the two pressure drop measurements.

Fluid injectivity, \( I \) is defined as the ratio of volumetric injection rate, \( q \) to the pressure drop, \( \Delta p \).

\[
I = \frac{q}{\Delta p}
\]

Relative Injectivity Change (RIC) after mineral precipitation was estimated from:

\[
RIC = 1 - \left( \frac{\Delta P_i}{\Delta P_f} \right)
\]

Where \( \Delta P_i \) is the liquid CO₂ pressure drop across the clean core and \( \Delta P_f \) is the pressure drop measured across the core after it was impaired by precipitated minerals.

**Mitigation technique:** The clean core sample was vacuum saturated with FW and aged for 14 days. The aged core was then prepared and flooded with about 50 PV supercritical CO₂ to vaporize brine and possibly precipitate salts into the pore spaces. Initial liquid CO₂ pressure drop across the impaired core was measured. The core was then flushed with about 30 PV of the diluent LSW brine at 0.05 ml/min in attempt to dissolve and washout precipitated minerals. The LSW-washed core was then vaporized with supercritical CO₂ to dryness. When all remaining brine was vaporized, liquid CO₂ pressure drop across the treated core was measured.

RIC after LSW treatment was calculated from:

\[
RIC_{LSW} = \left( \frac{\Delta P_{b}}{\Delta P_{a}} \right) - 1 \quad \text{for} \quad q_a = q_b
\]
Where $\Delta P_b$ is the liquid CO$_2$ pressure drop across the core immediately after impairment by precipitated minerals and $\Delta P_a$ is the liquid CO$_2$ pressure drop measured across the core after the impairment was treated by alternate CO$_2$ and LSW injection. CO$_2$ injectivity is improved if $\text{RIC}_{\text{LSW}} > 0$.

3. ANALYTICAL MODELING

Advection of the aqueous phase by supercritical CO$_2$ leaves immobile brine behind the two-phase front. The immobile brine is vaporized by injected CO$_2$, creating a dry-out zone near the injection end where salts are precipitated into the pores [2]. In this study, we assume that salt precipitation commences after all mobile brine is displaced out of the core. Salt is precipitated mainly in the dry-out region after vaporization of brine behind the two-phase front. The dry-out region extends further into the core as more brine is vaporized, creating a salt precipitation front around the injection vicinity.

Pruess [10] developed analytical model to estimate solid salt saturation in the dry-out zone from fractional flow theory and mass balance. We have adapted the model to estimate precipitated salt saturation in the dry-out zone. To satisfy conditions for fractional flow theory, the applicability of the model is restricted to constant CO$_2$ injection rate into 1-D linear geometry in a homogeneous porous medium with uniform initial conditions. The effect of capillary pressure was neglected.

![Fig. 2. Schematic of the saturation profile of gas-brine advection and vaporization process](image)

Figure 2 shows the saturation profile that characterize advection and vaporization of brine by supercritical CO$_2$. The injection end is at $x = 0$, the extent of dry-out and mineral precipitation is denoted by $x_d$, the two-phase front is at $x_f$ and $S_{g,d}$ denotes CO$_2$ saturation at the dry-out front. The objective is to estimate the solid saturation $S_s$, the fraction of pore space in the dry-out region occupied by solid salt and then use this parameter to estimate the impact on injectivity.

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The solid saturation was estimated from mass balance between injected CO₂ and displaced brine given by:

\[ S_s = (1 - S_{g,d}) \frac{\rho_{aq} X_s}{\rho_s} \]  

(4)

where:
- \( S_{g,d} \) – average gas phase saturation behind the dry-out front,
- \( \rho_{aq} \) – the aqueous phase density,
- \( \rho_s \) – density of the solid phase,
- \( X_s \) – the mass fraction of salt dissolved in aqueous phase.

\( S_{g,d} \) is the only unknown parameter in the equation. From the Buckley–Leverette solution, it can be shown that [15]:

\[ \frac{1}{\bar{S}_{g,d}} = \frac{1}{S_{g,d}} + \frac{1-f_d}{(df/dS)_{S_{g,d}}} \]  

(5)

where \( f_a \) is fractional flow of the gas phase at \( S_{g,d} \) and \((df/dS)_{S_{g,d}}\) is the derivative of fractional flow of gas at the dry-out front.

The gas phase saturation behind the dry-out zone, \( S_{g,d} \) was estimated by iterating the mass balance and fractional flow equations:

\[ \left(1-S_{g,d}\right)(df/dS)_{S_{g,d}} + f_d - 1 = F \]  

(6)

The coefficient \( F \) is given by:

\[ F = \frac{\rho_g Y_g}{\rho_{aq} (1-X_s - X_{CO2})} \]  

(7)

where:
- \( \rho_g \) – gas density,
- \( Y_g \) – the equilibrium mass fraction of water in the gas phase,
- \( X_{CO2} \) – the mass fraction of CO₂ dissolved in the aqueous phase.

Brooks–Corey type CO₂-brine relative permeability curves were used this work [16]. Brine and CO₂ relative permeability equations were defined as:

\[ K_{r,w} = \left( S_{w}^* \right)^{N_w} \]  

(8)

\[ K_{r,CO2} = K_{r,CO2} \left( S_{wi} \left(1-S_w^* \right)^2 \left[1-\left( S_w^* \right)^{N_{CO2}} \right] \right) \]  

(9)
The normalized saturation $S_w^*$ given by:

$$S_w^* = \frac{S_w - S_{wi}}{1 - S_{wi}}$$  \hspace{1cm} (10)

where:

- $K_{r,ws}$, $K_{r,CO2}$ - relative permeability to brine and CO$_2$, respectively,
- $K_{r,CO2}(S_{wi})$ - denotes the CO$_2$ permeability at irreducible brine saturation $S_{wi}$,
- $N_w$, $N_{CO2}$ - fitting parameters, the Corey exponents.

Krevor et al. [16] estimated $N_w = 6$ and $N_{CO2} = 5$ for Berea sandstone. In this work, $K_{r,CO2}(S_{wi}) = 0.95$ was assumed and $S_{wi} = 0.3$.

Bolton et al. [17] proposed a model for quantifying porosity reduction due to salt precipitation. The model is given here as:

$$\phi = \phi_0 (1 - S_s)$$  \hspace{1cm} (11)

where $\phi$ is porosity of the impaired porous medium and $\phi_0$ is porosity of the clean porous medium. Based on grain size distribution, the permeability of a porous medium can be estimated from the Kozeny–Carman grain model [18]. The equation is given by:

$$k = R_i^2 \left( \frac{\phi^3}{45 (1 - \phi)^2} \right)$$  \hspace{1cm} (12)

where $R_i$ is the initial local spherical radius in close packed structure.

The ratio of the permeability of impaired porous medium $k$ to the permeability of the clean porous medium $k_0$ can be derived from Equation (12) as:

$$\frac{k}{k_0} = \left( \frac{\phi}{\phi_0} \right)^2 \left( \frac{1 - \phi_0}{1 - \phi} \right)^2$$  \hspace{1cm} (13)

Equation (11) and (12) can be combined to give:

$$\frac{k}{k_0} = \frac{(1 - S_s)^3}{1 + (\phi_0 S_s / (1 - \phi_0))^2}$$  \hspace{1cm} (14)

For constant injection rates and fluid properties, it can be shown from Darcy’s equation that:

$$\frac{q}{\Delta P} = Ck$$  \hspace{1cm} (15)

where $C = \frac{A}{\mu L}$ is assumed to be constant.
Substituting Equation (15) into (1), RIC can be modeled by:

\[ \text{RIC} = 1 - \frac{I_f}{I_i} = 1 - \left( \frac{\Delta P_i}{\Delta P_f} \right) = \left( 1 - \frac{k}{k_0} \right) \]  

(16)

The computation process is straightforward. The solid saturation \( S_s \) is estimated from Equation (4) after \( \bar{S}_{g,d} \) is calculated. The permeability ratio \( k/k_0 \) is then computed from Equation (14) followed by estimation of the relative injectivity change, RIC from Equation (16).

**Simulation**

First, the FW saturated core is flooded with supercritical CO\(_2\) to dryness. The initial RIC is computed. The core is then saturated with LSW and final RIC determined. The difference between the initial and final RIC values is a measure of the impact of precipitated salts on CO\(_2\) injectivity. Assuming the diluent LSW dissolves all precipitates in the core, subsequent injection of CO\(_2\) into the LSW-filled core will precipitate the mineral contents of LSW into the core. However, LSW might not dissolve all precipitated minerals, the remaining solid saturation will be more than the original solid content of LSW. Therefore, the injectivity improvement can be estimated from the difference between the initial and final RIC. Table 4 shows some generic data and conditions used in the calculations.

**Table 4**

Some data used in the modeling process

<table>
<thead>
<tr>
<th>Modeling Data</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \rho_s )</td>
<td>1027 kg/m(^3)</td>
</tr>
<tr>
<td></td>
<td>( \rho_g )</td>
<td>640 kg/m(^3)</td>
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<tr>
<td></td>
<td>( \rho_{ag} )</td>
<td>1180 kg/m(^3)</td>
</tr>
<tr>
<td></td>
<td>( Y_g )</td>
<td>( 2.24 \times 10^{-3} )</td>
</tr>
<tr>
<td></td>
<td>( X_{CO2} )</td>
<td>( 1.57 \times 10^{-2} )</td>
</tr>
<tr>
<td></td>
<td>( X_s )</td>
<td>0.106</td>
</tr>
<tr>
<td></td>
<td>( T )</td>
<td>50°C</td>
</tr>
<tr>
<td></td>
<td>( P )</td>
<td>80 bar</td>
</tr>
</tbody>
</table>
4. RESULTS AND DISCUSSION

Impact of mineral precipitation on CO$_2$ injectivity

Regardless of the initial saturating brine salinity, salt precipitation could impair CO$_2$ injectivity (Fig. 3). When brine salinity was reduced by almost half (FW to LSW1), injectivity impairment declined only by 9 percentage points (36.3% to 27.3%). This confirms the reports that minimum precipitation around the inlet could induce marginal injectivity impairment [4, 7]. The impact of mineral precipitation on injectivity is therefore not linearly dependent on the initial saturating brine salinity. Figure 3 also show the simulation results at the experimental conditions.

At high brine salinity, the experimental results agree with the simulation results but the deviation become more significant as brine salinity declines. The model predicted 3.7% injectivity impairment for LSW2 but 58.8% impairment was observed in the experiments. We suggest that this deviation could be attributed to interaction between the saturating brine and the Berea core.

At very low brine salinity, LSW can inspire detachment and transport of colloidal particles, from the pore walls in sandstone [11, 13, 19]. Probably, mineral precipitation effect was very low as predicted by the model, but detached fine particles bridged the pore channels and reduced CO$_2$ injectivity. From the experimental results, decrease in initial brine salinity reduces the effect of salt precipitation on injectivity of CO$_2$. However, beyond certain brine salinity, the injected brine interacts with the porous medium, probably releasing colloids into the flowing stream, thereby further compounding injectivity loss.

Fig. 3. Effect of mineral precipitation on CO$_2$ injectivity. CO$_2$ was injected at 5 ml/min into saturated Berea Core
Injectivity impairment mitigation

We attempted to reduce the effect of precipitated minerals on CO\textsubscript{2} injectivity through alternate injection of CO\textsubscript{2} and LSW. LSW brine salinity, supercritical CO\textsubscript{2} injection rate and initial core permeability were optimized to study their impact on injectivity recovery.

**Brine salinity:** The relationship between injectivity change and diluent brine salinity is presented in Figure 4. In general, CO\textsubscript{2} injectivity improved from 8.66\% to 31.62\% when the diluent brine salinity was decreased stepwise from FW to LSW4. Below LSW3, no injectivity improvement was observed.

The solubility of precipitated minerals in the diluent LSW increased when brine salinity was reduced, because dilute solutions have more free water molecules to interact with precipitated minerals. At high diluent brine salinity, results from the model agrees well with the simulation data (Fig. 4). However, at very low brine salinity, the experimental data deviates significantly from the simulation results probably because the diluent interacts chemically with the rock matrix. Interaction between the porous medium and the diluent could induce clay swelling and colloidal transport, which have the tendency impair CO\textsubscript{2} injectivity. LSW4 diluent did not improve injectivity, probably because fines migration and clay swelling overshadowed injectivity improvement. Therefore, decrease in diluent salinity dissolves more precipitates and improves injectivity. However, below brine salinity of about 21.10\% g/l, injectivity did not improve because the diluent interacts with the porous medium chemically.
Supercritical CO$_2$ injection rate: Figure 5 show injectivity changes observed at various CO$_2$ injection rates. We found practically no injectivity change (31.62% to 30.05%) when CO$_2$ injection rate was increased from 1 ml/min to 5 ml/min. However, by raising injection rate from 10 ml/min to 25 ml/min, injectivity reduced by almost 40 percentage points.

![Figure 5](image_url)

**Fig. 5.** Effect of CO$_2$ injection rate on injectivity changes induced by alternate CO$_2$-brine injection in Berea core

High supercritical CO$_2$ injection rate might only speed up the advection of brine. However, alternating CO$_2$ and LSW injection mechanism enhance injectivity when the diluent dissolve precipitated minerals. The rate at which brine is displaced out of the porous medium, could affect precipitation rate, but this might not necessarily improve dissolution of precipitated minerals. Above CO$_2$ injection rate of about 5 ml/min, injectivity was further impaired probably because of heterogeneous distribution of precipitated minerals in the pores. At high injection rates, advection becomes predominant. Vaporization of brine is rapid, leading to heterogeneous distribution of precipitated salts which does not favour dissolution.

Initial core permeability: Three sandstone core samples with varying permeability but similar porosity were studied. The core was initially saturated with LSW2 and CO$_2$ injection rate of 5 ml/min was maintained throughout the experiments. CO$_2$ injectivity improved for high permeability sandstone cores (Fig. 6). Berea core sample (1484 mD) recorded the highest injectivity improvement (30.05%).

High permeability sandstone cores have open pore channels for fluid flow. The large pore channels favor dissolution of precipitates. In low permeability sandstone cores, the narrow pore throats, delay brine breakthrough and favor precipitation of minerals.
In addition, given the same precipitation rate, effect of precipitates on injectivity is expected to be higher in low permeable rocks because the narrow pore channels could be plugged. This could be a possible explanation of the observed trend.

![Fig. 6. Effect of initial core permeability](image)

5. CONCLUSIONS

The presence of adequate CO$_2$ injectivity is a prerequisite for CCS projects, and CO$_2$ injectivity has significant impact on the economics of CO$_2$ EOR projects. Mineral precipitation near injection wells impair CO$_2$ injectivity. CO$_2$ alternating LSW injection could reduce the impact of precipitated minerals on CO$_2$ injectivity.

The major challenge of this technique is the selection of optimal brine salinity and CO$_2$ injection rate to minimize formation damage. We have conducted laboratory experiments to investigate the diluent brine salinity and CO$_2$ injection rate required to reduce the impact of salt precipitation. The following findings standout:

- Alternate injection of CO$_2$ and LSW could reduce the impact of mineral precipitation and improve CO$_2$ injectivity. A maximum of about 30% injectivity improvement was attained in the laboratory experiments.
- Injectivity improved further as brine salinity decline. When brine salinity was below 21.102 g/l, CO$_2$ injectivity was further impaired probably due to fines migration and clay swelling.
- CO$_2$ injection rates above 5 ml/min did not improve injectivity.
- Injectivity improvement also depend on initial core permeability.

The findings are still in the preliminary stage, nevertheless the results and insights are useful for understanding the impact of mineral precipitation on CO$_2$ injectivity.
Acknowledgement

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REFERENCES


