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Novel approaches to lower reservoir pressure by accelerating convective mixing between brine and CO₂

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Public abstract

In this report, it is investigated whether it is possible to enhance dissolution of CO2 in brine using nanoparticles (NPs) as a remediation and/or mitigation option for unwanted migration of CO2. The idea is to inject a homogeneous mixture of NPs and CO2 into the stored CO2. The heavier NP-CO2 mixture spreads on the interphase between the CO2 and brine. The heavier NPs move into the brine together with the CO2 and increase the density of the brine. This will enhance the process of convective mixing which increases the dissolution rate of CO2. However, it was found that the method is very inefficient in terms of the amount of NPs needed compared to the increase in CO2 dissolution. For example, to achieve an increase of 50% in the CO2 dissolution rate, 1 kg of NP is needed to dissolve 3 kg extra CO2 for an example case at 1 km depth. This makes the method unattractive both technically and economically, because:

- a large effort is required for engineering NPs with the correct properties
- the risks associated: risk of clogging and pressure increase
- the method is expensive: for dissolving 5 Mton CO2 at doubled dissolution rate, costs in excess of 1 trillion € were estimated.
- the method is very slow (order 10-100 years).
<table>
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| This report is part of the research project MiReCOL (Mitigation and Remediation of CO\textsubscript{2} leakage) funded by the EU FP7 programme\textsuperscript{1}. Research activities aim at developing a handbook of corrective measures that can be considered in the event of undesired migration of CO\textsubscript{2} in deep subsurface reservoirs. MiReCOL results support CO\textsubscript{2} storage project operators in assessing the value of specific corrective measures if the CO\textsubscript{2} in the storage reservoir does not behave as expected. MiReCOL focuses on corrective measures that can be taken while the CO\textsubscript{2} is in the deep subsurface. The general scenarios considered in MiReCOL are 1) loss of conformance in the reservoir (undesired migration of CO\textsubscript{2} within the reservoir), 2) natural barrier breach (CO\textsubscript{2} migration through faults or fractures), and 3) well barrier breach (CO\textsubscript{2} migration along the well bore).

This report investigates the possibilities for enhancing dissolution of CO\textsubscript{2} in brine. Dissolution of CO\textsubscript{2} in brine has two safety advantages:
- The pressure is lowered.
- The dissolved CO\textsubscript{2} can no longer migrate as a separate phase but its migration is restricted to migration of the brine.

For enhancing CO\textsubscript{2} dissolution during the injection phase several possibilities are discussed in the literature:
- Alternate injection with water/brine (Emami-Meybodi et al., 2015)
- Co-injection of CO\textsubscript{2} with SO\textsubscript{2} (Crandell et al., 2010)
- Co-injection of CO\textsubscript{2} with nanoparticles (NPs) to enhance convective mixing (Javadpour and Nicot, 2011 and Singh et al., 2012)

From these methods, the last method was selected in MiReCOL to be investigated as potential remediation method in this work package. The proposed method enhances the natural process of convective mixing by increasing the density of the CO\textsubscript{2}-saturated brine by using NPs. Convective mixing can develop when CO\textsubscript{2} is stored on top of brine: the CO\textsubscript{2} dissolves into the underlying brine which increases the density of the brine. The heavier, CO\textsubscript{2}-saturated brine on top of the lighter, normal brine is unstable and at some point in time the layer of heavy brine becomes unstable and the heavy, CO\textsubscript{2}-saturated brine starts to move downward. As a result, fresh (unsaturated) brine is transported to the CO\textsubscript{2}-brine interface. In case of enhancement using NPs, the heavy NPs (e.g. metals and/or metaloxides which are in the order of 1-50 nm in size) move into the brine together with the CO\textsubscript{2}. This increases the density of the CO\textsubscript{2}-saturated brine which in turn increases the rate of convective mixing.

Natural CO\textsubscript{2} dissolution is a relatively slow process even when enhanced by convective mixing and is important for the long-term storage of CO\textsubscript{2} (Huppert and Neufeld, 2014). Therefore, this remediation strategy is aimed at undesired migrations of a relatively slow rate or as a complementary measure for another remediation strategy. Maybe it is also possible to use this for mitigation rather than remediation at a very early stage before an actual leak has developed.

To evaluate the feasibility of using NPs for remediation and/or mitigation, two aspects are evaluated:
- Placement of the NPs: how do you get the NPs where you need them
- Assuming that the NPs are where you need them, how much do they enhance convective

\textsuperscript{1} More information on the MiReCOL project can be found at [www.mirecol-co2.eu](http://www.mirecol-co2.eu).
mixing and thus increase the dissolution of CO₂ into the brine.

For the first aspect (placement), for both remediation and mitigation, it is most likely that the NPs are injected when (part of) the CO₂ is in place. This means that a mixture containing the NPs will need to be injected in such a way that the NPs reach the boundary between the CO₂ and the brine. A strategy to achieve this is discussed in section 2.1. To simulate the placement of the NPs on the boundary, numerical simulation is used. This method is discussed in section 2.3. The main point addressed by the NP placement simulation is:

- What is an acceptable density of the NP-CO₂ for injection?

For the acceptable density range, the NP-CO₂ (homogeneously mixed) should obviously be heavier than CO₂, but lighter than the brine. If the NP-CO₂ is too heavy, then it will move into the brine and not spread on the interface. If the NP-CO₂ is too light (i.e. density difference with the CO₂ is small), the spreading is not efficient.

For the second aspect (modelling convective mixing), a situation is assumed where a mixture of free CO₂ and NPs is present on top of brine (both stationary). In that case, the use of equations for the estimation of CO₂ dissolution resulting from convective mixing as derived by Szulczewski et al. (2013) is justified. This method is described in section 2.4.

The results of the analysis of both aspects are discussed in Chapter 3. Also some economic aspects and potential risks are discussed there. The report will be concluded with a discussion and conclusions.
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1 INTRODUCTION

This report is part of the research project MiReCOL (Mitigation and Remediation of CO₂ leakage) funded by the EU FP7 programme. Research activities aim at developing a handbook of corrective measures that can be considered in the event of undesired migration of CO₂ in deep subsurface reservoirs. MiReCOL results support CO₂ storage project operators in assessing the value of specific corrective measures if the CO₂ in the storage reservoir does not behave as expected. MiReCOL focuses on corrective measures that can be taken while the CO₂ is in the deep subsurface. The general scenarios considered in MiReCOL are 1) loss of conformance in the reservoir (undesired migration of CO₂ within the reservoir), 2) natural barrier breach (CO₂ migration through faults or fractures), and 3) well barrier breach (CO₂ migration along the well bore).

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slow rate or as a complementary measure for another remediation strategy. Maybe it is also possible to use this for mitigation rather than remediation at a very early stage before an actual leak has developed.

To evaluate the feasibility of using NPs for remediation and/or mitigation, two aspects are evaluated:

- Placement of the NPs: how do you get the NPs where you need them
- Assuming that the NPs are where you need them, how much do they enhance convective mixing and thus increase the dissolution of CO$_2$ into the brine.

For the first aspect (placement), for both remediation and mitigation, it is most likely that the NPs are injected when (part of) the CO$_2$ is in place. This means that a mixture containing the NPs will need to be injected in such a way that the NPs reach the boundary between the CO$_2$ and the brine. A strategy to achieve this is discussed in section 2.1. To simulate the placement of the NPs on the boundary, numerical simulation is used. This method is discussed in section 2.3. The main point addressed by the NP placement simulation is:

- What is an acceptable density of the NP-CO$_2$ mixture for injection?

For the acceptable density range, the NP-CO$_2$ (homogeneously mixed) should obviously be heavier than CO$_2$, but lighter than the brine. If the NP-CO$_2$ is too heavy, then it will move into the brine and not spread on the interface. If the NP-CO$_2$ is too light (i.e. density difference with the CO$_2$ is small), the spreading is not efficient.

For the second aspect, a situation is assumed where a mixture of free CO$_2$ and NPs is present on top of brine (both stationary). In that case, the use of equations for the estimation of CO$_2$ dissolution resulting from convective mixing as derived by Szulczewski et al. (2013) is justified. This method is described in section 2.4.

The results of the analysis of both aspects are discussed in Chapter 3. Also some economic aspects and potential risks are discussed there. The report will be concluded with a discussion and conclusions.
2 METHODS

2.1 Injection strategy of nanoparticles (NPs)

Since we are investigating the use of NPs for remediation and/or mitigation measures, the NPs are not injected together with the CO$_2$ from the start. The NPs need to be injected when (part of) the CO$_2$ is in place. For an effective remediation strategy it is necessary to place the NPs on the interface between brine and CO$_2$ where the CO$_2$ dissolution takes place. Two basic strategies for placing the NPs are:

1. Injection of a mixture of NPs and CO$_2$ (NP-CO$_2$) into the CO$_2$ phase with a density intermediate between CO$_2$ and brine. The NP mixture will move down through the CO$_2$ and spread on the CO$_2$-brine interface.

2. Injection of a mixture of NPs and CO$_2$ (NP-CO$_2$) into the brine phase with a density intermediate between CO$_2$ and brine. The NP mixture will move up through the brine and then spread on the interface.

The NPs cannot be injected alone but need to be injected in combination with another substance as a (homogeneous) mixture. Obvious candidates for mixing with the NPs are brine and CO$_2$, but other substances would also be possible (e.g. methane, nitrogen, alcohol). To simplify matters for now, we will assume that the NPs are injected together with CO$_2$. Since the NPs should have high density in order to increase the convective mixing, an appropriate mixture of NPs and CO$_2$ should result in a density which is intermediate to the CO$_2$ and brine. This will be investigated in chapter 3.1.

Placing strategy 1 (injection of NPs into the CO$_2$) is illustrated in Figure 2-1. For strategy 2, the injection phases and strategy are similar. In this report, we focus on strategy 1.

The placing of NP-CO$_2$ via injection can be divided in three phases (see Figure 2-1):

1. Injection phase: a homogeneous mixture of the CO$_2$ with NPs (NP-CO$_2$) is injected in supercritical phase in the CO$_2$. Flow in the reservoir is dominated by advection and pressure differences caused by injection. This means that the CO$_2$ moves laterally away from the well. Some losses and retention of NPs are to be expected.

2. Spreading phase: once injection is stopped the NP-CO$_2$ moves down due to the density difference with the surrounding supercritical CO$_2$. The flow is still dominated by advection. Once the NP-CO$_2$ reaches the interface with the brine, NPs will gradually move into the brine. This phase already starts during injection.

3. Dissolution phase: NPs move into the brine, effectively increase the density and thereby enhance convective mixing.

At this stage, the processes inside the well during injection are not investigated. It is assumed that it is possible to inject the required homogeneous NP-CO$_2$ mixture at the
required depth. As long as the CO\textsubscript{2} is super-critical (with relatively high density), it is likely that a sufficiently stable mixture can be created. This may however require engineering of the NPs, which can increase the cost of the particles.

Figure 2-1. Overview of the injection of CO\textsubscript{2} with NPs (NP-CO\textsubscript{2}) into CO\textsubscript{2} overlying brine, with three distinct phases of placing NP-CO\textsubscript{2}: (1) Injection phase, (2) spreading phase, (3) dissolution phase.

2.2 Properties of NP-CO\textsubscript{2}

Since the NPs will be present in both, CO\textsubscript{2} and brine, we define the following volume (V) fractions of NPs:

The volume fraction of NPs in brine saturated with CO\textsubscript{2} \((f_b)\) is defined as:

\[
f_b = \frac{V_{NP}}{V_{NPCO2satbrine}}
\]  \hspace{1cm} (1)

with

\[
V_{CO2satbrine} + V_{NP} = V_{NPCO2satbrine}
\]

The volume fraction of NPs in (free) CO\textsubscript{2} \((f_c)\) is defined as:
\begin{equation}
    f_c = \frac{V_{NP}}{V_{NPCO2}}
\end{equation}

with

\begin{equation}
    V_{CO2} + V_{NP} = V_{NPCO2}
\end{equation}

\section*{2.2.1 Density}

The density of CO$_2$ as a function of pressure and temperature is taken from Lemmon et al. (2015). The density of the CO$_2$-saturated brine is calculated from the correlation by Garcia (2001).

Density ($\rho$) of the NP mixtures is based on the equations provided by Javadpour and Nicot (2011):

\begin{equation}
    \rho_{NPCO2satbrine} = (1 - f_b)\rho_{CO2satbrine} + (f_b)\rho_{NP}
\end{equation}

\begin{equation}
    \rho_{NPCO2} = (1 - f_c)\rho_{CO2} + (f_c)\rho_{NP}
\end{equation}

\section*{2.2.2 Viscosity}

The viscosity of the CO$_2$ is taken from Lemmon et al. (2015). The viscosity of the brine is calculated from Batzle and Wang (1992). The viscosity of the CO$_2$-saturated brine is assumed to be the same as that of normal brine. Solubility of CO$_2$ in brine is calculated according to Duan et al. (2006).

The viscosity ($\mu$) of the NP-mixtures is based on the equations provided by Javadpour and Nicot (2011) using Einstein’s viscosity relation:

\begin{equation}
    \mu_{NPCO2satbrine} = (1 + 2.5f_b)\mu_{CO2satbrine}
\end{equation}

\begin{equation}
    \mu_{NPCO2} = (1 + 2.5f_c)\mu_{CO2}
\end{equation}

\section*{2.3 Reservoir simulation for NP placement}

As discussed in the introduction, the main point addressed by the NP placement simulations is:

- What is an acceptable density of the NP-CO$_2$ for injection?

To calculate the placement of the NP-CO$_2$, a numerical reservoir simulator is used (industry-standard code Eclipse 100, black-oil simulator). We assume that the CO$_2$ is stationary and is not moving up-dip any more. Since the reservoir simulator is not able to simulate NPs explicitly, a simplified approach is followed in which CO$_2$ is simulated as the gas phase, NP-CO$_2$ as the (dead) oil phase (with properties matching those of the
NP-CO₂) and brine as the water phase. Convective mixing is not included in these simulations, since the focus here is to investigate whether it is feasible to place the NP-CO₂ on the interphase between CO₂ and brine and what acceptable densities are to achieve this.

Below is a list of other processes which might be relevant, but are not taken into account.

- The degree of dispersion and stability of the NPs. Phase separation due to gravity might occur.
- NP losses to ambient CO₂ or brine other than on the interface, which changes the properties of the NPs-CO₂. In other words, the fraction NP in the NP-CO₂ is fixed.
- Retardation of the NPs (Kampel and Goldsztein, 2011)
- Miscibility: the phases CO₂ (simulated as gas phase) and NP-CO₂ (simulated as oil phase) are assumed to be immiscible.
- Clogging of pores: pore throats for high permeability sand are generally >1 µm, whereas the particles have size of 10-100 nm. In case of aggregation, the particle size gradually increases and might lead to clogging of the pore throats. This is undesirable. Additional stabilization/functionalization of the NPs with a partly CO₂-philic layer might be needed in that case. A potential candidate might be polyethylene glycol.
- Foam formation which reduces injectivity.

Most of these processes can be avoided to a large extent by proper engineering of the particles. Miscibility cannot be avoided, but is more important on long time scales. It is expected that this simplified approach provides sufficient information to reach the goal of these simulation, namely estimate a suitable density range.

For the reservoir simulation, the PVT properties of the NP-CO₂ are required as a function of pressure. To calculate this, a constant mass fraction of NPs is assumed and the corresponding properties calculated. The calculation of properties for CO₂ and NP-CO₂ has been described in Section 2.2. In Figure 2-2, Figure 2-3 and Figure 2-4 the resulting properties are presented as a function of pressure for an NP density of 5000 kg/m³ and mass fraction of 1E-4.
Figure 2-2. Density of CO\textsubscript{2} and NP-CO\textsubscript{2} as a function of pressure for a temperature of 40°C and 70°C for NP density of 5000 kg/m\textsuperscript{3} and mass fraction of 1E-4.

Figure 2-3. Viscosity of CO\textsubscript{2} and NP-CO\textsubscript{2} as a function of pressure for a temperature of 40°C and 70°C for NP density of 5000 kg/m\textsuperscript{3} and mass fraction of 1E-4.
To determine the range of acceptable densities for placement of the NPs, 5 cases are simulated. In Table 1 the settings of the 5 cases are presented.

Table 1. Overview of the reservoir input settings for five cases.

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<th>Case 1a</th>
<th>Case 1a _brine</th>
<th>Case 1b</th>
<th>Case 2a</th>
<th>Case 2b</th>
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<td>Depth</td>
<td>1000 m</td>
<td>2000 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>105 bar @ CO$_2$-brine contact</td>
<td>205 bar @ CO$_2$-brine contact</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>40 °C</td>
<td>70 °C</td>
<td></td>
<td></td>
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<td>Permeability (horizontal)</td>
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<td>1000 mD</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Permeability (vertical)</td>
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<td>100 mD</td>
<td></td>
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<td>porosity</td>
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<tr>
<td>CO$_2$ density (@ reservoir conditions)</td>
<td>656 kg/m$^3$</td>
<td>668 kg/m$^3$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NP density</td>
<td>5000 kg/m$^3$</td>
<td>7500 kg/m$^3$</td>
<td>5000 kg/m$^3$</td>
<td>7500 kg/m$^3$</td>
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<tr>
<td>Injection into phase</td>
<td>CO$_2$</td>
<td>brine</td>
<td>CO$_2$</td>
<td>CO$_2$</td>
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</table>
both cases (Figure 2-4). The mass fraction of NPs is 50% higher for the heavier particles.

2.4 Calculation of CO₂ dissolution flux with NPs

For the calculation of the dissolution flux of CO₂ into the brine (enhanced by convective mixing) that could be achieved by adding NPs, we can assume that NP-CO₂ is in contact with the brine. The CO₂ dissolution flux \( F_{CO₂} \) in case of convective mixing (also named the fingering regime) is calculated as presented by (Szulczewski et al., 2013):

\[
F_{CO₂} \approx 0.017 \ c_s \ V \quad (7)
\]

with

\[
V = \frac{\Delta \rho g k}{\mu \phi} \quad (8)
\]

Where:

- \( c_s \): saturated concentration of CO₂ [kg/m³]
- \( V \): characteristic velocity of the fingers [m/s]
- \( \Delta \rho \): density difference between CO₂-saturated brine and brine without CO₂ [kg/m³]
- \( g \): gravitational acceleration [m/s²]
- \( k \): permeability [m²]
- \( \mu \): dynamic viscosity [Pa·s]
- \( \phi \): porosity [-]

The properties affected by the NPs are \( V, \Delta \rho \), and \( \mu \). Thus the CO₂ dissolution flux with and without NPs can be calculated. Table 2 shows the input settings for the calculations. A density of 10.000 kg/m³ was used here to make the chance for success as large as possible.

Table 2. Input settings for calculating the efficiency of enhancing CO₂ dissolution by convective mixing.

<table>
<thead>
<tr>
<th>Property</th>
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<td>Pressure</td>
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<td>Temperature</td>
<td>40 °C</td>
</tr>
<tr>
<td>Vertical permeability</td>
<td>500 mD</td>
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<tr>
<td>Porosity</td>
<td>0.35</td>
</tr>
<tr>
<td>Salinity</td>
<td>3.5 %</td>
</tr>
<tr>
<td>Density NPs</td>
<td>10.000 kg/m³</td>
</tr>
</tbody>
</table>

2.4.1 Partitioning of NPs between CO₂ and brine

To calculate the properties of the NP-CO₂ and NP-CO₂ saturated brine for eq. 7 and eq. 8, the volume fraction of NPs is required. The volume fraction NPs in free CO₂ (\( f_c \) (eq. 1)) is determined by the injection strategy. However, the volume fraction NP in the brine (\( f_b \)) cannot be determined easily. It depends on the partitioning of the NPs over
the CO₂ and the brine, which depends on the properties of the surface of the NPs and the relative affinity for CO₂ and/or brine. Javadpour and Nicot (2011) assumed that the brine at the interface would get the same volume fraction of NPs as the injected NP-CO₂, or in other words \( f_b = f_c \). This presents a problem though: if the CO₂-saturated brine that moves away from the interface due to convection contains a volume fraction \( f_b = f_c \), then the CO₂ at the interface would quickly become depleted of NPs. In general three cases can be identified:

1. The rate of NPs moving to the brine is faster w.r.t. the CO₂.
2. The rate of NPs moving to the brine is the same w.r.t. the CO₂ (thus the amount of NPs that move into the brine can be calculated from the CO₂ solubility).
3. The rate of NPs moving to the brine is slower w.r.t. CO₂.

For case 1, NP-CO₂ at the CO₂-brine interface will become depleted of NPs (\( f_c \) will decrease). For the assumption under case 3, NPs will remain behind in the CO₂ (\( f_c \) will increase). For case 2, \( f_c \) will remain constant. So, even though the partitioning of the NPs between brine and CO₂ in no way depends on the solubility of CO₂, for evaluation purposes it is useful to derive \( f_b \) based on case 2 and calculate any other cases based on that \( f_b \). Thus \( f_b \) can be calculated from \( f_c \), the solubility of CO₂ and the different densities. The derivation will be presented below.

Please note that it is assumed that the NPs are stable particles and do not dissolve in either the CO₂ or the brine.

The solubility \( s \) of CO₂ in the brine is defined as:

\[
\frac{m_{CO_2}}{m_{brine}} = \frac{\rho_{CO_2} V_{CO_2}}{\rho_{brine} V_{brine}}
\]

with \( f_b \) defined in (Eq. 1).

With the definition of \( f_c \) (Eq. 2), this can be written as:

\[
f_b = f_c \times \frac{V_{NP CO_2}}{V_{NP CO_2 sat brine}} = f_c \times \frac{V_{NP} + V_{CO_2}}{V_{NP} + V_{CO_2 sat brine}}
\]

As an intermediate step we multiply with \( 1/V_{brine} \), resulting in:

\[
f_b = f_c \times \frac{V_{NP} / V_{brine} + V_{CO_2} / V_{brine} + V_{CO_2 sat brine} / V_{brine}}{V_{brine}}
\]

The four fractions in the equation (9) above can be rewritten into known variables. This will be explained below. From the definition of solubility \( s \) above, it follows that:

\[
\frac{V_{CO_2}}{V_{brine}} = s \frac{\rho_{brine}}{\rho_{CO_2}}
\]

From the definition of \( f_c \):

\[
V_{NP} = f_c (V_{NP} + V_{CO_2})
\]
\[ V_{NP} - f_c V_{NP} = V_{NP} (1 - f_c) = f_c V_{CO2} \]  
(14)

\[ \frac{V_{NP}}{V_{brane}} = \frac{f_c \cdot V_{CO2}}{1 - f_c V_{brane}} \]  
(15)

And

\[ \frac{V_{CO2 sat brine}}{V_{brane}} = \frac{(1 + s) \rho_{brane}/\rho_{CO2 sat brine}}{m_{brane}/\rho_{brane}} = \frac{(1 + s) \rho_{brane}}{\rho_{CO2 sat brine}} \]  
(16)

Substituting Eq. 10, 13 and 14 in Eq. 9 results in the equation to calculate the volume fraction of NPs in brine \((f_b)\) based on the volume fraction in the CO\(_2\) \((f_c)\) and the solubility of CO\(_2\) in brine:

\[ f_b = f_c \times \frac{\left( f_c \left( \frac{\rho_{brane}}{\rho_{CO2}} \right) \right)^{s}}{\left( \frac{\rho_{brane}}{\rho_{CO2}} \right)^{s} + (1 + s) \left( \frac{\rho_{brane}}{\rho_{CO2 sat brine}} \right)} \]  
(17)
3 RESULTS AND DISCUSSION

3.1 NP Placement

Table 3 shows the results of the cases described in Table 1. In section 2.3, the simulation approach was described.

The radius listed in the last column is the maximum radius reached by the NP-CO$_2$ after 2 years (1 year of injection and a year time for spreading). The sensitivity of spreading to the density of the injected NP-CO$_2$ is not very large. So for acceptable spreading, a density of NP-CO$_2$ between 750 and 950 kg/m$^3$ at reservoir conditions is probably acceptable. Figure 3-2 shows the density of NP-CO$_2$ as a function of the volume fraction of the NPs in the injected CO$_2$ at reservoir conditions. From this plot, the acceptable range for the volume fraction of the NPs in the NP-CO$_2$ to be used for the calculations of the increase in CO$_2$ dissolution flux in the next section, can be derived. For these calculation a density of the NPs of 10.000 kg/m$^3$ was used in order to get the highest possible benefit from the NPs.

Table 3. Results of the placement simulations.

<table>
<thead>
<tr>
<th>Case</th>
<th>Density NP</th>
<th>Density NP-CO$<em>2$ @ $P</em>{reservoir}$</th>
<th>Radius (after 2 yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1a</td>
<td>5000 kg/m$^3$</td>
<td>785 kg/m$^3$</td>
<td>420 m</td>
</tr>
<tr>
<td>Case 1a_brine</td>
<td>5000 kg/m$^3$</td>
<td>785 kg/m$^3$</td>
<td>400 m</td>
</tr>
<tr>
<td>Case 1b</td>
<td>7500 kg/m$^3$</td>
<td>872 kg/m$^3$</td>
<td>440 m</td>
</tr>
<tr>
<td>Case 2a</td>
<td>5000 kg/m$^3$</td>
<td>844 kg/m$^3$</td>
<td>400 m</td>
</tr>
<tr>
<td>Case 2b</td>
<td>7500 kg/m$^3$</td>
<td>946 kg/m$^3$</td>
<td>400 m</td>
</tr>
</tbody>
</table>

The radius presented in Table 3 is after 2 years (of which only in the first year injection occurred). The spreading continues after this time. For example for case 1a, after another year of spreading the radius has grown with another ~40 m. This is similar for the other cases. However, the assumptions of immiscible flow and no loss of particles become less valid as spreading continues.
Figure 3-1. Spreading 2 years after the start of injection for case 1 (Table 3) with NP-CO$_2$ injection in a vertical well with NP density of 7500 kg/m$^3$ (horizontal grid block size = 40 m). The cross section shows the CO$_2$ in red, the NP-CO$_2$ in green and in blue the brine.

Figure 3-2. Density of NP-CO$_2$ as a function of the volume fraction of NPs with a density of 10,000 kg/m$^3$ (all at reservoir conditions) for case 1 (1 km depth) and case 2 (2 km depth).

To check whether injection strategy 2 (injection into the brine) significantly affects the results, case1a was also simulated for injection into the underlying brine. The differences were small: for the same settings, the NP-CO$_2$ spread a bit further for the injection in CO$_2$ than for the injection in brine (420 m away from the well after 2 years.
for injection into CO₂ (Figure 3-3) versus 400 m away from the well for injection into brine (Figure 3-4). Also, more NP-CO₂ was trapped due to residual trapping in the case of injection into the brine.

Figure 3-3. Spreading 2 years after the start of injection for case 1a for injection in the CO₂ (see Table 3). The cross section shows the CO₂ in red, the NP-CO₂ in green and in blue the brine.

Figure 3-4. Spreading 2 years after the start of injection for case 1a_brine with injection into the brine below the CO₂. The cross section shows the CO₂ in red, the NP-CO₂ in green and in blue the brine.

3.2 Efficiency of increasing CO₂ dissolution flux

To determine the efficiency of the mitigation measure the next step is to calculate, for the values of $f_c$ determined in the previous section, the increase in convective mixing
and in CO₂ dissolution. To characterize the efficiency, the following numbers are calculated:

- Percentage increase in CO₂ dissolution flux (flux in kg/m²/yr) (I):

\[
I = 100\% \times \left( \frac{F_{CO₂, NP} - F_{CO₂}}{F_{CO₂}} \right)
\]

(18)

Where:

\( F_{CO₂, NP} \) : CO₂ dissolution flux with NP-CO₂ (kg/m²/yr)
\( F_{CO₂} \) : CO₂ dissolution flux with only CO₂ (kg/m²/yr)

- Ratio of additional CO₂ dissolution flux and the required NP flux to reach that CO₂ flux (R):

\[
R = \left( \frac{F_{CO₂, NP} - F_{CO₂}}{F_{NP}} \right)
\]

(19)

Where:

\( F_{NP} \) : flux NPs in the flux F_{CO₂, NP} (kg/m²/yr)

- Ratio of the additional CO₂ dissolution flux and the CO₂ input required to inject the relevant amount of NPs (\( R_{CO₂} \)) (also expressed as a flux in kg/m²/yr):

\[
R_{CO₂} = \left( \frac{F_{CO₂, NP} - F_{CO₂}}{F_{NP} \times \frac{(1 - f_{c,m})}{f_{c,m}}} \right)
\]

(20)

Where \( f_{c,m} \) is the mass fraction of NP in NP-CO₂, calculated from:

\[
f_{c,m} = f_c \times \frac{\rho_{NP}}{\rho_{NP, CO₂}}
\]

(21)

The three numbers defined above (Eq. 18-20) are presented as a function of \( f_c \) (at downhole conditions) in Figure 3-5 to Figure 3-7 for case 1 (see Table 2 for details on the input). The values of \( f_c \) are chosen to get acceptable densities of the NP-CO₂ in terms of placement (see Section 3.1 and Figure 3-2). Four different levels of partitioning in brine were investigated: 100%, 50%, 20% and 10%. 100% means that the volume fraction of the NPs with respect to the CO₂ in the CO₂-saturated brine is the same as the volume fraction in the free CO₂. In the other cases, the volume fraction NPs in brine is reduced compared to that scenario.
Figure 3-5. Percentage increase in CO$_2$ dissolution flux ($I$, Eq. 18) as a function of $f_c$ for 4 different scenarios of partitioning of NPs over CO$_2$ and brine (100% is equal partitioning, 10% indicates a strong preference for the CO$_2$ phase).

Figure 3-6. Ratio of additional CO$_2$ dissolution flux and the required NP flux ($R$, Eq. 19) as a function of $f_c$ for 4 different scenarios of partitioning of NPs over CO$_2$ and brine (100% is equal partitioning, 10% indicates a strong preference for the CO$_2$ phase).
Additional CO$_2$ dissolution flux compared to the CO$_2$ input associated with the input in NPs ($R_{\text{CO}_2}$, Eq. 20) as a function of $f_c$ for 4 different scenarios of partitioning of NPs over CO$_2$ and brine (100% is equal partitioning, 10% indicates a strong preference for the CO$_2$ phase).

The results in the Figure 3-5 and Figure 3-6 show a clear trade-off: with more NPs moving into the brine, the increase in dissolved CO$_2$ becomes larger, but the efficiency decreases. The efficiency with which the NPs are used is low: even for the most efficient cases only 4.5 kg of CO$_2$ is dissolved additionally for every kg of NP added (per m$^2$ per year). Figure 3-8 illustrates this trade-off in one figure.

Figure 3-7 shows the amount of CO$_2$ necessary for injection with the NPs compared to the amount of CO$_2$ dissolved extra. Values above 1 mean that more CO$_2$ is dissolved than added. For all the cases below 1, more CO$_2$ is added when injecting the NPs than is additionally dissolved. This means that for many cases more CO$_2$ needs to be added than is dissolved. This is not a problem if the method is used in cases where CO$_2$ injection for storage is continued: a mitigation measure rather than remediation (see also the discussion in the Introduction and the next section). However, the amount of NPs to be injected is very large in any case.
Figure 3-8. Illustration of the trade-off between a large increase in dissolution and efficient use of the NPs.

The efficiency of the method in terms of pressure decrease has not been simulated. Since NP require to be co-injected with a solvent/carrier medium, typically CO\textsubscript{2}, the method requires injection of large volumes, initial pressure increase can be expected. If pressure increase is an issue, this method is obviously not suitable.

### 3.3 NP injection from the start

So far only the injection of NPs as a mitigation or remediation option have been discussed: i.e. when (part of) the CO\textsubscript{2} has already been injected. Javadpour and Nicot (2011) investigate the co-injection of NPs with CO\textsubscript{2} from the start of the injection of CO\textsubscript{2}. Javadpour and Nicot (2011) stated that for co-injection of NPs from the start only a small volume fraction in the CO\textsubscript{2} was needed (0.001) to achieve an increase in convective mixing of 50\%, suggesting that the process is quite efficient. The main reason for the difference with the results shown in this paper is the partitioning: Javadpour and Nicot assumed that the volume fraction NPs in the brine would be identical to the volume fraction NPs in the CO\textsubscript{2} (see section 2.2.3), whereas we assume that the NPs and CO\textsubscript{2} move into the brine together at the same volume fraction. With the assumption of Javadpour and Nicot, the CO\textsubscript{2} would become depleted of NPs very quickly. A second difference is that we compare the mass of the required NPs to the mass of CO\textsubscript{2}. Due to the large difference in density between CO\textsubscript{2} and NPs (roughly a factor of 10), the mass fraction NPs in CO\textsubscript{2} is much larger than the volume fraction.

Thus for upfront injection, the required amounts and efficiency of NPs are the same as for injection when the CO\textsubscript{2} is in place. A disadvantage of injecting the NPs with CO\textsubscript{2} from the start is that usually the plume moves up dip first, which might result in loss of
NPs. An advantage is that the presence of the NPs can reduce the time necessary for convective mixing to start.

An extreme option, especially for deep injection would be to add so many NPs that the density of the NP-CO$_2$ would become heavier than the brine and would sink rather than rise enhancing storage safety.

### 3.4 Associated risks

To evaluate the potential of this technique for remediation purposes, associated risks of the method need to be evaluated. An important side effect, is the rise in pressure caused by this method on the short term due to the required injection of quite large volumes. The amount of NPs to be injected is large, certainly if you also consider the amount of gas that needs to be co-injected with the NPs. The effect of the rise in pressure might be mitigated by brine withdrawal at the same time as (continued) injection of CO$_2$.

Another potential risk is loss of injectivity due to clogging of pores. This might happen if the selected NPs are too large compared to the pore throats (e.g. Mohamed, 2011) or if they aggregate. See also Section 2.3.

### 3.5 Cost

The costs of NPs is an important part of the feasibility of the suggested approach. Since we are particularly aiming for high density NPs, such as metal NPs (Pb, Fe, Cu, Ag or Au). The costs of such NPs is in the order of 5 – 25 k€/kg.\(^3\) The costs of the common metal NPs (Pb, Fe and Cu) is in the lower range, while the noble metal NPs (Ag and Au) are clearly in the upper price range. On the other end of the price spectrum are clay nanoparticles. They are used in a variety of applications, among which is the oil and gas industry. The price for these mineral NPs is in the order of 0.1 k€/kg.\(^4\) The price is lower than the metal NPs. However, the density of minerals is significantly lower than for metals and therefore they might be less effective in enhancing convective mixing. Given the range of possible prices for NPs and the need for a high density, a price of 1 k€/kg is assumed for further calculations.

Example calculation:

The goal is to dissolve 5 Mton CO$_2$ at doubled dissolution rate at a pressure of 100 bar and temperature of 40°C (density CO$_2$ is 629 kg/m$^3$). For an average thickness of the CO$_2$ layer of 10m, the surface area of CO$_2$ is 7.95E5 m$^2$. From Figure 3-5, it can be seen that this is possible in two ways which are summarized in Table 4.

---


Table 4. Example of calculation of cost for use of NPs.

<table>
<thead>
<tr>
<th></th>
<th>Partitioning 100%</th>
<th>Partitioning 50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_c$ (reservoir conditions)</td>
<td>0.014</td>
<td>0.027</td>
</tr>
<tr>
<td>Density NPs (kg/m$^3$)</td>
<td>10.000</td>
<td>10.000</td>
</tr>
<tr>
<td>Density NP-CO$_2$ (kg/m$^3$)</td>
<td>760</td>
<td>882</td>
</tr>
<tr>
<td>CO$_2$ dissolution flux (kg/m$^2$/yr)</td>
<td>8.89</td>
<td>8.79</td>
</tr>
<tr>
<td>Time to full dissolution (yrs)</td>
<td>707</td>
<td>715</td>
</tr>
<tr>
<td>NP flux (kg/m$^2$/yr)</td>
<td>2.01</td>
<td>1.94</td>
</tr>
<tr>
<td>Co-injected CO$_2$ flux (kg/m$^2$/yr)</td>
<td>8.89</td>
<td>4.40</td>
</tr>
<tr>
<td>Required Mass NP (kg)</td>
<td>1.13E9</td>
<td>1.10E9</td>
</tr>
<tr>
<td>Price NP (€)</td>
<td>1.13E9</td>
<td>1.10E9</td>
</tr>
</tbody>
</table>

From this table, it is clear that the cost are prohibitive: for dissolving 5 Mton CO$_2$ already more than 1 Mton NP is necessary which would cost 1 trillion € at a price of 1 €/kg, which doesn’t even include the cost of transport and the required injection wells.

Even when using waste (depleted uranium oxides) as suggested by Javadpour and Nicot (2011), costs are associated with the NPs. Creating particles of the right size can be expensive and is not straightforward (Hasan et al., 2011). For example, Javadpour and Nicot (2011) cite the work by Hastings et al. (2008), in which particles are created. However the created particles are in the µm range rather than in the nm range, which would be too large to inject in a reservoir because of the risk of clogging the pores.
4 CONCLUSIONS

In this report it was investigated whether injecting NPs to enhance CO$_2$ dissolution via convective mixing is a viable mitigation strategy. However, it was found that the method is very inefficient in terms of the amount of NPs needed compared to the increase in CO$_2$ dissolution. For example, to achieve an increase of 50% in the CO$_2$ dissolution rate, 1 kg of NP is needed to dissolve 3 kg extra CO$_2$ for an example case at 1 km depth. This makes the method unattractive both technically and economically, because:

- a large effort is required for engineering NPs with the correct properties
- the risks associated: risk of clogging and pressure increase
- the method is expensive: for dissolving 5 Mton CO$_2$ at doubled dissolution rate, costs in excess of 1 trillion € were estimated.
- the method is very slow (order 10-100 years).

The only way to make this work applicable is to also enhance the solubility of the CO$_2$ at the same time.
REFERENCES


Szulczewski, M.L., M.A. Hesse and R. Juanes (2013) carbon dioxide dissolution in