Mitigating CO 2 Leakage by Immobilizing CO 2 into Solid Reaction Products

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Mitigating CO₂ leakage by immobilizing CO₂ into solid reaction products

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Abstract

In the unlikely case of CO₂ leakage from a storage reservoir, it is desirable to close the leak efficiently and permanently. This could be done by injecting a reactive solution into the leak path, thereby immobilizing migrating CO₂ by consuming the gas and forming solid reactants. With regard to permanent closure, it is important to consider materials that are stable in the long-term, ensuring permanent CO₂ containment. Numerical modelling was applied to assess the feasibility of injecting calcium-rich water as a CO₂-reactive solution to form calcite. A scenarios analyses of key parameters showed that the success of leakage remediation can be up to 95% when carefully balancing the injection rate and distance versus the permeability and leakage rate.

Keywords: CO₂ leakage remediation; Chemical clogging; Reactive transport modelling; CO₂ storage

1. Introduction

To store CO₂ permanently in the subsurface, reservoirs are selected that provide physical containment of CO₂. In the unlikely event of localized leakage from a CO₂ storage site, a corrective measures plan must be in place and appropriate remediation measures should be initiated. Flow mitigation measures need to be developed to demonstrate possibilities for preventing CO₂ migration to overlying aquifers or to the surface, ensuring the

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contribution of the stored CO_2 to reduced global warming [1,2]. We present a method for CO_2 mobility control by injecting a CO_2-reactive and CO_2-consuming solution into the CO_2 leak path to form solid reactants that clog the pore space, reduce permeability and minimize leakage. This work is part of the EU FP-7 MIRECOL project which aims at creating a toolbox of techniques to mitigate and/or remediate undesired migration or CO_2 leakage out of the envisaged containment. Knowledge and experience on the mitigation of CO_2 leakage will help to build confidence in the safety of deep subsurface CO_2 storage.

Immobilizing migrating CO_2 by forming solid reactants is a relatively new field. Forming mineral solid reactants will have the advantage of creating a naturally stable barrier against CO_2 flow. Experience with unintentional precipitation (scaling and formation damage) as commonly encountered in the oil and gas or geothermal industries, sheds some light onto the options of possible solid reactants. Frequently occurring scales associated with oil and gas production are calcite, anhydrite, barite, celestite, gypsum, iron sulphide and halite [3]. Re-injection of production water is prone to scaling of calcite, while strontium, barium and calcium sulphates are more often observed during seawater injection [4,5]. Low enthalpy geothermal water re-injection may cause precipitation of carbonates, silica and metal compounds [6,7 and references therein]. Considering CO_2 storage, (slow) mineralization reactions between the stored CO_2 and the host rock may occur in the longer term. Much research has been done on this topic since these reactions provide permanent trapping and increased the storage safety [e.g. 8]. CO_2 mineralization reactions may have the additional benefits of CO_2 consumption as well as clogging for leakage remediation.

Considering intentional clogging for flow control, Wasch et al. [9] proposed controlled precipitation of salt as a preventative measure against possible leakage of CO_2 along wellbores. Nasr-El-Din et al. [10] proposed injecting a fluid that is chemically incompatible with the reservoir brine in order to induce mineral precipitation for selecting plugging and flow control. Previous work on forming solid reactants specifically for leakage remediation concerns calcite and silica. Bio-mineralization has been proposed for engineering biofilms covering grains, subsequently forming carbonate by ureolysis [11,12]. Carbonate can also be directly formed by injecting reactive suspensions or solutions into the CO_2 containing environment [13]. Ito et al. [13] report on experiments and modelling of a chemical substance that will react with CO_2 to form a barrier for further CO_2 leakage. They injected both silica and calcium grouts into a synthetic porous medium of glass beads. The experimental results support the feasibility of the method for reactive clogging of a high permeable leak path. Druhan et al. [14] investigated numerically the formation of amorphous silica adapted for a higher molecular volume analogous to silica polymers to stimulate clogging.

We considered a calcium-rich reactive solution that reacts immediately upon contact with CO_2 forming calcite which is stable at reservoir conditions. This approach has the advantage that reactions can be modelled with available software and databases without modifications. The production and practical use of such a fluid is beyond the scope of this study. Leakage remediation was modelled in three steps. First, a CO_2 leak was defined within the caprock. A buoyancy and/or a pressure gradient drives CO_2 upwards which forms a plume of CO_2 in the aquifer above the leaking caprock. Second, the injection of a CO_2-reactive solution into the plume near the leak was simulated, creating conditions in favour of forming solid reactants above the leak. Third, a post-injection equilibration phase was simulated. This last step indicates if further migration of CO_2 is successfully prevented by clogging.

2. Methods

2.1. Simulator

The simulations were performed with the TOUGHREACT reactive transport flow simulator, using the Petrasim interface. TOUGHREACT has been developed for coupled modelling of subsurface multiphase fluid and heat flow, solute transport, and chemical reactions by introducing reactive transport into the flow simulator TOUGH2 [15]. TOUGH2 is a numerical simulation program for multi-dimensional fluid and heat flow of multiphase, multicomponent fluid mixtures in porous and fractured media [16]. We used the ECO2N fluid property module for CO_2 and brine mass transfer including the thermodynamics and thermophysical properties of H_2O-NaCl-CO_2 mixtures [17]. Mineral reaction kinetics are included using reaction rates of Palandri and Kharaka [18].

2.2. Model setup

A 3D model was developed of an aquifer overlying a CO_2 reservoir and one cell connecting the two layers, representing a caprock leakage pathway such as a permeable fault or a leaking wellbore (Figure 1a). For simplicity, the caprock cells were disabled except for the vertical leak path. The model dimensions are 200*200*140 meter and the model was arbitrarily located at 2000 m depth. The mesh contains 11 layers in the z direction and 22 cells in the x and y direction, with grid refinement in the top aquifer to obtain more detail at the location of leakage and injection (optimized within the 8000 active cells as allowed by TOUGHREACT). The lateral boundary conditions are open (i.e. given an infinite volume factor) assuming an infinite reservoir and aquifer compared to the small 200 m model. The top and lower boundary conditions are closed, assuming the presence of impermeable bounding formations.

The rock properties were based on the P18 field in the Netherlands offshore with a reservoir porosity of 15% and a horizontal (kh) and vertical (kv) permeability of 20 and 2 mD respectively (Permeability expressed in Darcy or milliDarcy (mD), with 1 Darcy equivalent to $9.9 \cdot 10^{-13}$ m²). For relative permeability, Corey curves were selected with a residual liquid saturation of 0.18 and a residual gas saturation of 0.121. For the capillary pressure a Leverett's function was applied using a P0 of $1 \cdot 10^6$. For simplicity, the flow properties of the overburden aquifer, leak and reservoir were taken equal, only for the leak the vertical permeability is taken the same as the horizontal permeability. A scenarios analysis on key parameters such as permeability was performed and will be discussed in the relevant sections on leakage, remediation and equilibration results.

The initial conditions for model initialization are 200 bar pressure, $1 \cdot 10^{-10}$ gas saturation and a 0.06 salt mass fraction. The temperature is selected to be 80 °C and non-isothermal behaviour is neglected. The model is first run for initialization, in order to distribute the pressure, gas saturation and brine composition with depth according gravitational forces. Secondly the CO_2 storage conditions were applied to the reservoir and the leak was enabled through the caprock. A CO_2 plume is therefore present in the top aquifer as an initial condition (Figure 1b). This represents the status in the subsurface after leakage detection by monitoring techniques and before action would be taken to remediate leakage. Different CO_2 storage conditions and were simulated to assess their effect on leakage, remediation and equilibration.
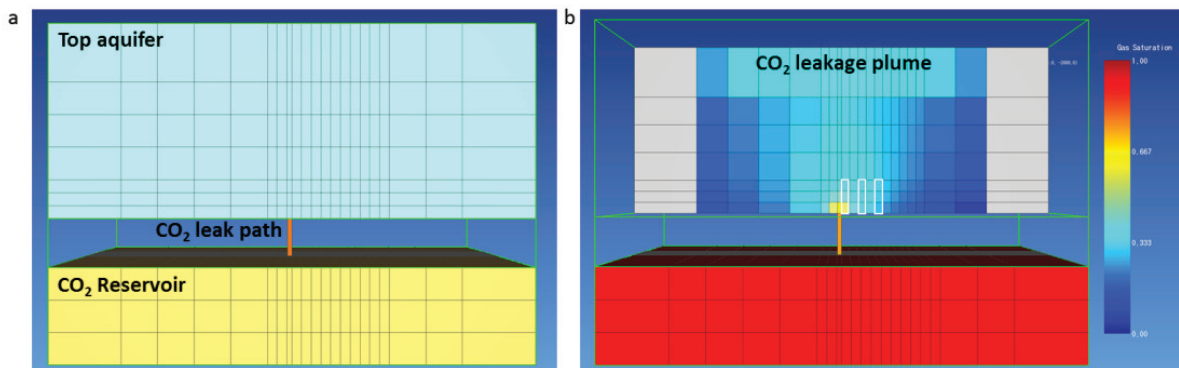
Fig. 1. (a) The model with a top aquifer overlying a CO_2 reservoir and a leak through the caprock; (b) Cross section in the top aquifer showing the plume of CO_2 above the leak. The three white rectangles indicate the cells for the three injection locations of the remediation fluid into the CO_2 plume.

The initial formation water in the aquifer above the caprock was calculated by equilibrating pure brine with a simple sandstone mineralogy (Table 1). Only the water is used for further modelling, reservoir rock – fluid/gas reactions are neglected given short time frame of interest for leakage remediation. We injected a calcium saturated solution to stimulate calcite precipitation when reacted with dissolved CO_2 (Equation 1). The composition of the injected reactive solution was computed by equilibrium with lime (CaO) and has a calcium concentration of 0.68 mol/kg water and a pH of 12.

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \tag{1}$$

Table 1. Chemical characteristics.

Mineralogical composition	Formula	Volume fraction
Quartz(alpha)	SiO_2	0.7
Microcline	$K(AlSi_3)O_8$	0.1
Illite(Al)	$K_{0.85}Al_{2.85}Si_{3.15}O_{10}(OH)_2$	0.1
Albite(high)	$NaAlSi_3O_8$	0.1
Formation water composition		mol/L
Cl		1
Na		$9.99 \cdot 10^1$
Si		$7.30 \cdot 10^4$
K		$1.09 \cdot 10^3$
Al		$3.04 \cdot 10^7$
pH		8.03

Porosity changes due to mineral dissolution or precipitation are calculated by TOUGHREACT using mineral specific molar volumes. All cells were assigned a porosity-permeability relationship to model the effect of precipitation and related porosity decrease on the flow of CO_2. This relationship is a large unknown for fluid-rock interactions and their effect on fluid flow, and depends on rock type, pore morphology and type of chemical reactions. The most commonly used relationship for porous media is the one by Verma-Pruess (Equation 2) as implemented in TOUGHREACT [20]. The relation is based on a porous medium consisting of pore throats and pore bodies. A small change in porosity can result in a large change in permeability, reflecting the process of pore throat blockage by precipitates which reduces flow although the bulk of the pore space is left unfilled. The relation uses two parameters, a critical porosity (the porosity below which the permeability is reduced to zero) and a power law exponent (defining the rate at which the permeability decreases). We assumed a critical porosity of 12% as a 100% remediation success, and a power law exponent of 8. These numbers are rock dependent and probably not known for many aquifers, hence the effect is studied in a sensitivity analyses.

$$\frac{k}{k_i} = \left(\frac{\phi - \phi_c}{\phi_i - \phi_c}\right)^n \tag{2}$$

With k being permeability, k_i for initial permeability, ϕ for porosity, ϕ_i for the initial porosity, ϕ_c for the critical porosity and n for the power law exponent.

3. Results

A scenario analysis is performed to assess the effectiveness of the remediation method and to evaluate the uncertainty related to the key parameters. The scenarios represent a range of possible characteristics of the storage reservoir and the leak itself that could affect the success of the leakage remediation method. These key parameters include: reservoir pressure, reservoir gas saturation, aquifer and leak permeability, leakage rate, injection rate and injection distance from the leak path. The success of leakage remediation is defined as the change in CO_2 leakage rate and the amount of calcite porosity clogging straight above the leak. This will indicate the effectivity and applicability of the leakage remediation method. The results of the different model scenarios will be discussed for the leakage, remediation and equilibration stage.

3.1. Leakage stage

The leakage rate is controlled by the pressure difference between the reservoir and the top aquifer, their flow properties and the properties of the CO_2. To consider different leakage rates for subsequent leakage remediation, several simulations were run with varying properties. A range in permeabilities is considered to represent relevant values, high enough to allow efficient water injection and up to values of a reasonable reservoir rock (Table 2). CO_2 storage conditions were implemented for two different types of storage sites (Table 3). The first represents aquifer-storage where the pressure increases during CO_2 injection, yielding an overpressure. The second represents a depleted gas field which is filled until hydrostatic pressure is regained. Simulations for aquifer-storage were performed with gas saturations of 0.9 and 0.3 to represent end members of gas saturation in a storage reservoir; high close the well and low further into the CO_2 plume. For storage in a depleted gas field, a range is not relevant and simulations were only performed with a gas saturation of 0.9.

Table 2. Permeability scenarios.

Permeability Scenario	Reservoir & Aquifer		Leak
	Kh (mD)	Kv (mD)	Kv (mD)
1	20	2	20
2	200	20	200
3	400	40	400
4	800	80	800

Table 3. Reservoir scenarios.

Reservoir scenario	Reservoir type	
	Pressure	Gas saturation
a	20 bar overpressure	Saturated (0.9)
b	hydrostatic	Saturated (0.9)
c	20 bar overpressure	Under-saturated (0.3)

Since we aim to study remediation for the case of an existing leak, we allow the leakage rate and related plume in the overlying aquifer to develop for a period of 10 years. This period should allow for a plume to become large enough to be detected by conventional monitoring techniques. For reservoir scenario a (overpressured, high gas saturation) the resulting leakage rate ranges from 0.27 to 10.93 mega ton per year for different permeabilities (1a to 4a, Table 4). Basically, twice the permeability yields twice as fast leakage. This linear relation is shown for all three reservoir scenarios, although the absolute leakage rates are far lower for b and c. This is due to the absence of a pressure gradient for the hydrostatic scenarios, with CO_2 migration only driven by buoyancy (1b to 4b, Table 4), and due to the lower gas content (1c to 4c, Table 4). The low saturation scenarios 1c to 4c yield mobile water and hence leakage of water (and dissolved CO_2) as well as gaseous CO_2. Since the overpressured, high saturation scenarios 1a to 4a yield the most variation in leakage rates, these 4 scenarios were selected for further modelling of leakage remediation.

Table 4. Leakage scenarios and resulting leakage rates for varying permeabilities (reservoir and aquifer kh being equal to the leak kv) and reservoir CO_2 gas saturation (Sg) and pressure (P).

Leakage scenarios	Permeability scenarios		Reservoir scenarios		Leakage rates	
					Gas (mton/yr)	Water (mton/yr)
1a	*1*	Leak kv 20 mD	*a*	0.9 Sg, P + 20 bar	0.27	0
2a	*2*	Leak kv 200 mD	*a*	0.9 Sg, P + 20 bar	2.71	0
3a	*3*	Leak kv 400 mD	*a*	0.9 Sg, P + 20 bar	5.39	0
4a	*4*	Leak kv 800 mD	*a*	0.9 Sg, P + 20 bar	10.93	0
1b	*1*	Leak kv 20 mD	*b*	0.9 Sg, P hydrostatic	0.02	0
2b	*2*	Leak kv 200 mD	*b*	0.9 Sg, P hydrostatic	0.18	0
3b	*3*	Leak kv 400 mD	*b*	0.9 Sg, P hydrostatic	0.36	0
4b	*4*	Leak kv 800 mD	*b*	0.9 Sg, P hydrostatic	0.72	0
1c	*1*	Leak kv 20 mD	*c*	0.3 Sg, P + 20 bar	0.01	0.01
2c	*2*	Leak kv 200 mD	*c*	0.3 Sg, P + 20 bar	0.12	0.13
3c	*3*	Leak kv 400 mD	*c*	0.3 Sg, P + 20 bar	0.24	0.26
4c	*4*	Leak kv 800 mD	*c*	0.3 Sg, P + 20 bar	0.47	0.52

3.2. Remediation stage

After simulating leakage for a period of 10 years, the calcium-rich solution is injected into the aquifer close to the leak. The injection rate and distance from the leak are parameters that can to a certain degree be controlled by the operator. We investigate a range to take into account the uncertainty linked to the seismic resolution or other monitoring techniques (not allowing for a precise determination of the location of the leak), and uncertainty in permeability and pressure response of the aquifer (causing injection not be executed as planned). The three selected injection locations are indicated in a cross-section of the model, also showing the CO_2 plume (Figure 1b), with distances of injection to the leak point of 3, 11 and 19 m. The selected injection rates range between 3, 15, 30 and 60 kg/s (with 60 kg/s being approximately 100 m^3/hr of fluid down the well) and are considered to be realistic injection rates. The remediation scenarios are run for four of the leakage scenarios described above, thus considering four permeability values and corresponding leakage rates as starting points for remediation (1a to 4a, Table 4). The remediation scenarios are combinations of 4 permeabilities, 4 injection rates and 3 injection locations, yielding 48 scenarios.

First, the characteristics of remediation are described for a scenario of injection at 11 m distance from the leak with an injection rate of 15 kg/s and using leakage scenario 2a (Table 4). Since the gas in the plume above the leak is pushed away by injection of the reactive solution, the pressure rises (Figure 2a) and the gas saturation drops around the injection point (Figure 2b). The high pH calcium solution (Figure 2c) is injected into the CO_2 plume where the dissolved CO_2 (Figure 2d) combines with the dissolved calcium (Figure 2e) to form solid calcite (Figure 2f). As long as it remains open, the leak provides additional CO_2 for the formation of calcium carbonate. This is favorable for the remediation process since this calcite forms right above the leak, clogging the pore space and decreasing porosity (Figure 2g) and permeability (Figure 2h).

Remediation in the different scenarios is compared for the change in leakage rate and the calcite porosity clogging above the leak. For the 48 remediation scenarios this is reported in Table 5 and 6. Results are given for the end of the remediation process, i.e. when the permeability becomes too low for further injection. Note that some scenarios could not be run since the low permeability did not allow for high injection rates, suggesting that 20 mD is near the low permeability limit of injection. The change in leakage rate after the remediation procedure suggests that for all considered permeabilities (and respective initial leakage rates) a 100% remediation success can be achieved given a right combination of injection distance and injection rate (Table 5). For higher permeabilities, higher injection rates are required to achieve full leakage reduction. Furthermore, injection close to the leak point generally increases the percentage of leakage reduction. For the calcite in the cell above the leak, there is a sweet spot of high calcite precipitation for medium to high permeabilities, low to medium injection rates and injection close to the well (Table 6).

Several scenarios show a change of leakage rate of more than -100 % indicating that flow is inverted through the leak path due to the pressure of water injection. Although there is no more leakage during the remainder of the remediation procedure, flow is evidently still possible through the leak. This conclusion is confirmed by the amount of calcite in the cell above the leak, which can be relatively low (insufficient for porosity clogging) for scenarios that showed a more than 100% decrease in leakage rate and *appeared* to be successful (Table 5). Clearly, the amount of calcite formed in the cell above the leak (Table 6) and the change in leakage rate (Table 5) do not necessarily correlate. This can be explained since remediation during injection is a combined chemical and hydraulic process, which implies that flow through the leak is suppressed by a reduction in permeability and by the additional pressure of water injection. Different scenarios have varying relative contributions of hydraulic and chemical remediation to the reduction of leakage. Therefore the final leakage reduction should be determined without the hydraulic component to assess the actual leakage reduction and success of remediation. This is especially important since none of the scenarios reaches the critical porosity of 12% for complete clogging below which permeability is assumed to be zero (i.e. a critical volume of calcite above $3.0 \cdot 10^{-2}$, Table 6). The simulations on the post-injection stage are presented in section 3.3.
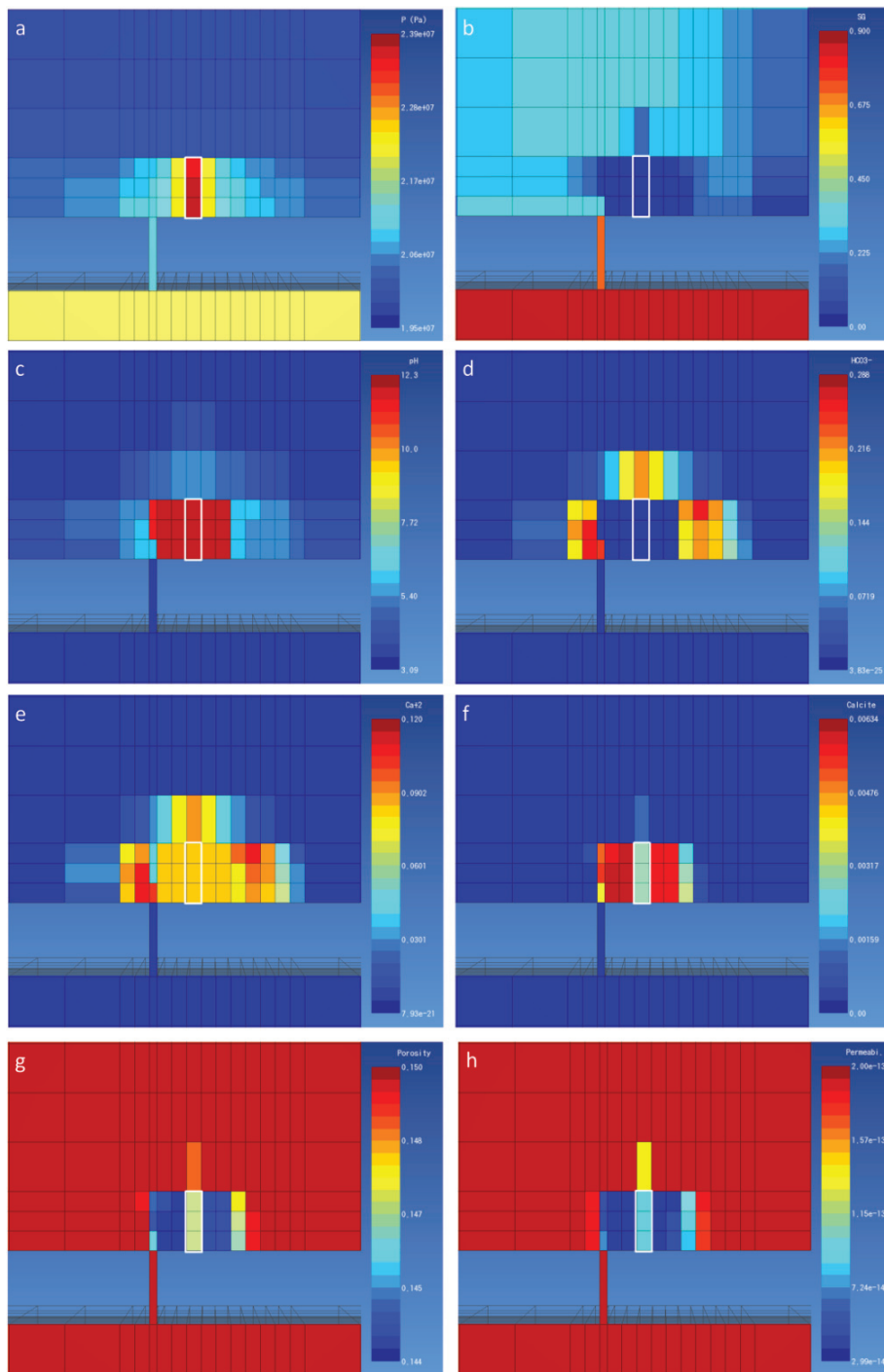
Fig. 2. Results for several parameters in 90 by 90 m details of a y-axis cross section through the centre of the model. Injection of the CO_2 reactive solution is characterized by: a) pressure increase, b) gas saturation decrease, c) high pH zone within the low pH CO_2 plume, d/c) high HCO_3^- and Ca^+ concentrations at the front of the injected solution, e) resulting calcite precipitation, g/h) related porosity & permeability decrease.

Table 5. The key scenario parameters are shown on the left for injection distance and permeability and on top for the injection rates. The resulting change in leakage rate (%) for all the combinations of parameters is shown in the coloured cells. The colours indicate a ranking from more (green) to less (red) successful scenarios and scenarios that did not run are shown in grey.

Injection distance (m)	Permeability kh, kv (mD)	Injection rate (kg/s)			
		3	15	30	60
3	20, 2	-103			
3	200, 20	-100	-102	-101	-97
3	400, 40	-68	-100	-102	-101
3	800, 80	-41	-100	-100	-108
11	20, 2	-101	-113		
11	200, 20	-39	-100	-100	-107
11	400, 40	-22	-83	-97	-100
11	800, 80	-14	-47	-76	-85
19	20, 2	-64	-114		
19	200, 20	-28	-65	-72	-102
19	400, 40	-13	-43	-45	-72
19	800, 80	-3	-23	-19	-40

Table 6. The key scenario parameters are shown on the left for injection distance and permeability and on top for the injection rate. The resulting calcite precipitation (volume factor) above the leak for all the combinations of parameters is shown in the coloured cells. The colours indicate a ranking from more (green) to less (red) successful scenarios and scenarios that did not run are shown in grey.

Injection distance (m)	Permeability kh, kv (mD)	Injection rate (kg/s)			
		3	15	30	60
3	20, 2	5.1E-03			
3	200, 20	1.8E-02	4.4E-03	3.9E-03	9.7E-04
3	400, 40	1.5E-02	1.3E-02	3.7E-03	4.2E-03
3	800, 80	1.3E-02	1.7E-02	1.3E-02	2.1E-03
11	20, 2	7.8E-03	5.5E-03		
11	200, 20	1.1E-02	1.9E-02	7.7E-03	3.9E-03
11	400, 40	9.2E-03	1.4E-02	1.1E-02	6.2E-03
11	800, 80	8.7E-03	1.2E-02	1.3E-02	9.9E-03
19	20, 2	1.8E-05	9.8E-06		
19	200, 20	4.8E-03	7.9E-03	7.9E-04	6.6E-05
19	400, 40	1.7E-03	7.5E-03	4.9E-04	5.2E-05
19	800, 80	3.4E-04	6.7E-03	3.5E-05	1.9E-05

3.2.1. Sensitivity to the porosity-permeability relationship

The sensitivity of leakage reduction towards the porosity-permeability relationship was assessed by varying the Verma-Pruess relation input parameters, the critical porosity and the power law component. All porosity permeability relationships were tested for the scenario of 200 mD permeability with 3 m distance and 3 kg/s injection. With a higher power law exponent, the permeability reduction is larger when porosity reduces. This is illustrated by the similar calcite content but lower permeability for higher power law exponents (12-6 and 12-10 versus the base case 12-8, Table 7). With a lower critical porosity, more calcite needs to precipitate to clog the pore space and hence the remediation method would be less effective although the calcite content is higher (11-8 and 13-8 versus the base case 12-8, Table 7). The sensitivity study indicates the importance of the porosity-permeability relationship in the effectivity and applicability of the remediation method. With a more favorable porosity-permeability relationship for clogging, the remediation results as described in Table 5 could be more positive given the same calcite content (Table 6).

Table 7. Remediation results for different porosity-permeability relationships. The first number in the scenario name is the critical porosity for complete permeability reduction, the second the power law exponent.

Scenario	Change in leakage rate (%)	Calcite (Volume Fraction)	Permeability (mD)
12-8	-100.0	1.79E-02	0.14
12-6	-79.1	1.86E-02	0.60
12-10	-100.0	1.77E-02	0.026
11-8	-76.0	2.02E-02	0.73
13-8	-100.0	1.45E-02	0.006

3.3. Equilibration stage

To assess the final success of leakage remediation – attributed only to chemical clogging – an equilibration stage of up to 100 days is modelled after the remediation stage. Flow is simulated according to the pressure gradients created during injection of the reactive solution and the changed permeability due to calcite precipitation, but now without the pressure of injection. Whether leakage will commence again depends on proper placement and durability of the calcite barrier. In Figure 3, three scenarios (of equal initial permeability and leakage rate but different injection rates and distances) are presented to illustrate different outcomes of the equilibration stage. During remediation the scenario of Figure 3a shows a gradual decline of the leakage rate to zero while calcite increases. The scenario is quite successful since during the equilibration stage the leakage builds up to only 20% of the initial value while calcite remains roughly constant. The cartoon of Figure 3a shows the proper placement of the calcite barrier (in purple) above the caprock leak preventing flow of CO_2 (in green) through the leak. The scenario of Figure 3b shows faster leakage reduction during remediation to below zero, indicating flow of the reactive solution into the leak. As a result, CO_2 supply is blocked and not enough calcite can precipitate. The cartoon of Figure 3b shows the flow through the leak (in blue) and the improper placement of the barrier with insufficient calcite precipitation above the leak. In the equilibration stage leakage commences again (even causing some additional calcite precipitation) resulting in a final reduction of 37%. The scenario of 3c illustrates unsuccessful remediation with almost no calcite above the leak since clogging occurred before the leak was reached, as illustrated in the cartoon in Figure 3c. Although varying in success, the scenarios showed no significant calcite dissolution within the simulation time of 100 days.

Since the 19 m injection scenarios resulted in little to no calcite precipitation in the remediation stage (all comparable to Figure 3c) these scenarios were not considered further for the equilibration phase. The 37 remaining scenarios show a large variation in leakage reduction (Table 8). For all equilibration scenarios leakage re-establishes to a certain degree, as was expected from the injection stage which indicated a lack of complete clogging. The most successful scenarios are characterised by a medium to high permeability and a low injection rate. The most successful scenarios after equilibration also have the highest calcite precipitation above the leak (Table 6 compared

to Table 8). The fastest injection rate and the lowest permeability (corresponding to a low initial leakage rate) yield little success in remediation. Some of these scenarios yielded complete leakage reduction during remediation due to the pressure of water injection (Table 5) but only limited leakage reduction after equilibration (Table 8). These scenarios had a large hydraulic and small chemical component in leakage remediation and when no more water is injected, only the chemical remediation remains. It can be concluded that the success of leakage remediation during injection is very different from the actual success after equilibration. The simulations show some additional calcite precipitation, but more importantly no dissolution of calcite. The most numerically stable scenarios were run for 1000 year and showed no significant dissolution above the leak, indicating that the calcite barrier can remain stable in the long-term.
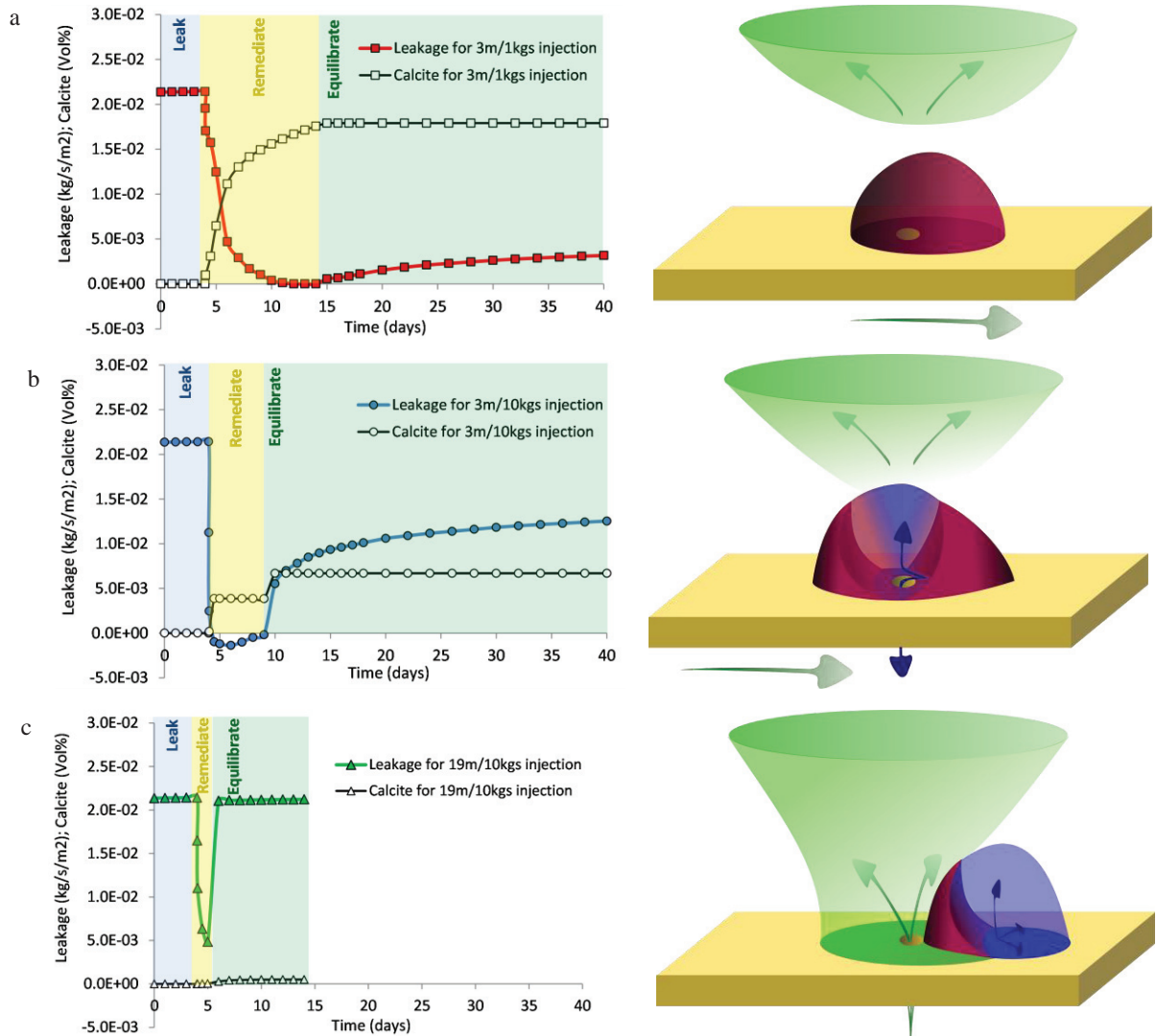

Fig. 3. For three scenarios a,b and c, the leakage and calcite precipitation data during leakage, remediation and equilibration is presented on the left and a cartoon on the right illustrates the different outcomes of leakage remediation. 3a shows successful clogging with increasing calcite precipitation (3a left) forming a calcite barrier above the leak (in purple, 3a right) preventing further migration of CO_2 (in green). 3b shows partially successful clogging with a small amount of calcite above the leak (3b left) and flow of the reactive solution through the leak (in blue, 3b right) preventing sufficient supply of CO_2 to form calcite. 3c shows premature calcite clogging preventing the reactive solution to reach the leak (3c right). Hence during remediation the leakage rate fully re-establishes (3c, left).

Table 8. Overview of the change in leakage rate for the different scenarios indicating the remediation success after an equilibrium phase. Scenarios in grey failed to run. The colours show the relative ranking from the best (green) to the worst remediation results (red).

Injection distance (m)	Permeability kh, kv (mD)	Injection rate 1 (kg/s/cell)	5 (kg/s/cell)	10 (kg/s/cell)	20 (kg/s/cell)
3	20, 2	-33			
3	200, 20	-80	-12	-37	
3	400, 40	-45	-47	-11	-0.1
3	800, 80	-24	-59	-47	-4
11	20, 2	-17	-14		
11	200, 20	-16	-95	-8	-6
11	400, 40	-7	-32	-10	-4
11	800, 80	-1	-14	-22	-0.2

4. Discussion

The numerical study on injecting calcium-rich water to form leakage-blocking calcite indicated the requirement of CO_2 supply from the leak for sufficient calcite formation – in addition to the CO_2 already present in the plume above the leak – which is the main disadvantage of the proposed technique. It requires a delicate balance between the injection rate, leakage rate and injection distance in order to achieve sufficient pore blockage. The work of Druhan et al. [19] also identified the balance between the flow rate through the leak and fluid injection rate as a major impact factor in the successful placement of the sealant. Setting a reactive solution at the right location remains a challenge, regardless of the reactant used. The use of swelling silica polymers as used by Druhan et al. [19] would promote the remedial method in the sense that less reactant is required to be put in place. However, the stability of such a polymer in the long term is currently not proven. Besides swelling, delayed precipitation of the solid reactant might take away some difficulties of the remediation method as proposed in this report. Instead of the reactivity according to the equilibrium constant and the kinetic parameters, engineered solutions with delaying additives could open opportunities for a simpler injection concepts as the solid reactant will not precipitate directly upon contact with CO_2. This would reduce the level of complexity regarding flow properties of the aquifer and the leak, parameters which are not easily obtained. For this reason, the use of substances that increase in volume with some delay would be beneficial for this method, since the solution has time to reach the leak where it can subsequently react to form solids and clog the leakage pathway. However, the method becomes less efficient with distance as it takes increasingly more volume of reactive solution to reach the leak. The volume of the injected fluid and injection time will govern the cost of the remediation method and are therefore crucial for the feasibility of this technique.

We chose to inject the reactive solution in the aquifer above the leak. This method would have several advantages over injection into the reservoir itself. First of all, the caprock does not have to be penetrated by a new well, and hence additional leakage risk for the storage reservoir can be avoided. Second, gravitational effects of the dense liquid help suppressing the leaking gas. In contrast, injection below the caprock may cause the liquid to sink and move away from the leak as buoyant CO_2 flows upwards. Third, the pH within the aquifer remains higher after remediation, preventing dissolution of the solid reactant, whereas calcite could more easily re-dissolve under acid conditions in the reservoir. A disadvantage of injection above the leak is that the characteristics of the aquifer may be poorly known while – especially for a depleted gas field – flow properties and the pressure response are far better understood for the reservoir itself. With regards to the stability of the placed barrier, preliminary simulations indicate the long-term >1000 year stability of the precipitated calcite, showing no significant dissolution. The presently used models do however not include reactivity of the aquifer rock or groundwater flow, which may affect these results.

This study shows that remediation of unwanted CO_2 flow from the target reservoir through the caprock to an overlying aquifer could be successful. Yet, large uncertainties in the success of remediation are related to the porosity-permeability relation of calcite precipitation (or of any other solid reactant). The actual volume of solid reactant required for full clogging also depends heavily on the porosity-permeability relationship. As mentioned by Druhan et al. [19] and Ito et al. [18], the porosity-permeability relation is of utmost importance for predicting effective leakage remediation. The sensitivity presented in this paper showed a difference from hardly any remediation to a 100% leakage reduction during remediation depending on the porosity-permeability relation parameters. In the case of intentional salt clogging [9], the same challenge was encountered. It remains a topic of discussion as to which degree precipitation in the pore space reduces the flow of gas and water. More insights in the porosity-permeability relations need to be obtained through well-designed experimental and modelling studies.

5. Conclusion

The use of calcite as a solid reactant is a promising method for leakage remediation due to the natural stability of calcite in the subsurface. Induced calcite precipitation could be used for the formation of a strong, stable and durable barrier against unwanted migration of CO_2. TOUGHREACT was applied to simulate the injection of a calcium-rich solution in the vicinity of a CO_2 leak, causing precipitation of calcite, blocking of pore space resulting in a reduction of CO_2 leakage. Leakage reduction results were obtained during and after the remediation process. These showed that during the remediation process, CO_2 leakage is reduced by both the pressure of water injection (hydraulic remediation) as well as by clogging of the pore space by calcite precipitation (chemical remediation). However, only the clogged pore space remains effective for leakage mitigation after injection. Simulating an equilibration stage after injection showed that without sufficient calcite clogging, leakage will re-establish to a certain degree. The equilibration stage is crucial to assess the success of remediation. Concerning the longevity of leakage reduction, even for re-established leakage the placed calcite barrier remains stable and is not significantly dissolved.

The scenario analysis of varying key parameters showed a large variation in the amount of calcite precipitation around the leak. The results indicated that injection of the reactive solution into the CO_2 plume above the caprock leak does not yield enough calcite for sufficient porosity clogging without additional supply of CO_2 by the leak itself. Hence, the leak should be temporarily maintained to allow the gradual build-up of calcite until sufficient porosity clogging is achieved. This situation requires that key parameters such as the injection rate and injection distance are well attuned to the leakage rate and permeability to achieve a high degree of leakage remediation. The most successful scenarios are characterized by a medium to high permeability and a low injection rate and can yield a final leakage reduction of up to 95%.

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