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Accelerating dissolution of CO_2 in brine by enhancing convective mixing as a potential remediation option

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Abstract

This paper presents a study into the possibility to enhance dissolution of CO2 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 interface 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 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: a large effort is required for engineering NPs with the correct properties, the risks associated are clogging and pressure increase, and the method is expensive.

Keywords: remediation; CCS; convective mixing

1. Introduction

In the event of undesired migration of CO_2 in deep subsurface reservoirs, remediation of some sort may be required. This paper investigates the possibilities for enhancing dissolution of CO_2 in brine as a remediation measure. Dissolution of CO_2 in brine has two safety advantages:

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- 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 [1];
- Co-injection of CO_2 with SO_2 [2];
- Co-injection of CO_2 with nanoparticles (NPs) to enhance convective mixing [3,4].

From these methods, the last method was selected in the project MiReCOL (Mitigation and Remediation of CO_2 leakage) to be investigated as potential remediation method. The MiReCOL project, which is funded by the EU FP7 programme, aims at developing a handbook of corrective measures that can be considered in the event of undesired migration of CO_2 in deep subsurface reservoirs [5,6]. 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 in the form of fingers. 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 only for the long-term storage of CO_2 [7]. Therefore, this remediation strategy is aimed at undesired migrations at 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 to accurately place the NPs;
- Assuming that the NPs are in position, 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. Although not required, it is assumed for now that the NPs are co-injected as a homogeneous mixture with CO_2: NP-CO_2. The main point addressed for the NP placement is the acceptable density of the NP-CO_2 for injection. This is discussed in section 2.1.

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. [8] is justified. This method is described in section 2.2.

The results of the analysis are discussed in Section 3. In section 4, some economic aspects and potential risks are discussed.

Nomenclature

F	flux [kg/m^2/yr]
I	increase in CO_2 dissolution flux (%)
R	ratio of increase in CO_2 dissolution flux over NP flux (-)
R_{CO2}	ratio of increase in CO_2 dissolution flux over input of CO_2
V	volume [m^3]
c_s	saturated concentration of CO_2 [kg/m^3]

f_b volume fraction of NPs in brine saturated with CO_2 [-]
f_c volume fraction of NPs in CO_2 [-]
$f_{c,m}$ mass fraction of NPs in NP-CO_2 [-]
g gravitational acceleration [m^2/s]
k permeability [m^2]
s solubility of CO_2 in brine [kg/kg]
v characteristic velocity of the fingers [m/s]
μ dynamic viscosity [Pa·s]
φ porosity [-]
ρ density [kg/m^3]
Δρ density difference between CO_2-saturated brine and brine without CO_2 [kg/m^3]

Abbreviations
NP(s) nanoparticle(s)
NP-CO_2 homogeneous mixture of CO_2 and NPs

Subscripts
CO2 CO_2
CO2Satbrine brine saturated with CO_2
NP nano particle
NPCO2 homogeneous mixture of NP and CO_2
NPCO2Satbrine brine saturated with CO_2 and NPs
brine brine

2. Methods

2.1. NP Placement

The placing of NP-CO_2 via injection can be divided in three phases (see Fig. 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.

For the acceptable density range, the NP-CO_2 should obviously be heavier than CO_2, 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-CO_2 is too light (i.e. density difference with the CO_2 is small), the spreading is not efficient. Numerical modelling showed that a density of NP-CO_2 between 750 and 950 kg/m^3 at reservoir conditions is acceptable. For more details see [9].
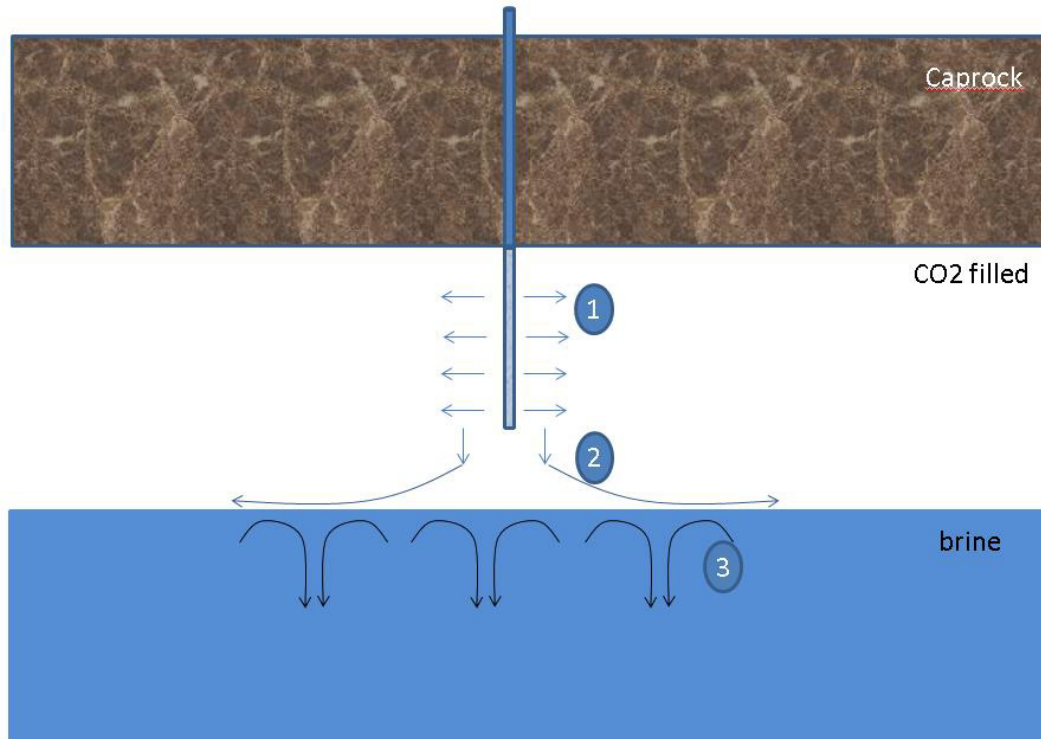
Fig. 1. Overview of the injection of CO_2 with NPs (NP-CO_2) into CO_2 overlying brine, with three distinct phases of placing NP-CO_2: (1) Injection phase, (2) spreading phase, (3) dissolution phase.

2.2. Enhanced convective mixing

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 assume that NP-CO_2 is in contact with the brine. The CO_2 dissolution flux (F_{CO2} in kg/m^2/s) in case of convective mixing (also named the fingering regime) is calculated as presented by Szulczewski et al. [8]:

$$F_{CO2} \approx 0.017 \, c_s v \tag{1}$$

Where v is the characteristic velocity of the fingers given by:

$$v = \frac{\Delta \rho g k}{\mu \varphi} \tag{2}$$

The properties affected by the NPs are $\Delta \rho$ and μ and as result v and F_{CO2}. How the density and viscosity change as a result of the NPs is shown below. First, 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:

$$f_b = {V_{NP}} \big/ {V_{NPCO2satbrine}} \tag{3}$$

with

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

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

$$f_c = V_{NP} \big/ V_{NPCO2} \tag{4}$$

with

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

The density of CO_2 as a function of pressure and temperature is taken from Lemmon et al. [10]. The density of the CO_2-saturated brine is calculated from the correlation by [11]. Density (ρ) of the NP mixtures is based on the equations provided by Javadpour and Nicot [3]:

$$\rho_{NPCO2satbrine} = (1 - f_b)\rho_{CO2satbrine} + (f_b)\rho_{NP} \tag{5}$$

$$\rho_{NPCO2} = (1 - f_c)\rho_{CO2} + (f_c)\rho_{NP} \tag{6}$$

The viscosity of the CO_2 is taken from Lemmon et al. [10]. The viscosity of the brine is calculated from Batzle and Wang [12]. 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. [13]. The viscosity (μ) of the NP-mixtures is based on the equations provided by Javadpour and Nicot [3] using Einstein's viscosity relation:

$$\mu_{NPCO2satbrine} = (1 + 2.5\, f_b)\mu_{CO2satbrine} \tag{7}$$

$$\mu_{NPCO2} = (1 + 2.5\, f_c)\mu_{CO2} \tag{8}$$

To calculate these properties of the NP-CO_2 and NP-CO_2 saturated brine, the volume fraction of NPs is required. The volume fraction NPs in free CO_2 (f_c (eq. 4)) 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 [3] 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: 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 does not depends on the solubility (s) of CO_2, for evaluation purposes it is useful to derive f_b based on case 2 and calculate 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 as given in Eq. 9. The derivation is presented in [9].

$$f_b = f_c \times \frac{\left(\frac{f_c}{1-f_c}+1\right)\left(\rho_{brine}/\rho_{CO2}\right)s}{\frac{f_c}{1-f_c}\left(\rho_{brine}/\rho_{CO2}\right)s + (1+s)\left(\rho_{brine}/\rho_{CO2satbrine}\right)} \tag{9}$$

With these inputs, the CO_2 dissolution flux with and without NPs can be calculated. Table 1 shows the input settings for the calculations.

Table 1. Input settings for calculating the efficiency of enhancing CO_2 dissolution by convective mixing.

Pressure	10 MPa (100 bar)
Temperature	40 °C
Vertical permeability	$0.5 \cdot 10^{-12}$ m^2 (500 mD)
Porosity	0.35
Salinity	3.5 %
Density NPs	10.000 kg/m^3

To characterize the efficiency, the following three numbers are defined:

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

$$I = 100\% * \left((F_{CO2,NP} - F_{CO2})/F_{CO2} \right) \tag{10}$$

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):

$$R = \left(F_{CO2,NP} - F_{CO2} \right)/F_{NP} \tag{11}$$

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):

$$R_{CO2} = \left(F_{CO2,NP} - F_{CO2} \right)/\left(F_{NP} * \frac{(1-f_{c,m})}{f_{c,m}} \right) \tag{12}$$

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

$$f_{c,m} = f_c * \frac{\rho_{NP}}{\rho_{NPCO2}} \tag{13}$$

3. Results

The three numbers defined in Eq. 9-11 are presented as a function of f_c (at downhole conditions) in Fig. 2 to Fig. 4. The values of f_c are chosen to get acceptable densities of the NP-CO_2 in terms of placement (750 to 950 kg/m^3) given the density of the NPs. 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.

The results in Fig. 2 and Fig. 3 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).

Fig. 5 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). However, the amount of NPs to be injected is large in any case.
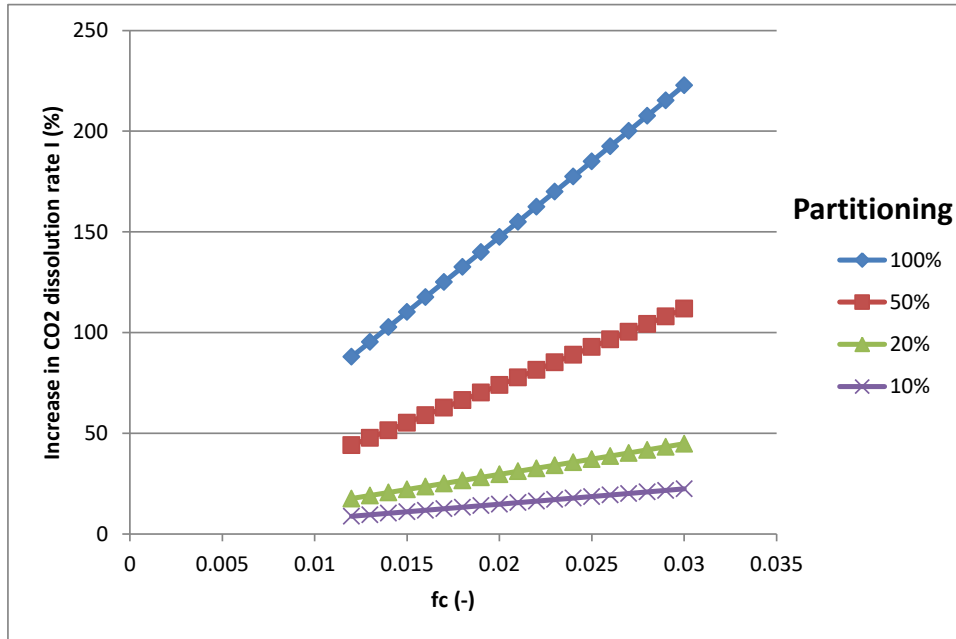

Fig. 2. Percentage increase in CO_2 dissolution flux (I, Eq. 10) as a function of f_c for 4 different scenarios of partitioning of NPs over CO_2 and brine (100% is equal partitioning, 10% indicates a strong preference for the CO_2 phase).
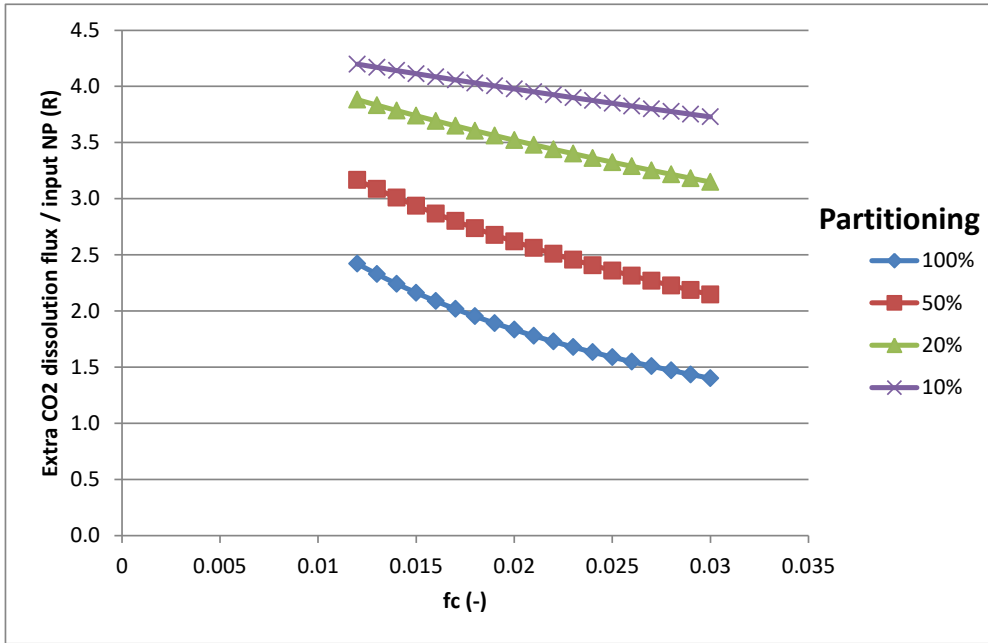
Fig. 3. Ratio of additional CO_2 dissolution flux and the required NP flux (R, Eq. 11) as a function of f_c for 4 different scenarios of partitioning of NPs over CO_2 and brine (100% is equal partitioning, 10% indicates a strong preference for the CO_2 phase).
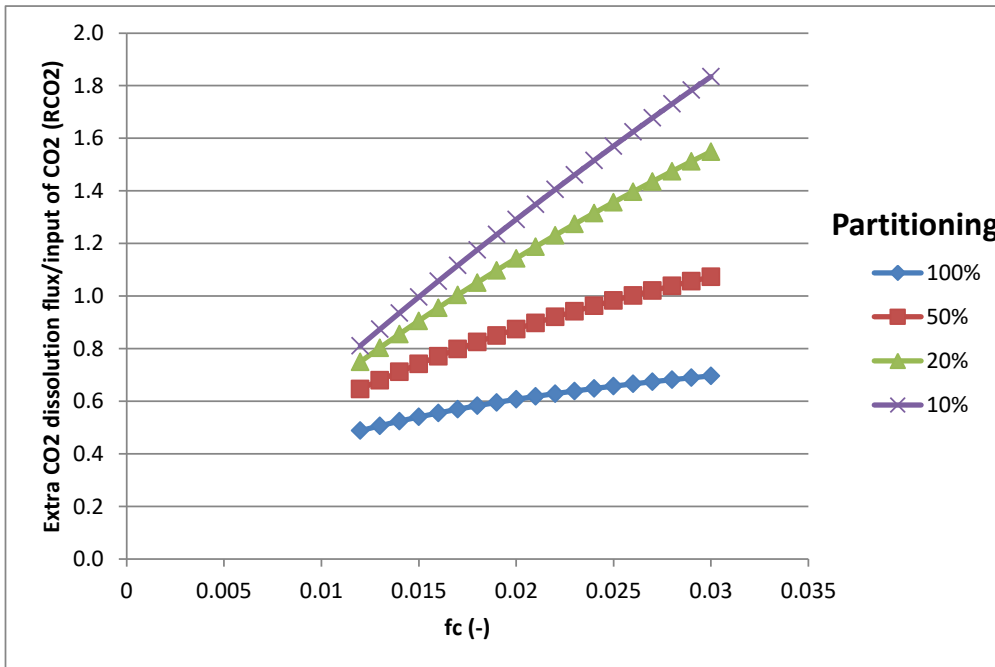

Fig. 4. Additional CO_2 dissolution flux compared to the CO_2 input associated with the input in NPs (R_{CO2}, Eq. 12) as a function of f_c for 4 different scenarios of partitioning of NPs over CO_2 and brine (100% is equal partitioning, 10% indicates a strong preference for the CO_2 phase).

4. Discussion

An important potential risk of this method is the increase 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 one also considers the amount of gas that needs to be co-injected with the NPs. The effect of the increase 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. [14]) or if they aggregate.

Cost is an important aspect of the feasibility of NPs as a corrective measure. 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 about 5000 – 25000 €/kg [15]. 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 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 100 €/kg [16]. 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 1000 €/kg is assumed for further calculations.

The cost of using NPs as a remediation option is derived with an example calculation.
The goal is to dissolve 5 Mt CO_2 at doubled dissolution rate at a pressure of 10 MPa (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 10 m, the surface area of CO_2 is $7.95 \cdot 10^5$ m^2. From Fig. 2, it can be seen that a doubled dissolution rate (100% increase) can be achieved in two ways: for 100% partitioning with $f_c = 0.014$ and with 50% with $f_c = 0.027$. The calculation of the cost for these two cases is summarized in Table 2.

Table 2. Example calculation of cost for use of NPs for two cases for dissolving 5 Mt CO_2.

	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, Mt)	$1.13 \cdot 10^9$, 1.13 Mt	$1.10 \cdot 10^9$, 1.10 Mt
Cost NP (€)	$1.13 \cdot 10^{12}$	$1.10 \cdot 10^{12}$

From this table, it is clear that the cost are prohibitive: for dissolving 5 Mt CO_2 already more than 1 Mt NP is necessary, which would cost 1 trillion € at a price of 1000 €/kg. At a greatly reduced cost of 1 €/kg, the cost would still be more than a billion € for 5 Mt CO_2. Even when using waste (depleted uranium oxides) as suggested by Javadpour and Nicot [3], costs are associated with the NPs. Creating particles of the right size can be expensive and is not straightforward [17]. For example, Javadpour and Nicot [3] cite the work by Hastings et al. [18], in which particles are created. However the particles created 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.

One aspect of the NPs on convective mixing was not discussed so far: due to the presence of the NPs convective mixing will start earlier. This advantage however is small compared to the total amount of CO_2 to be dissolved.

4. Conclusions

In conclusion, enhancing convective mixing using nanoparticles was found to be an inefficient remediation method. 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 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 prohibitively expensive;
- the method is slow (order 10-100 years).

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