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Public abstract

In this report, it is investigated whether it is possible to enhance dissolution of CO_2 in brine using nanoparticles (NPs) as a remediation and/or mitigation option for unwanted migration of CO_2. The idea is to inject a homogeneous mixture of NPs and CO_2 into the stored CO_2. The heavier NP-CO_2 mixture spreads on the interphase between the CO_2 and brine. The heavier NPs move into the brine together with the CO_2 and increase the density of the brine. This will enhance the process of convective mixing which increases the dissolution rate of CO_2. 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).

Public introduction (*)

This report is part of the research project MiReCOL (Mitigation and Remediation of CO_2 leakage) funded by the EU FP7 programme[1]. Research activities aim at developing a handbook of corrective measures that can be considered in the event of undesired migration of CO_2 in deep subsurface reservoirs. MiReCOL results support CO_2 storage project operators in assessing the value of specific corrective measures if the CO_2 in the storage reservoir does not behave as expected. MiReCOL focuses on corrective measures that can be taken while the CO_2 is in the deep subsurface. The general scenarios considered in MiReCOL are 1) loss of conformance in the reservoir (undesired migration of CO_2 within the reservoir), 2) natural barrier breach (CO_2 migration through faults or fractures), and 3) well barrier breach (CO_2 migration along the well bore).

This report investigates the possibilities for enhancing dissolution of CO_2 in brine. Dissolution of CO_2 in brine has two safety advantages:

- The pressure is lowered.
- The dissolved CO_2 can no longer migrate as a separate phase but its migration is restricted to migration of the brine.

For enhancing CO_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_2 with SO_2 (Crandell et al., 2010)
- Co-injection of CO_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_2-saturated brine by using NPs. Convective mixing can develop when CO_2 is stored on top of brine: the CO_2 dissolves into the underlying brine which increases the density of the brine. The heavier, CO_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_2-saturated brine starts to move downward. As a result, fresh (unsaturated) brine is transported to the CO_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_2. This increases the density of the CO_2-saturated brine which in turn increases the rate of convective mixing.

Natural CO_2 dissolution is a relatively slow process even when enhanced by convective mixing and is important for the long-term storage of CO_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

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[1] More information on the MiReCOL project can be found at www.mirecol-co2.eu.

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 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 (modelling convective mixing), 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.

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1 INTRODUCTION

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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_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.

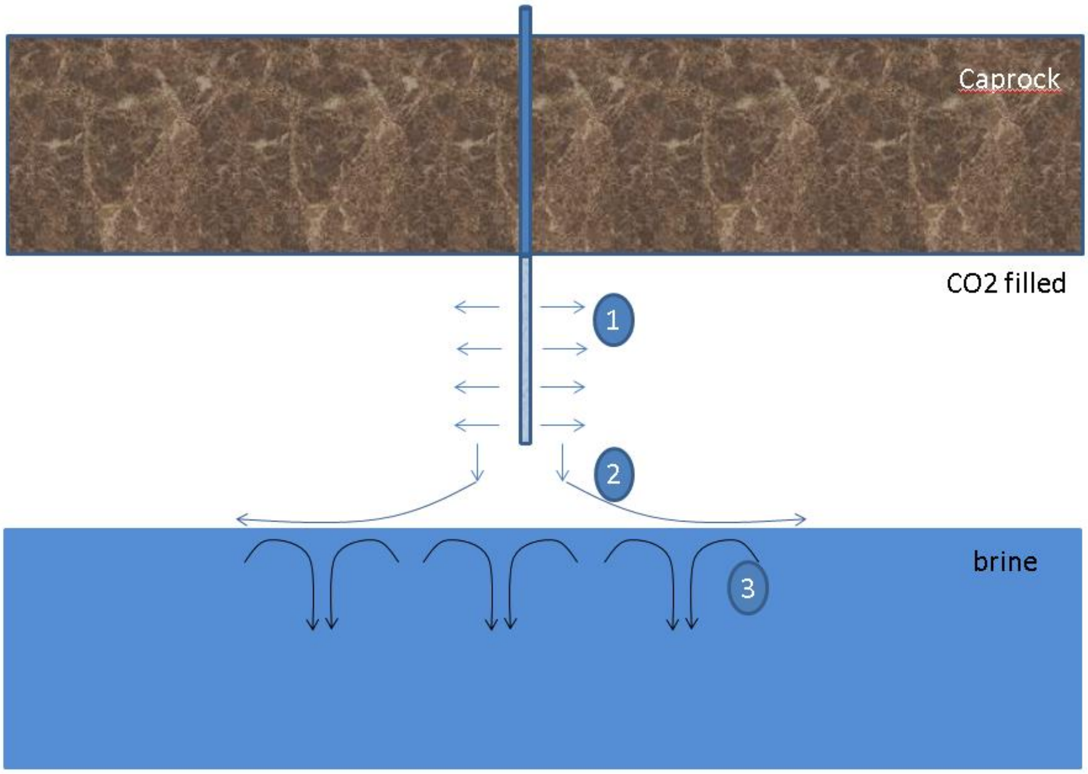

Figure 2-1. Overview of the injection of CO_2 with NPs (NP-CO_2) into CO_2 overlying brine,with three distinct phases of placing NP-CO_2: (1) Injection phase, (2) spreading phase, (3) dissolution phase.

2.2 Properties of NP-CO_2

Since the NPs will be present in both, CO_2 and brine, we define the following volume (V) fractions of NPs:

The volume fraction of NPs in brine saturated with CO_2 (f_b) is defined as:

$$f_b = {}^{V_{NP}}/_{V_{NPCO2satbrine}} \tag{1}$$

with

$$V_{CO2satbrine} + V_{NP} = V_{NPCO2satbrine}$$

The volume fraction of NPs in (free) CO_2 (f_c) is defined as:

$$f_c = {}^{V_{NP}}/_{V_{NPCO2}} \tag{2}$$

with

$$V_{CO2} + V_{NP} = V_{NPCO2}$$

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 (ρ) of the NP mixtures is based on the equations provided by Javadpour and Nicot (2011):

$$\rho_{NPCO2satbrine} = (1 - f_b)\rho_{CO2satbrine} + (f_b)\rho_{NP} \tag{3}$$

$$\rho_{NPCO2} = (1 - f_c)\rho_{CO2} + (f_c)\rho_{NP} \tag{4}$$

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 (μ) of the NP-mixtures is based on the equations provided by Javadpour and Nicot (2011) using Einstein's viscosity relation:

$$\mu_{NPCO2satbrine} = (1 + 2.5\, f_b)\mu_{CO2satbrine} \tag{5}$$

$$\mu_{NPCO2} = (1 + 2.5\, f_c)\mu_{CO2} \tag{6}$$

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-CO_2) 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-CO_2 on the interphase between CO_2 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 CO_2 or brine other than on the interface, which changes the properties of the NPs-CO_2. In other words, the fraction NP in the NP-CO_2 is fixed.
- Retardation of the NPs (Kampel and Goldsztein, 2011)
- Miscibility: the phases CO_2 (simulated as gas phase) and NP-CO_2 (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 CO_2-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-CO_2 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 CO_2 and NP-CO_2 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/m^3 and mass fraction of 1E-4.

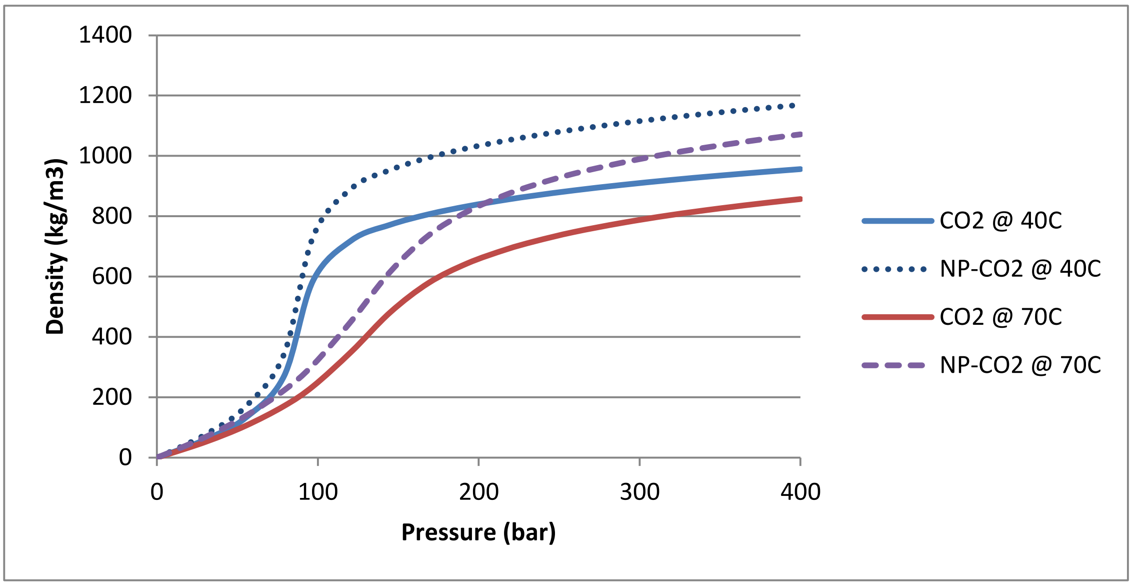

Figure 2-2. Density of CO_2 and NP-CO_2 as a function of pressure for a temperature of 40°C and 70°C for NP density of 5000 kg/m^3 and mass fraction of 1E-4.

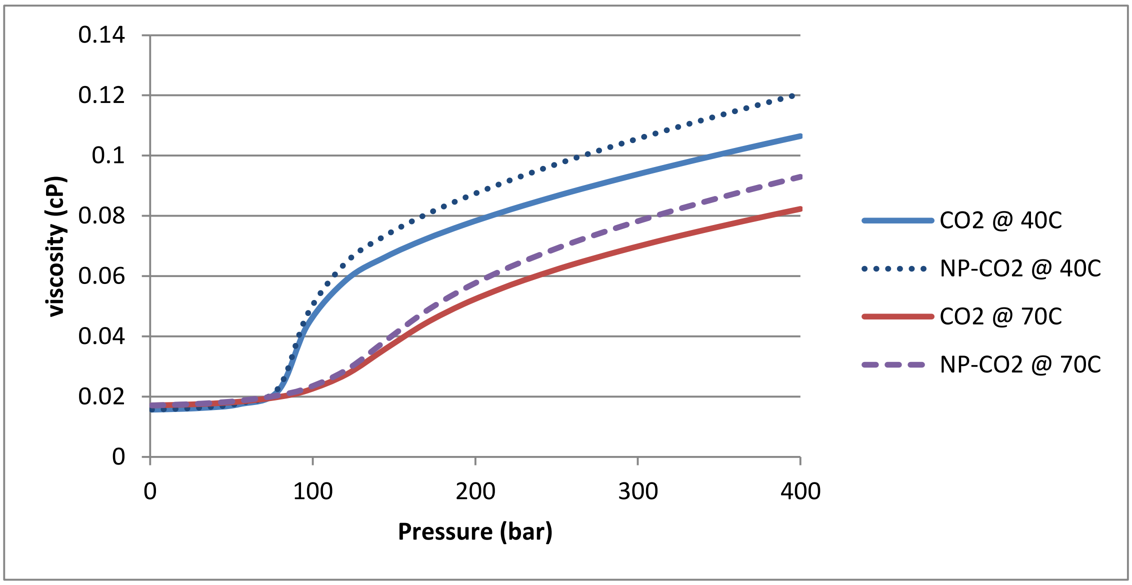

Figure 2-3. Viscosity of CO_2 and NP-CO_2 as a function of pressure for a temperature of 40°C and 70°C for NP density of 5000 kg/m^3 and mass fraction of 1E-4.

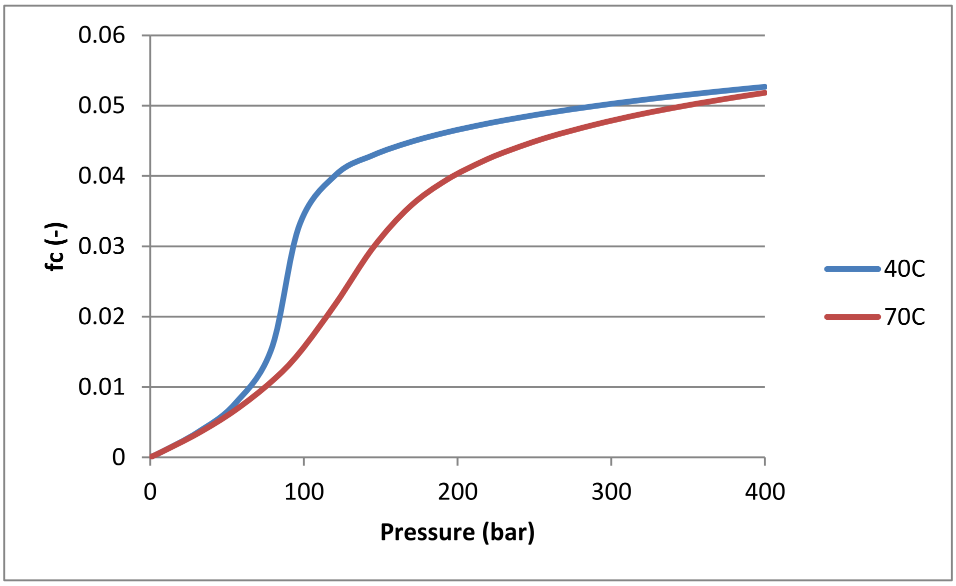

Figure 2-4. Volume fraction NPs in NP-CO_2 (f_c) as a function of pressure for temperatures of 40°C and 70°C for NP density of 5000 kg/m^3 and mass fraction of $1 \cdot 10^{-4}$.

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.

	Case 1a	**Case 1a_brine**	**Case 1b**	**Case 2a**	**Case 2b**
Depth	1000 m			2000 m	
Pressure	105 bar @ CO_2-brine contact			205 bar @ CO_2-brine contact	
Temperature	40 °C			70 °C	
Permeability (horizontal)	1000 mD			1000 mD	
Permeability (vertical)	100 mD			100 mD	
porosity	0.2			0.2	
CO_2 density (@ reservoir conditions)	656 kg/m^3			668 kg/m^3	
NP density	5000 kg/m^3		7500 kg/m^3	5000 kg/m^3	7500 kg/m^3
Injection into phase	**CO_2**	**brine**	**CO_2**	**CO_2**	

The placing was simulated as follows: first one year of injection into the CO_2 at a rate of $1 \cdot 10^6$ sm^3/day in a vertical injection well, then another year of spreading of the NP-CO_2 without further injection. Two different NPs were tested: one with a density of 5000 kg/m^3 (properties in Figure 2-2, Figure 2-3 and Figure 2-4) and one with a density of 7500 kg/m^3 (Javadpour and Nicot, 2011). The volume fraction of the NPs is the same in both cases (Figure 2-4). The mass fraction of NPs is 50% higher for the heavier particles.

2.4 Calculation of CO_2 dissolution flux with NPs

For the calculation of the dissolution flux of CO_2 into the brine (enhanced by convective mixing) that could be achieved by adding NPs, we can assume that NP-CO_2 is in contact with the brine. The CO_2 dissolution flux (F_{CO2}) in case of convective mixing (also named the fingering regime) is calculated as presented by (Szulczewski et al., 2013):

$$F_{CO2} \approx 0.017\, c_s V \qquad (7)$$

with

$$V = \frac{\Delta\rho g k}{\mu\varphi} \qquad (8)$$

Where:

c_s : saturated concentration of CO_2 [kg/m^3]
V : characteristic velocity of the fingers [m/s]
$\Delta\rho$: density difference between CO_2-saturated brine and brine without CO_2 [kg/m^3]
g : gravitational acceleration [m/s^2]
k : permeability [m^2]
μ : dynamic viscosity [Pa·s]
φ : porosity [-]

The properties affected by the NPs are V, $\Delta\rho$ and μ. Thus the CO_2 dissolution flux with and without NPs can be calculated. Table 2 shows the input settings for the calculations. A density of 10.000 kg/m^3 was used here to make the chance for success as large as possible.

Table 2. Input settings for calculating the efficiency of enhancing CO_2 dissolution by convective mixing.

Pressure	100 bar
Temperature	40 °C
Vertical permeability	500 mD
Porosity	0.35
Salinity	3.5 %
Density NPs	10.000 kg/m^3

2.4.1 Partitioning of NPs between CO_2 and brine

To calculate the properties of the NP-CO_2 and NP-CO_2 saturated brine for eq. 7 and eq. 8, the volume fraction of NPs is required. The volume fraction NPs in free CO_2 (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 CO_2 and the brine, which depends on the properties of the surface of the NPs and the relative affinity for CO_2 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-CO_2, or in other words $f_b = f_c$. This presents a problem though: if the CO_2-saturated brine that moves away from the interface due to convection contains a volume fraction $f_b = f_c$, then the CO_2 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 CO_2.
2. The rate of NPs moving to the brine is the *same* w.r.t. the CO_2 (thus the amount of NPs that move into the brine can be calculated from the CO_2 solubility).
3. The rate of NPs moving to the brine is *slower* w.r.t. CO_2.

For case 1, NP-CO_2 at the CO_2-brine interface will become depleted of NPs (f_c will decrease). For the assumption under case 3, NPs will remain behind in the CO_2 (f_c will increase). For case 2, f_c will remain constant. So, even though the partitioning of the NPs between brine and CO_2 in no way depends on the solubility of CO_2, 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 CO_2 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 CO_2 or the brine.

The solubility *s* of CO_2 in the brine is defined a:

$$s = \frac{m_{CO2}}{m_{brine}} = \frac{\rho_{CO2} V_{CO2}}{\rho_{brine} V_{brine}} \qquad (9)$$

with f_b defined in (Eq. 1).

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

$$f_b = f_c \times \frac{V_{NPCO2}}{V_{NPCO2satbrine}} = f_c \times \frac{V_{NP} + V_{CO2}}{V_{NP} + V_{CO2satbrine}} \qquad (10)$$

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

$$f_b = f_c \times \frac{V_{NP}/V_{brine} + V_{CO2}/V_{brine}}{V_{NP}/V_{brine} + V_{CO2satbrine}/V_{brine}} \qquad (11)$$

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:

$$V_{CO2}/V_{brine} = s\, \rho_{brine}/\rho_{CO2} \qquad (12)$$

From the definition of f_c:

$$V_{NP} = f_c (V_{NP} + V_{CO2}) \qquad (13)$$

$$V_{NP} - f_c V_{NP} = V_{NP}(1 - f_c) = f_c V_{CO2} \tag{14}$$

$$V_{NP}/V_{brine} = \frac{f_c}{1-f_c}\frac{V_{CO2}}{V_{brine}} \tag{15}$$

And

$$V_{CO2satbrine}/V_{brine} = \frac{(1+s)m_{brine}/\rho_{CO2satbrine}}{m_{brine}/\rho_{brine}} = (1+s)\,\rho_{brine}/\rho_{CO2satbrine} \tag{16}$$

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:

$$f_b = f_c \times \frac{\left(\frac{f_c}{1-f_c}+1\right)\left(\rho_{brine}/\rho_{CO2}\right)s}{\frac{f_c}{1-f_c}\left(\rho_{brine}/\rho_{CO2}\right)s + (1+s)\left(\rho_{brine}/\rho_{CO2satbrine}\right)} \tag{17}$$

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.

Case	Density NP	Density NP-CO_2 @ $P_{reservoir}$	Radius (after 2 yrs)
Case 1a	5000 kg/m^3	785 kg/m^3	420 m
Case 1a_brine	5000 kg/m^3	785 kg/m^3	400 m
Case 1b	7500 kg/m^3	872 kg/m^3	440 m
Case 2a	5000 kg/m^3	844 kg/m^3	400 m
Case 2b	7500 kg/m^3	946 kg/m^3	400 m

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.

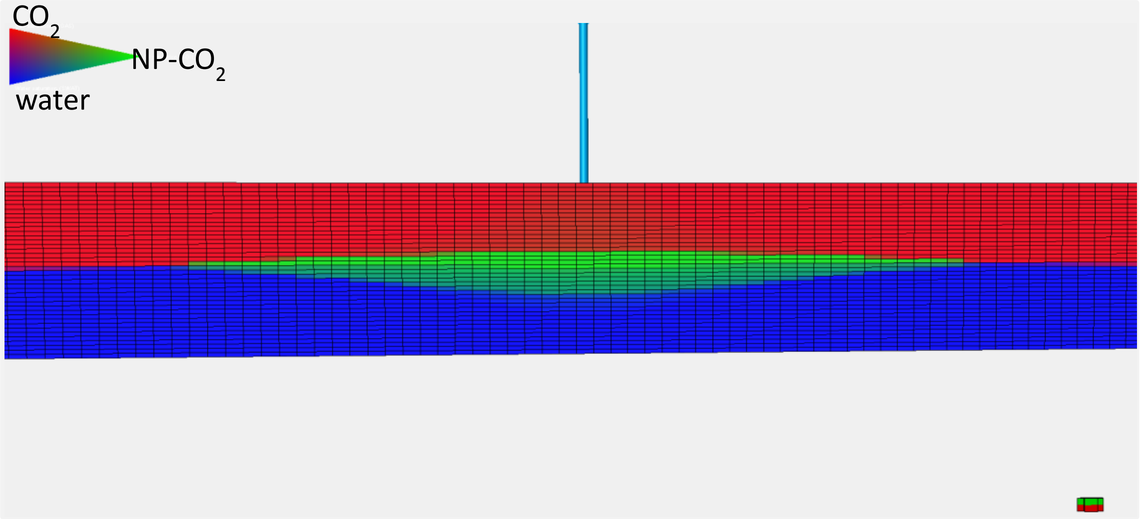

Figure 3-1. Spreading 2 years after the start of injection for case 1 (Table 3) with NP-CO_2 injection in a vertical well with NP density of 7500 kg/m3 (horizontal grid block size = 40 m). The cross section shows the CO_2 in red, the NP-CO_2 in green and in blue the brine.

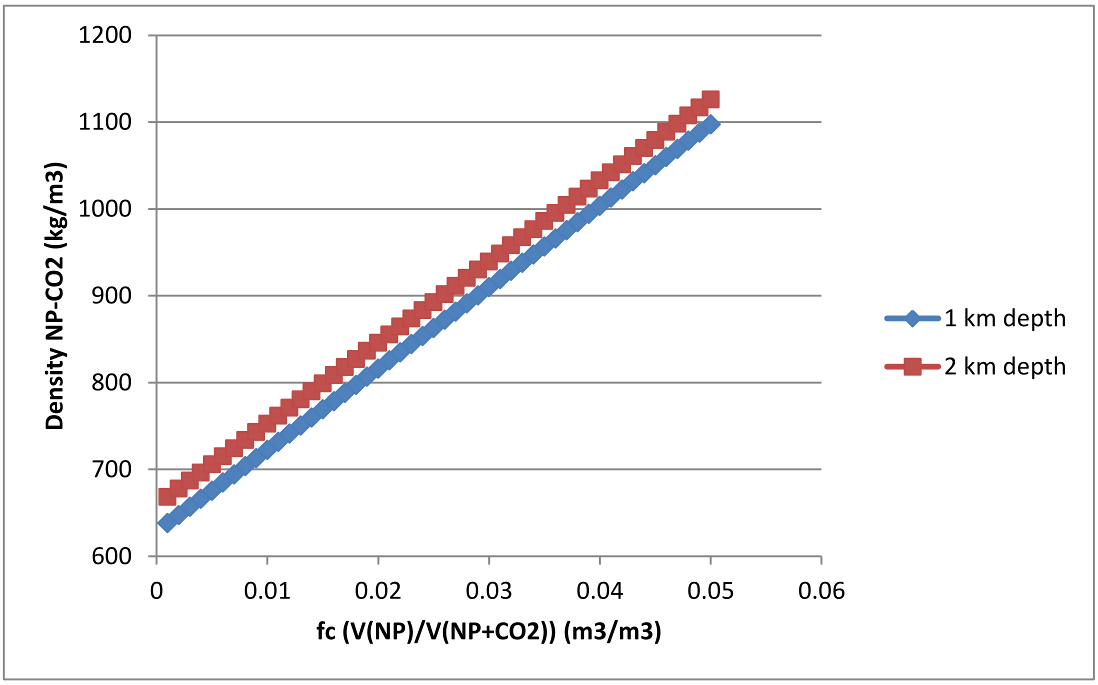

Figure 3-2. Density of NP-CO_2 as a function of the volume fraction of NPs with a density of 10.000 kg/m^3 (all at reservoir conditions) for case 1 (1 km depth) and case 2 (2 km depth).

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 CO_2 (Figure 3-3) versus 400 m away from the well for injection into brine (Figure 3-4)). Also, more NP-CO_2 was trapped due to residual trapping in the case of injection into the brine.

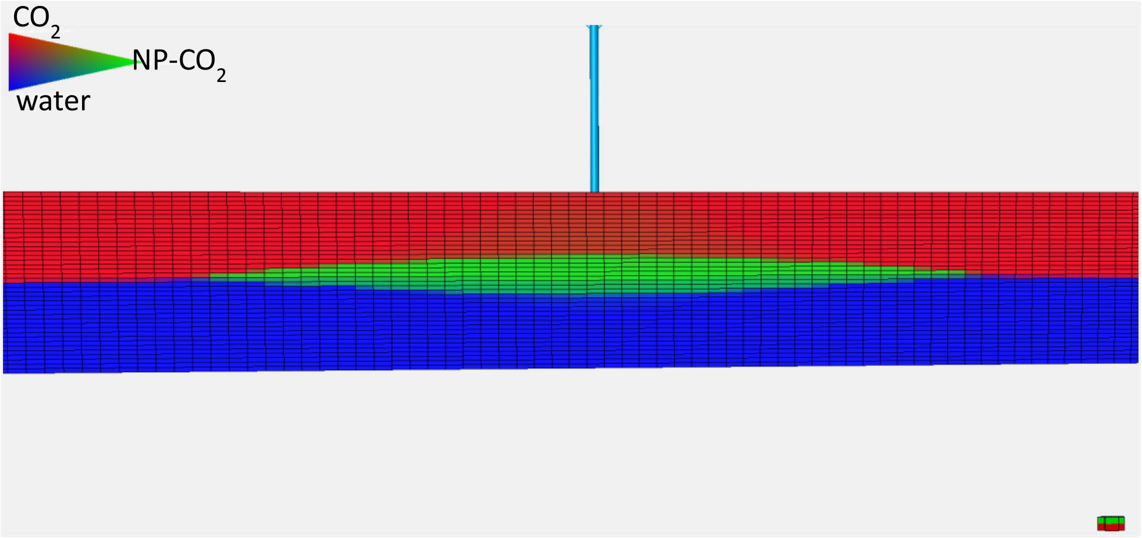

Figure 3-3. Spreading 2 years after the start of injection for case 1a for injection in the CO_2 (see Table 3). The cross section shows the CO_2 in red, the NP-CO_2 in green and in blue the brine.

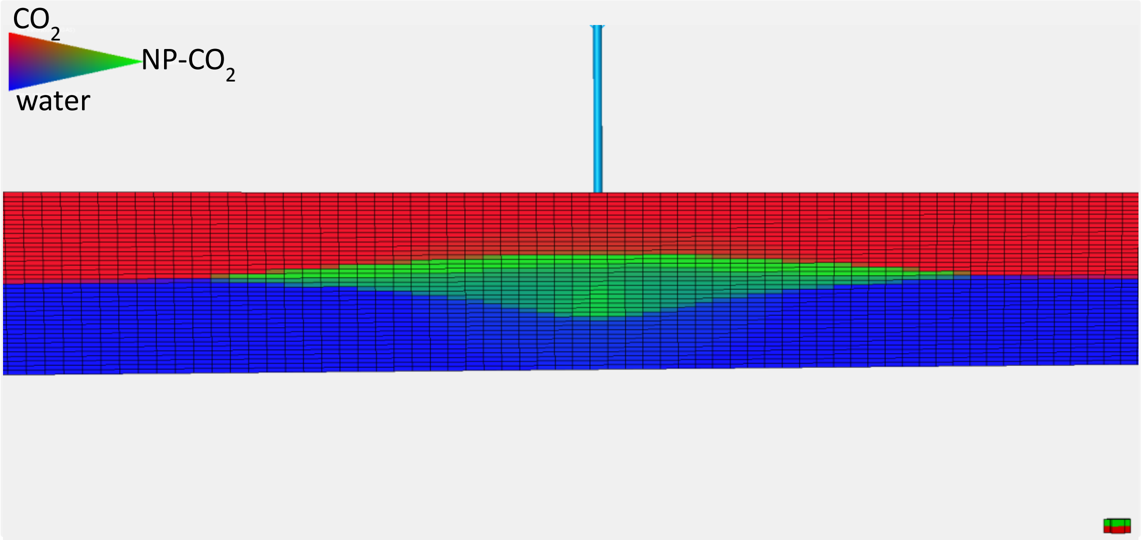

Figure 3-4. Spreading 2 years after the start of injection for case 1a_brine with injection into the brine below the CO_2. The cross section shows the CO_2 in red, the NP-CO_2 in green and in blue the brine.

3.2 Efficiency of increasing CO_2 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 CO_2 dissolution. To characterize the efficiency, the following numbers are calculated:

- Percentage increase in CO_2 dissolution flux (flux in kg/m^2/yr) (I):

$$I = 100\% * ((F_{CO2,NP} - F_{CO2})/F_{CO2}) \qquad (18)$$

Where:

$F_{CO2,\,NP}$: CO_2 dissolution flux with NP-CO_2 (kg/m^2/yr)
F_{CO2} : CO_2 dissolution flux with only CO_2 (kg/m^2/yr)

- Ratio of additional CO_2 dissolution flux and the required NP flux to reach that CO_2 flux (R):

$$R = (F_{CO2,NP} - F_{CO2})/F_{NP} \qquad (19)$$

Where:

F_{NP} : flux NPs in the flux $F_{CO2,\,NP}$ (kg/m^2/yr)

- Ratio of the additional CO_2 dissolution flux and the CO_2 input required to inject the relevant amount of NPs (R_{CO2}) (also expressed as a flux in kg/m^2/yr):

$$R_{CO2} = (F_{CO2,NP} - F_{CO2})/\left(F_{NP} * \frac{(1-f_{c,m})}{f_{c,m}}\right) \qquad (20)$$

Where $f_{c,m}$ is the mass fraction of NP in NP-CO_2, calculated from:

$$f_{c,m} = f_c * \frac{\rho_{NP}}{\rho_{NPCO2}} \qquad (21)$$

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-CO_2 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 CO_2 in the CO_2-saturated brine is the same as the volume fraction in the free CO_2. In the other cases, the volume fraction NPs in brine is reduced compared to that scenario.

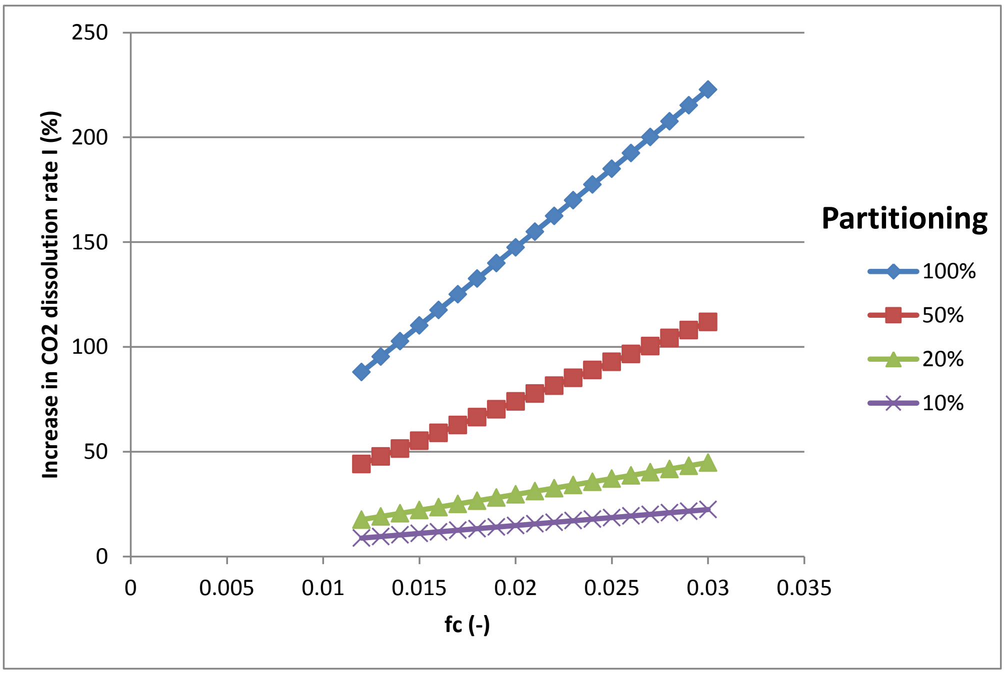

Figure 3-5. Percentage increase in CO_2 dissolution flux (I, Eq. 18) as a function of f_c for 4 different scenarios of partitioning of NPs over CO_2 and brine (100% is equal partitioning, 10% indicates a strong preference for the CO_2 phase).

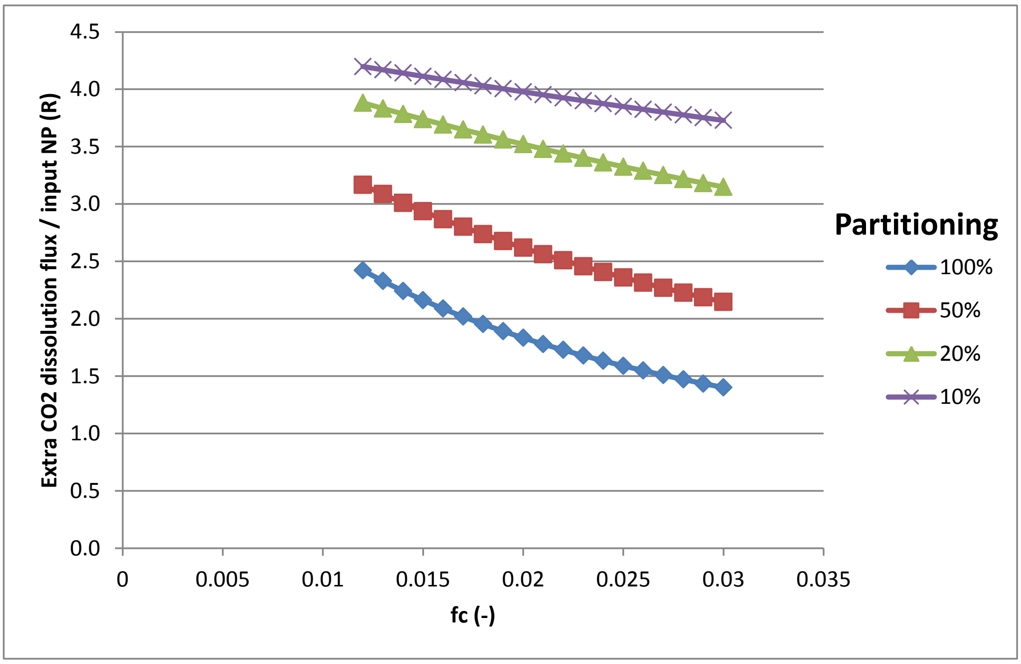

Figure 3-6. Ratio of additional CO_2 dissolution flux and the required NP flux (R, Eq. 19) as a function of f_c for 4 different scenarios of partitioning of NPs over CO_2 and brine (100% is equal partitioning, 10% indicates a strong preference for the CO_2 phase).

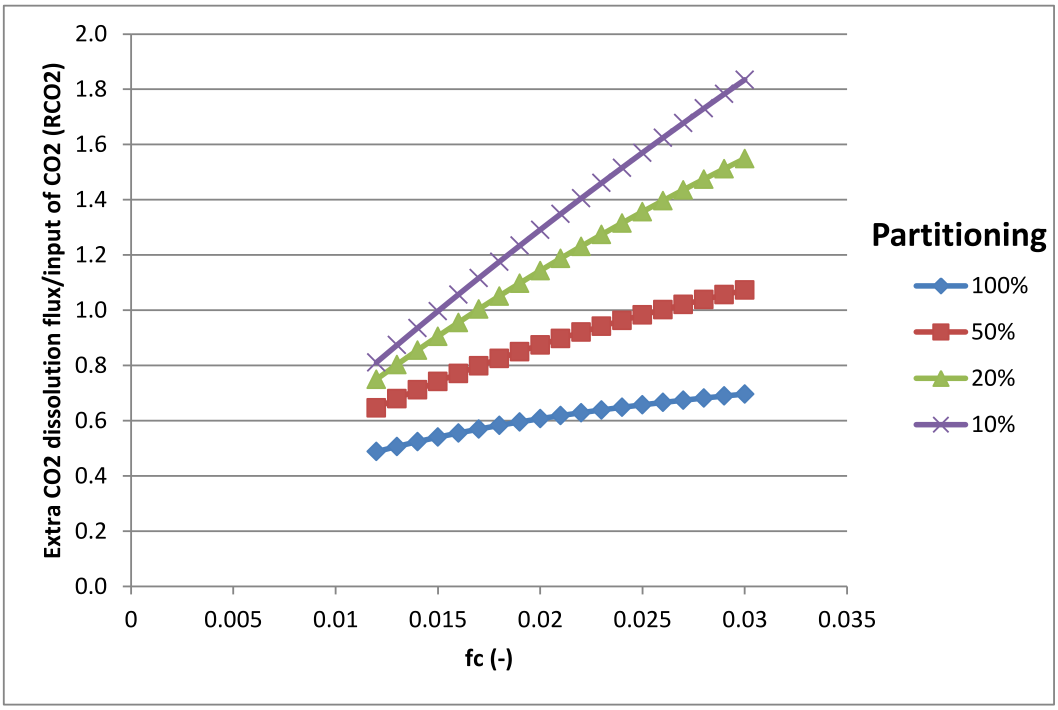

Figure 3-7. Additional CO_2 dissolution flux compared to the CO_2 input associated with the input in NPs (R_{CO2}, Eq. 20) as a function of f_c for 4 different scenarios of partitioning of NPs over CO_2 and brine (100% is equal partitioning, 10% indicates a strong preference for the CO_2 phase).

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.

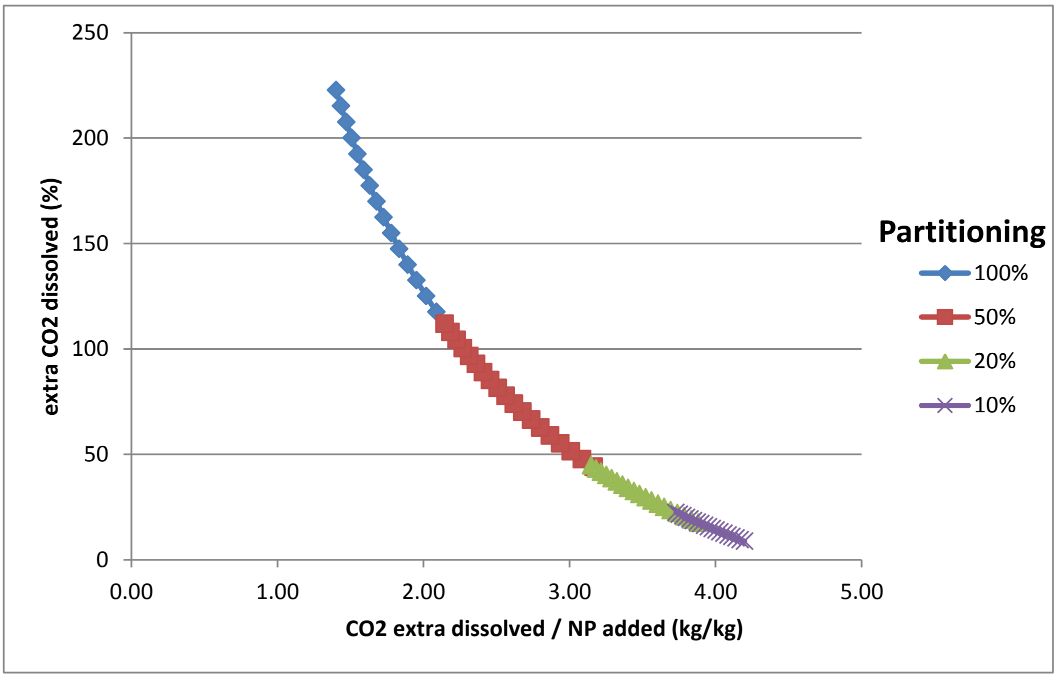

Figure 3-8. Illustration of the trade-off between a large increase in dissolution and efficient use of the NPs.

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_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_2 has already been injected. Javadpour and Nicot (2011) investigate the co-injection of NPs with CO_2 from the start of the injection of CO_2. Javadpour and Nicot (2011) stated that for co-injection of NPs from the start only a small volume fraction in the CO_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_2 (see section 2.2.3), whereas we assume that the NPs and CO_2 move into the brine together at the same volume fraction. With the assumption of Javadpour and Nicot, the CO_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 CO2. Due to the large difference in density between CO_2 and NPs (roughly a factor of 10), the mass fraction NPs in CO_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_2 is in place. A disadvantage of injecting the NPs with CO_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.

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[3] http://www.sigmaaldrich.com/materials-science/nanopowders & nanoparticle dispersions

[4] https://www.sigmaaldrich.com/catalog/product/aldrich/682659?lang=en&region=NL

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

	Partitioning 100%	**Partitioning 50%**
f_c (reservoir conditions)	0.014	0.027
Density NPs (kg/m^3)	10.000	10.000
Density NP-CO_2 (kg/m^3)	760	882
CO_2 dissolution flux (kg/m^2/yr)	8.89	8.79
Time to full dissolution (yrs)	707	715
NP flux (kg/m^2/yr)	2.01	1.94
Co-injected CO_2 flux (kg/m^2/yr)	8.89	4.40
Required Mass NP (kg)	1.13E9	1.10E9
Price NP (€)	1.13E9	1.10E9

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.

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