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Public abstract

This report is part of the research project MiReCOL (Mitigation and Remediation of CO_2 leakage) funded by the EU FP7 program[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 the 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).

In the unlikely case of localized CO_2 leakage from a storage reservoir, it is desirable to close the leak quickly, efficiently and permanently. This could be done by injection of material in the leak path, thereby blocking the flow. With regard to permanent closure, it is straightforward to look into materials that occur naturally in the subsurface, since they are stable in the long-term, ensuring permanent CO_2 containment in the storage site. This report describes a numerical modelling approach to assess the feasibility of injecting lime-saturated water as a CO_2-reactive solution to form -calcite, block CO_2 flow and remediate leakage. We performed reactive transport simulations with the software TOUGHREACT. A 3D model was developed of a CO_2 reservoir at the bottom, an aquifer at the top and a cell connecting the two layers, representing a caprock leakage pathway (such as a permeable fault or along a wellbore). A CO_2 plume was developed in the top aquifer by defining a leak in the caprock. The initial state of a CO_2 plume present takes into account the time required for a plume to become large enough to be detected by monitoring techniques.

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

A scenario analysis was performed to assess the effectivity and efficiency of the remediation method and evaluate the uncertainty related to the key parameters. The scenarios represent a range of possible characteristics of the storage reservoir and the leak that could affect the leakage remediation method. The key parameters include: reservoir pressure, gas saturation below the leak, permeability, leakage rate, injection distance from the leak and injection rate. Results for leakage reduction were obtained during and after remediation. This showed that leakage is affected by the injection of water and pressure changes (hydraulic remediation) as well as clogging of the pore space (chemical remediation). Of the two, only the chemical part remains after injection is stopped. Modelling showed that injection of the reactive solution in a CO_2-containing rock does not yield enough calcite, while full porosity clogging requires additional supply of CO_2 by the leak itself. Hence the leak should be maintained to allow the build-up of calcite until full porosity clogging is achieved. This situation requires a balance of injection rate, leakage rate, injection rate and reaction rate. The scenarios analysed indicated certain combinations of conditions and parameters which promoted chemical clogging. Scenarios showed a success of leakage remediation varying between 0 and 95%. The degree of leakage reduction can be used to calculate the likelihood of success of remediation and provide input for the MiReCOL webtool. This tool will help site owners to find appropriate remediation methods in the unlikely case that CO_2 leakage occurs.

Public introduction (*)

CO_2 capture and storage (CCS) has the potential to reduce significantly the carbon emission that follows from the use of fossil fuels in power production and industry. Integrated demo-scale projects are currently being developed to demonstrate the feasibility of CCS and the first such projects are expected to start operating in Europe under the Storage Directive in the period 2015 – 2020. For the license applications of these projects a corrective measures plan is mandatory, describing the measures to be taken in the unlikely event of CO_2 leakage. This project will support the creation of such corrective measures plans and help to build confidence in the safety of deep subsurface CO_2 storage, by laying out a toolbox of techniques available to mitigate and/or remediate undesired migration or leakage of CO_2. The project is particularly aimed at (new) operators and relevant authorities.

The MiReCOL project investigates various techniques for control of CO_2 migration including: i) injection strategy, ii) gel or foam injection, iii) water or brine injection and iv) injection of chemicals which react with CO_2 and precipitate it as a solid.

The results of this work will contribute to later activities that will assess the effectiveness and consequences of all leakage mitigation measures, leading to the production of a Corrective Measures Handbook.

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1 INTRODUCTION

To store CO_2 permanently in the subsurface, reservoirs are selected that provide physical and chemical containment of CO_2. However, future control on the movement of CO_2 is asked for in the unlikely case that CO_2 migrates out of its intended storage reservoir. Flow control measures are developed to demonstrate possibilities for preventing CO_2 leakage to overlying aquifers or to the surface, safeguarding the contribution of the stored CO_2 in reducing global warming. Immobilizing migrating CO_2 by consuming the gas and forming solid reactants is a relatively new field. Flow control by precipitating solids in the pore space has been practiced in the oil and gas industry in the context of ‘water shut-off’, blocking water production from high permeable layers and enhancing oil production from low permeable layers. Plugging agents such as foams and polymers are generally used, but for permanent CO_2 immobilization they lack the proven long-term stability in the subsurface. Forming mineral solid reactants will have the advantage of creating a naturally stable barrier against CO_2 flow.

Experience with unintentional precipitation or scaling and formation damage, as commonly encountered in the oil and gas or geothermal industries, sheds some light onto the possibilities for forming solid reactants. Minerals observed to form ‘naturally’ within the reservoir may all be potential candidates for controlled precipitation. Frequently occurring scales associated with oil and gas production are calcite, anhydrite, barite, celestite, gypsum, iron sulphide and halite (Cowan and Weintritt, 1976). Re-injection of production water is prone to scaling of calcium carbonate (Rocha et al., 2001, Moghadasi et al 2004, Birkle et al., 2008), while strontium, barium and calcium sulphates are more relevant for seawater injection (Delshad & Pope, 2003, Mota et al., 2004, Bedrikovetsky et al., 2006). Water injection in geothermal systems may involve precipitation of carbonates, silica (polymorphs), metal compounds (oxides hydroxides sulphides sulphate) and clays (e.g. Kuhn et al., 1997, Tarcan, 2005, Izgec et al. 2005, Regenspurg et al., 2010). The possibilities of precipitation due to water injection have been recognized by Nasr-El-Din et al. (2004), who aimed to achieve selective plugging by introducing fluid which is chemically incompatible with the reservoir brine, thereby causing mineral precipitation. In addition to fluid-fluid reactions, fluid-gas interaction may promote mineralization. Linked to well abandonment after CO_2 storage Wasch et al. (2013) proposed controlled intentional clogging with salt to prevent possible leakage of CO_2. Salt will precipitate when the solubility is exceeded due to evaporation into injected dry gas. This process is similar to salt scaling in natural gas and oil production (e.g. Kleinitz et al., 2001) and CO_2 injection in saline aquifers (e.g. Pruess and Müller, 2009, Zeidouni et al., 2009) and depleted gas fields (Giorgis et al., 2007 and Tambach et al., 2014). After injection, slower mineralization reactions between the stored CO_2 and the host rock may occur on the longer term. Much research has been done on this topic since these reactions provide permanent trapping and increased the storage safety (e.g. of Gaus, 2010).

Previous work on the induced formation of solid reactants for leakage remediation concerns calcite or silica. Bio-mineralization has been proposed for engineering biofilms covering grains subsequently forming carbonate by ureolysis (Mitchell et al., 2009, Cunningham et al., 2011). Carbonate can also be directly formed by injecting reactive suspensions or solutions into the CO_2 containing environment (Ito et al., 2014). Ito et al., (2014) report 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 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. (2014) numerically investigated amorphous silica formation adapted for a higher molecular volume analogues to silica polymers. We investigated the feasibility of injecting a CO_2-reactive and CO_2-consuming reactive solution. Lime-saturated water is selected which reacts readily upon contact with CO_2. This approach has the advantage that reactions can be modelled with available software and databases without modifications. Furthermore a solution will have a low viscosity, which simplifies injection. The production and practical use of such a fluid is beyond the scope of this study. The results derived for the lime solution will provide general insight in leakage mitigation using non-swelling CO_2 reactive substances.

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 modeling of subsurface multiphase fluid and heat flow, solute transport, and chemical reactions by introducing reactive transport into the flow simulator TOUGH2 (Xu et al., 2006). TOUGH2 is a numerical simulation program for multi-dimensional fluid and heat flow of multiphase, multicomponent fluid mixtures in porous and fractured media (Pruess et al., 1999). 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 (Pruess, 2005). The mineral reaction kinetics are included for the solid reactant using reaction rates of Palandri and Kharaka (2004).

2.2 Workflow

2.2.1 Mesh making

The model was developed to represent a CO_2 storage site with a CO_2 storage reservoir, a caprock and an overlying aquifer (Figure 1, image 0). The dimensions are 200*200*140 meter and the model was arbitrarily located between 2000 and 2140 m depth. Vertical sub-layering was chosen to obtain more detail in the top aquifer where leakage remediation is required (Table 1). For the x,y direction a custom regular grid was defined (

Table 2). Note that the grid is asymmetric and has finer gridding at the right side where injection is envisaged. We developed a model to find an optimum between model size and grid refinement within the maximum of 8000 active cells allowed by TOUGHREACT.

Table 1. Model layering (z direction).

	Total thickness (m)	*Number of layers*	*Layer thickness (m)*
Top aquifer	80	1	24
		3	13 1/3
		3	5 1/3
Caprock	20	1	20
Storage reservoir	40	3	13 1/3

Table 2. Cell sizes in the x and y direction.

number of cells	1	4	2	1	10	2	1	1
cell size (m)	30	15	4	2	4	15	30	30

The rock properties were based on the P18 field with a reservoir porosity of 15% and flow properties as listed in Table 3. Preliminary modelling showed that the permeability of the aquifer is the limiting factor for the leakage rate and a higher permeability for the leak path through the caprock does not increase the leakage rate significantly. Hence for simplicity the flow properties of the aquifer, caprock (leak) and reservoir were taken equal. Only for the leak the vertical permeability is not decreased by a factor of ten.

Table 3. Rock properties.

	Permeability	
	(mD)	(m^2)
Horizontal (kh)	20	2E-14
Vertical (kv)	2	2E-15
	Relative permeability	
	Slr	Sgr
Corey's Curves	0.18	0.121
	Capillary pressure	
	P0	Slr
Leverett's function	1.00E+06	0.18

2.2.2 Initialization of conditions prior to CO_2 storage

The initial conditions for model initialization are 200 bar pressure, 1E-10 gas saturation and a 0.06 salt mass fraction. Note that the gas saturation is close to zero and hence resembles an aquifer before CO_2 storage. The temperature is selected to be 80 °C and non-isothermal behaviour is neglected. The model is run for 20,000 years for initialization, distributing the pressure, gas saturation and brine composition with depth according gravitational forces. The caprock was set to permeable to allow for pressure distribution. The resulting pressure with depth is shown in Figure 1.

2.2.3 Initialization of chemistry and conditions after CO_2 storage

The initialized conditions of the previous step were used and chemical properties were included. The whole model was assigned the same formation water. The formation water composition was calculated in a separate batch model, equilibrating NaCl brine with a simple sandstone mineralogy (
Table 4 and Table 5). Only the water is used for further modelling, reservoir rock – fluid/gas reactions are neglected given short time of interest for leakage remediation. To aid chemical convergence a mineralogy was defined with only (nearly inert) quartz.
The reservoir is subsequently filled with CO_2 by assigning the cells a gas saturation of 80%. Two situations were considered: a) hydrostatic pressure in the reservoir as for storage in a depleted gasfield and b) 20 bar overpressure to represent aquifer storage (Figure 1, images 2a/2b). The caprock was disabled and the leak pathway was assigned a zero permeability to obtain initial containment of CO_2 in the reservoir. The model was ran for 2 years to initialize pressure and gas saturation, furthermore the water chemistry in the reservoir was allowed to equilibrate with CO_2.

Table 4. Mineralogy for calculating of the formation water.

Mineral	*Volume fraction*
Quartz(alpha)	0.7
Microcline	0.1
Illite(Al)	0.1
Albite(high)	0.1

Table 5. Formation water composition.

Formation water (mol/L)	
Cl	1
Na+	9.99E-01
H4SiO4	7.30E-04
K+	1.09E-03
Al	3.04E-07
pH	8.03

2.2.4 Initialization of the CO_2 Leak

The initialized conditions of the previous step were used and the caprock leak cell was enabled with a permeability equal to the horizontal permeability the aquifer. The lateral boundary conditions are open (i.e. given a 1E50 volume factor) to allow free flow away and towards the leak. Top and lower boundary conditions are closed, assuming impermeable bounding formations. The leakage rate is allowed to develop following the pressure and saturation conditions and the flow properties. Buoyancy drives CO_2 upwards forming a plume of CO_2 in the aquifer above the leak (Figure 1, image 3). Since MiReCOL aims to supply mitigation methods for the case of an existing leak, we allow a plume to develop for a period of 10 years. This period is arbitrarily chosen, but should allow for a leak to become substantially large enough to be detected by monitoring even though the flow rate is small.

2.2.5 Injection of the lime-saturated fluid

After the CO_2 plume is established, a CO_2 reactive fluid is injected (Figure 1, image 4). We study injection into an aquifer above the storage reservoir. This method would have several advantages over injection in the reservoir itself. The caprock does not have to be penetrated by a new well, and hence no additional leakage risk is created. Gravitational effects of the dense liquid help suppress 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. A disadvantage of injection above the leak is that the characteristics of the top aquifer may be poorly known while – especially for a depleted gas field – flow properties and pressure response are far better understood for the reservoir itself.

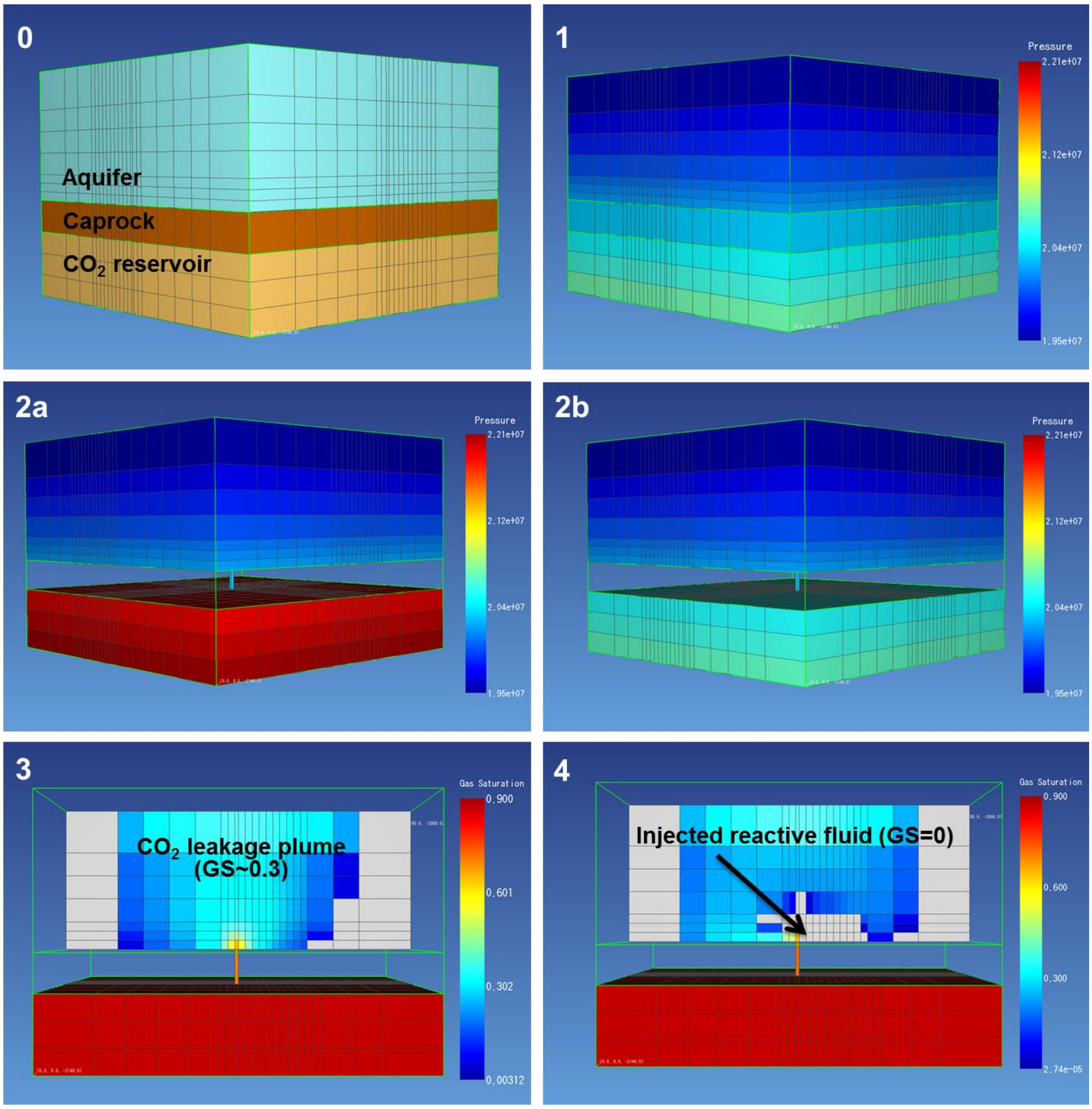

Figure 1. Step 1 to 4 of the workflow.

Injection of the solution is implemented by defining a *source* cell with a specific (lime-saturated) water flux. Note that the injection rate is constant and cannot be defined as being dependent on pressure with TOUGHREACT. As a result, pressure rises due to water injection. When the area above the leak is near complete clogging, injection becomes difficult and pressure may rise severely, while in reality the injection rate would be lowered and eventually stopped when reaching a certain pressure. Note that models are run until permeability and pressure changes hamper further injection, affecting the remediation time.

We used a calcium solution (lime-equilibrated) to stimulate calcite when reacted with dissolved CO_2 (Equation 1). The reactive solution has a calcium concentration of 0.68 mol/kg water and a pH of 12. All cells were assigned a porosity-permeability relationship to model the effect of precipitation on the CO_2 leakage. We used the porosity permeability relationship of Verma-Pruess as implemented in TOUGHREACT

(Xu et al., 2006). The relation uses two parameters, a critical porosity (the porosity at 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%, 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.

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

2.2.6 Equilibration stage

After injection of the reactive solution an equilibration stage is run to establish equilibrium after the remediation stage. After injection is stopped, flow occurs according to the pressure and saturation gradients created during injection of the reactive solution. This step will indicate if leakage will commence again or if further migration of CO_2 is prevented and is crucial to assess the success of remediation and the longevity of leakage reduction.

2.3 Scenarios

Several factors determine whether or not the solid reactant successfully remediates unwanted migration of CO_2. For successful clogging there should be a balance between the injection rate, leakage rate and reaction rate to ensure that sufficient solids form at the right location. The leakage rate is controlled by the pressure difference between the reservoir and the top aquifer, and by the flow properties of the leak. To consider a range in leakage rates, several simulations were run with varying key parameters.

2.3.1 Injection rate & distance

The injection rate and distance from the leak are parameters that are not site specific but can, to a certain degree, be controlled by the operator. We investigated 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 2). The distance of injection to the leak point is 3, 11 and 19 meters (based on the cell centres). The selected injection rates range between 1 and 20 kg/s/cell and are considered to be achievable injection rates. Injection is specified for a column of three cells representing a perforation interval of 15 meters. Note that the total injection should be summed for the three injection cells, and hence for a rate of 10 kg/s/cell this is 30 kg/s in total, which is approximately 100 m3/hr of fluid down the well.

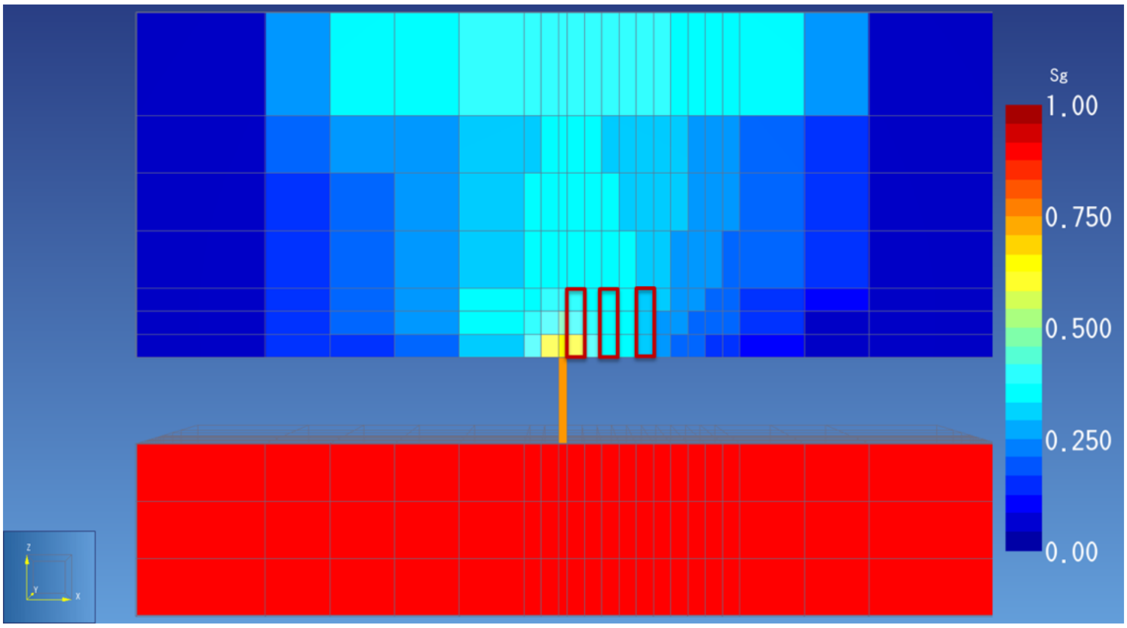

Figure 2. Cross section of the model with red squares indicating the three perforation intervals for injection of the reactive solution. The colour scale is for gas saturation, indicating the CO_2 plume above a leak path and the CO_2 reservoir below.

2.3.2 Permeability, pressure & gas saturation

The range in permeability scenarios is assumed to represent relevant values, not too low that water injection becomes challenging and up to values of a reasonable reservoir rock (Table 6). Pressure conditions will be different for different types of storage sites. We distinguished between overpressurised and hydrostatic pressures. The first represents aquifer storage where the pressure increases during CO_2 injection. Hydrostatic pressure conditions are as would be expected for CO_2 storage in a depleted gas field where an empty field is filled until hydrostatic pressure is regained. We used two saturations, close to fully saturated (Sg of 0.9) and 30% gas saturated. These values represent end members of gas saturation in a storage reservoir, high close the well and low further into the CO_2 plume. The selected pressure and saturation conditions yield three scenarios (Table 7). Although pressure boundary conditions also affect the leakage rate, open boundary conditions are used assuming an infinite aquifer and reservoir with respect to the 200 m cube model.

Table 6. Scenarios for permeability of the reservoir, aquifer and leak.

Permeability scenario	***Reservoir/ aquifer*** **Kh (mD)**	**Kv (mD)**	***Leak*** **Kh (mD)**
1	20	2	20
2	200	20	200
3	400	40	400
4	800	80	800

Table 7. Scenarios for CO_2 conditions in the reservoir.

Reservoir **scenario**	***Reservoir type***	
	Pressure	**Gas saturation**
a	20 bar overpressure	Saturated (0.9)
b	hydrostatic	Saturated (0.9)
c	20 bar overpressure	Undersaturated (0.3)

3 LEAKAGE REMEDIATION BY SOLID REACTANTS

3.1 The process of reactive clogging

The characteristics of clogging are discussed for a scenario of injection at 11 m distance from the leak with an injection rate of 5 kg/s/cell in an overpressurized reservoir of 200 mD permeability. Since gas in the pore space is pushed away by injection of the reactive solution, the pressure rises (Figure 3 a) and the gas saturation drops (Figure 3 b). The 10 bar pressure rise falls within the approximately 20% pressure increase allowable for water injection.

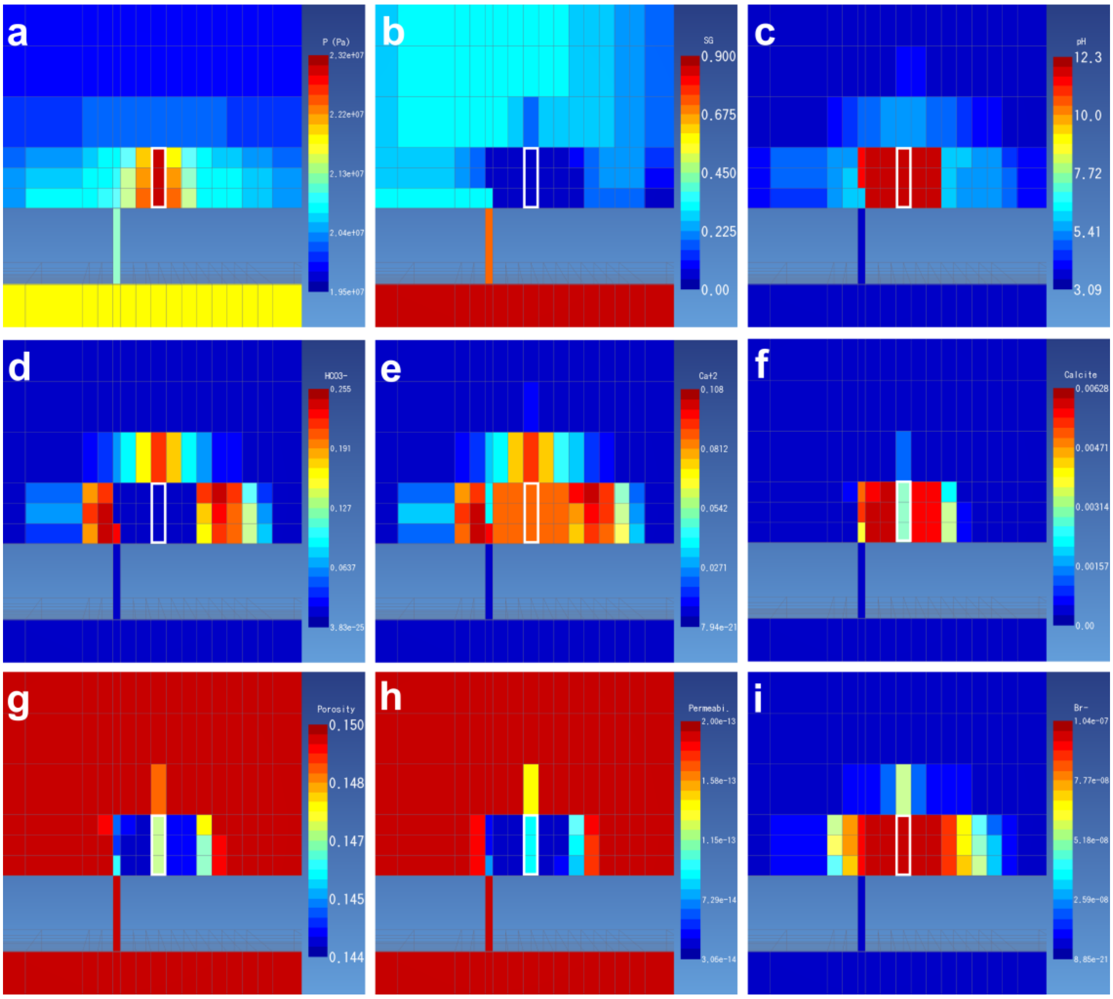

Figure 3. Results for several parameters in 80 by 90 m details of a y-axis cross section through the centre of the model. Injection of the CO_2 reactive solution is characterized by: a) pressure increase, b) gas saturation decrease, c) high pH zone within the low pH CO_2 plume, d/c) high HCO_3^- and Ca^+ concentrations at the front of the injected solution, e) calcite precipitation, g/h) porosity and permeability decrease due to calcite precipitation, i) co-injected Br^- tracer showing the extent of the injected fluid.

The high pH calcium solution (Figure 3 c) is injected into the CO_2 plume where the dissolved CO_2 (Figure 3 d) combines with calcium (Figure 3 e) to form calcite (Figure 3 f). Since most dissolved CO_2 is consumed by the reaction, new calcite forms at the front of the injected solution where HCO_3^- is still present. In addition, the leak itself provides 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 3 g) and permeability (Figure 3 h).

Successful remediation is defined as mitigation of unwanted migration of CO_2 by blocking the pore space. This is shown by the reduction in flow rate through the leak path and calcite precipitation above the leak (Figure 4 and Figure 5). The first drop in leakage rate is due to the injected water and the related pressure increase. At this stage, the reactive solution did not reach the leak yet (Figure 5, t = 0.5 day). The second reduction in flow occurs when the reactive fluid reaches the leak point and calcite starts to precipitate and clog the pore space (Figure 4 and Figure 5, t = 3 days). With continuous injection, the flow of CO_2 changes direction as it is pushed downwards (Figure 5, t = 6 days). The leakage rate is reduced to zero (Figure 4), suggesting successful remediation. The success of the remediation could be expressed as the degree of leakage reduction from the initial flow rate to the flow rate at the end of remediation. In this case that would be 100%.

To test whether the mitigation of unwanted CO_2 migration remains successful in time, the flow is studied after injection is stopped (when the permeability becomes too low for further injection). For this stage some leakage is re-established after the complete leakage reduction during remediation (Figure 6). This can be explained since the remediation during injection is a combined chemical and hydraulic process, meaning that flow through the leak is suppressed by a reduction in permeability and by the additional pressure of water injection. When no more water is injected, the chemical remediation remains, which yields in this case a leakage reduction of 95%. Hence the actual success of remediation is 95% instead of a 100%.

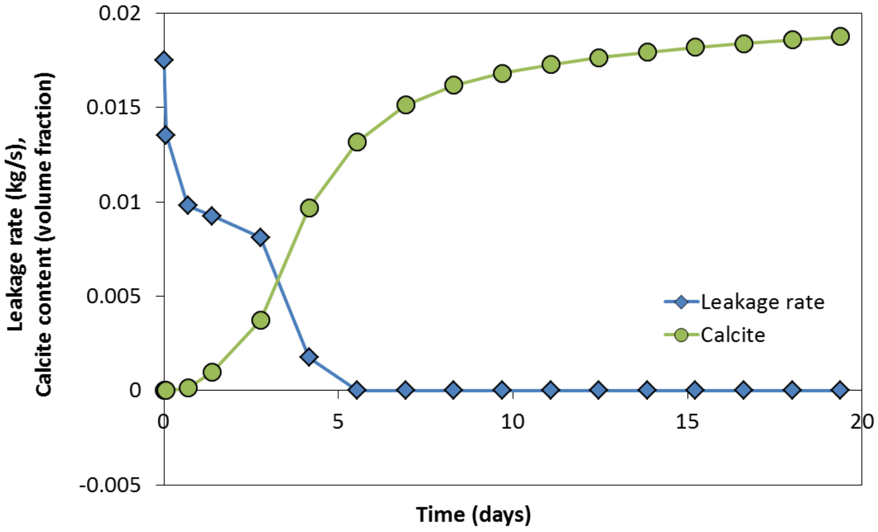

Figure 4. Graph of the leakage rate through the caprock (z direction) and the calcite content in the cell above the leak (same scale used). With time, more calcite precipitates and the leakage rate decreases.

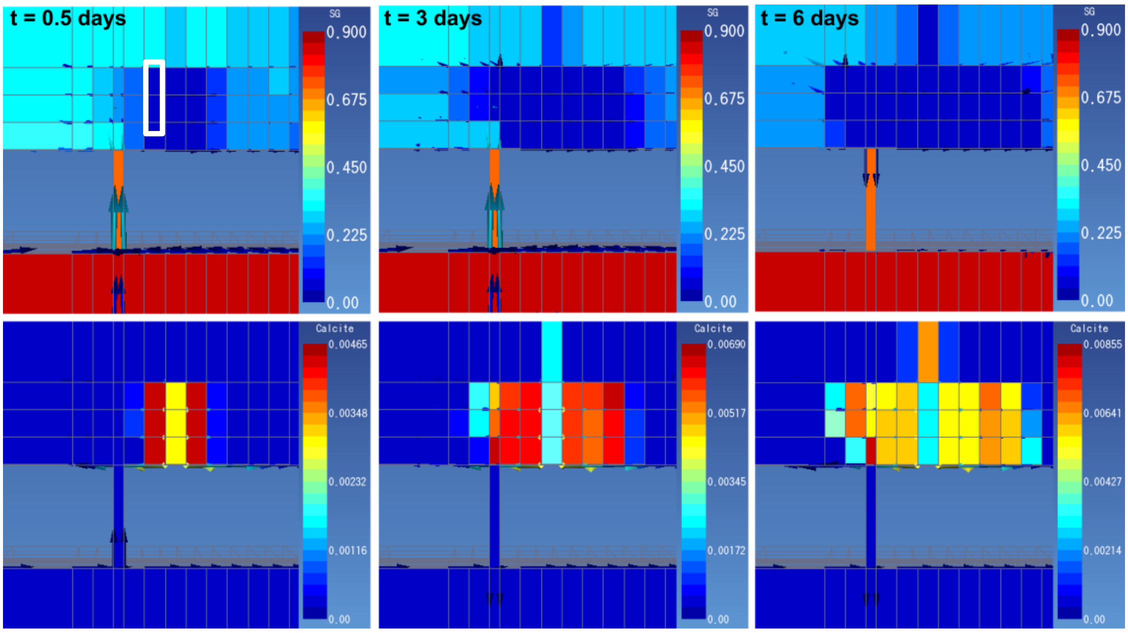

Figure 5. Gas saturation (in colour) and flow (vectors) for three time steps and associated calcite precipitation below. As more reactive solution is injected, it reaches the leak (t = 2 days) and overflows it (t = 6 days). Direct CO_2 leakage into the solution above, increases calcite forming until gas flow is inverted after 6 days of injection.

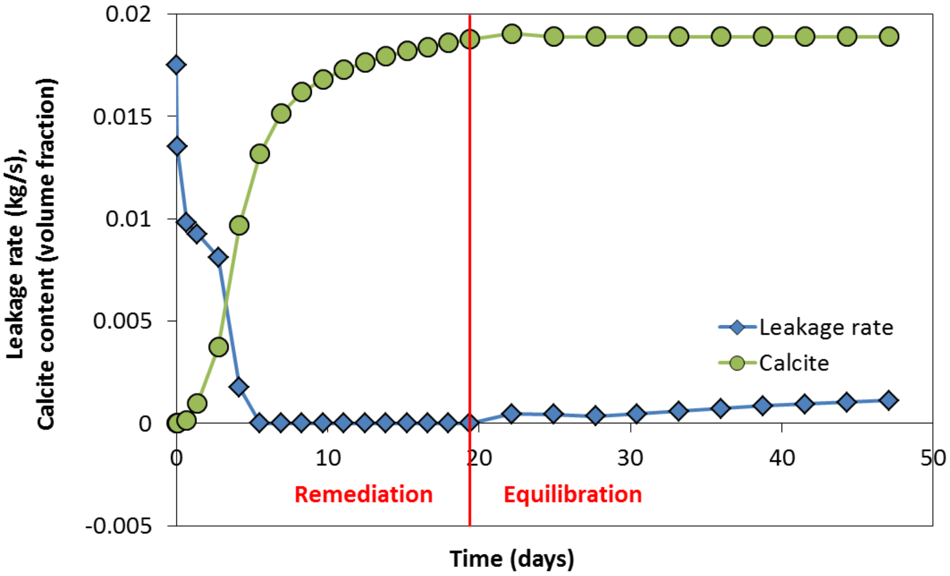

Figure 6. Graph of the leakage rate through the caprock (z direction) and the calcite content in the cell above the leak (same scale used). With time after remediation, calcite remains stable while leakage re-established to some degree.

4 UNCERTAINTY ANALYSIS

4.1 Leakage scenarios

Scenarios for the *initial* leakage rate were based on the different pressure conditions and the geological variability as defined in section 2.3.2. For the ‘overpressurized, high gas saturation reservoir’ scenarios the leakage rates range from 0.27 to 10.93 mton for different permeabilities (1a to 4a, Table 8). Basically, double the permeability yields twice as fast leakage. This linear relation is shown for all three reservoir types, although the absolute leakage rates are far lower. The lower leakage rate is due to the smaller pressure gradient for the hydrostatic scenarios (1b to 4b, Table 8) and due to the lower gas content for the low saturation scenarios (1c to 4c, Table 8). The low saturation scenarios yield mobile water and hence leakage of water (and dissolved CO_2) as well as gaseous CO_2. Since the overpressurized, high saturation scenarios 1a to 4a yield the most variation in leakage rates, these 4 scenarios were selected for the uncertainty assessment. Each scenario is applied to the three storage types (Table 8).

Table 8. Leakage scenarios and resulting leakage rates for the combinations of 4 permeability and 3 reservoir scenarios. SG is the CO_2 gas saturation.

Leakage scenario name	Permabillity Scenario	Aquifer Kh (mD)	Aquifer Kv (mD)	Leak Kh (mD)	Reservoir scenario		Leakage rates Gas (mton/yr)	Leakage rates Water (mton/yr)
1a	*1*	20	2	20	*a*	0.9 SG, P + 20 bar	**0.27**	**0**
2a	*2*	200	20	200	*a*	0.9 SG, P + 20 bar	**2.71**	**0**
3a	*3*	400	40	400	*a*	0.9 SG, P + 20 bar	**5.39**	**0**
4a	*4*	800	80	800	*a*	0.9 SG, P + 20 bar	**10.93**	**0**
1b	*1*	20	2	20	*b*	0.9 SG, P hydrostatic	**0.02**	**0**
2b	*2*	200	20	200	*b*	0.9 SG, P hydrostatic	**0.18**	**0**
3b	*3*	400	40	400	*b*	0.9 SG, P hydrostatic	**0.36**	**0**
4b	*4*	800	80	800	*b*	0.9 SG, P hydrostatic	**0.72**	**0**
1c	*1*	20	2	20	*c*	0.3 SG, P+20 bar	**0.01**	**0.01**
2c	*2*	200	20	200	*c*	0.3 SG, P+20 bar	**0.12**	**0.13**
3c	*3*	400	40	400	*c*	0.3 SG, P+20 bar	**0.24**	**0.26**
4c	*4*	800	80	800	*c*	0.3 SG, P+20 bar	**0.47**	**0.52**

4.2 Remediation scenarios

4.2.1 Effect of permeability, injection rate and injection distance

The remediation scenarios were run for four of the leakage scenarios described above, thus considering four permeability’s and corresponding leakage rates as starting points for remediation (1a to 4a, Table 8). The remediation scenarios are combinations of 4 injection rates and 3 injection locations, yielding 48 scenarios. The success of these scenarios at the end of the injection process, in terms of the change in leakage rate, is reported in Table 9. Note that the low permeability did not allow high injection rates, and hence these scenarios could not be run. Leakage can be reduced more than a 100 per cent if flow is inverted through the leak path. For all permeabilities and related leakage rates, a full decrease in leakage rate can be achieved given a right combination of injection distance and injection rate. For higher permeabilities, higher injection rates are required to achieve successful remediation. This is most pronounced for the highest permeability, yielding complete success only for injection at 3 meter distance. It appears that injection close to the leak point or faster injection will generally increase the likelihood of success for leakage reduction during the remediation procedure.

Table 9. Scenario overview for the change in leakage rate (%). The colours show a ranking from more (green) to less (red) successful scenarios. Scenarios that did not run are shown in grey.

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	-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 10. Scenario overview for calcite precipitation (volume factor) above the leak. The colours show a ranking from more (green) to less (red) successful scenarios. Scenarios that did not run are shown in grey.

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	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

As mentioned before, stopping flow through the leak path is a combined effect of injection of water and clogging of the pore space by the solid reactant. Comparing the amount of calcite formed above the leak (Table 10) and the change in leakage rate (Table 9) clearly indicates that the two do not necessarily correlate. This will have an effect on the equilibration stage, as described in the section 4.3. Especially for injection far from the leak point (19 meter scenario), some scenarios were successful in leakage remediation but have a very small contribution of chemical remediation (i.e. calcite clogging). Since none of the scenarios reaches the critical volume of calcite of 3.0E-2 (which yields a porosity reduction of 15% to the critical value of 12% after which permeability is assumed to be zero) as we defined for complete permeability impairment, chemical remediation was always less than a 100% (Table 10). There is a sweet spot of high calcite precipitation for medium to high permeabilities (and initial corresponding leakage rate) with low to medium injection rates. It cannot be concluded that higher permeability or faster injection will necessarily be better, but *the combination has to be right*. However, injection at 19 m distance yields little calcite precipitation above the leak, indicating that the remediation method needs to be practiced close to the leak point at least < 20 m.

Since the combination of injection rate and location for the specific aquifer conditions is of such importance, Figure 7 shows the processes of successful or unsuccessful leakage reduction. We discuss 1) successful clogging with significant calcite precipitation above the leak, 2) partially successful clogging with calcite precipitation but also premature suppression of leakage, stopping further supply of CO_2 and 3) unsuccessful scenarios with calcite porosity clogging before the leak point was reached. The calcite volume fraction in Figure 7 shows the gradually increasing calcite formation for the effective scenario, whereas calcite precipitation stops for the partially successful scenario. This can be explained by the gas saturation, which is reduced to zero and hence no more CO_2 is available for calcite precipitation after all dissolved CO_2 is consumed (Figure 7, middle graph). This indicates that the hydraulic component of remediation should not be too large, as water suppressing the gas migration also stops new supply of CO_2. Since the leakage rate reduces to zero for both the successful and partially successful scenarios, both appear to be effective in remediation during injection. The figures on the right in Figure 7 clearly illustrate how scenarios can be unsuccessful (bottom figure) as calcite clogging simply occurs at the wrong location. The calcite distribution of the partially successful scenario shows less calcite in the cell above the leak compared to the successful one, but more calcite clogging at a larger distance around the leak. Looking at only the calcite above the leak will therefore not tell the whole story of leakage remediation. Another step of simulations is required to assess if the effectivity of the remediation after the procedure is stopped, which will be discussed in the next chapter.

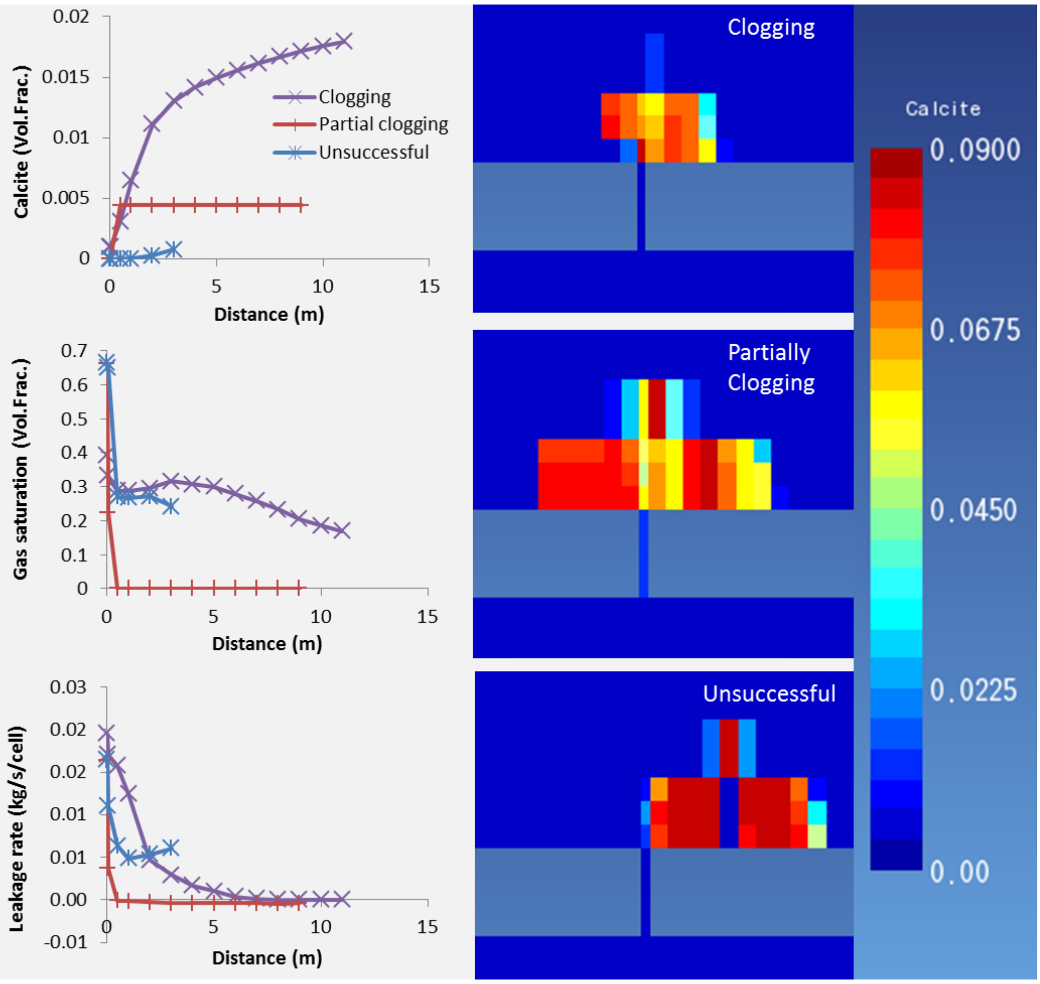

Figure 7. Three examples of scenarios yielding unsuccessful (2a-19m-10kgs), partially successful (2a-3m-5kgs) and unsuccessful (2a-3m-1kgs) leakage reduction. The graphs on the left show, from top to bottom, the calcite content and gas saturation above the leak and the leakage rate through the leak path. The figures on the right visualize the calcite precipitation in 80 m details of y-axis cross sections of the model.

4.2.2 Effect of reservoir pressure and gas saturation

The previous scenarios were all for the high pressure and gas saturation reservoir (a, Table 8). The hydrostatic (b) and low saturation conditions (c) were tested for the scenario of 200 mD permeability with 11 m distance 5 kg/s/cell injection. The change in leakage rate for the base case reservoir scenario *a* was 100%, for *b* this is -103.8% and for *c* -83.5% for gas and -95.6% for water leakage. Hence *c* is the least effective, but the calcite content shows that b and c are actually both less successful than *a* (Figure 8). These reservoir scenarios have a much lower initial leakage rate (Table 8) and hence CO_2 leakage is more easily suppressed by water injection, limiting the CO_2 supply and calcite precipitation. These scenarios require lower injection rates to achieve the balance between fast enough injection to reach the leak but slow enough to allow for CO_2 supply until clogging is complete.

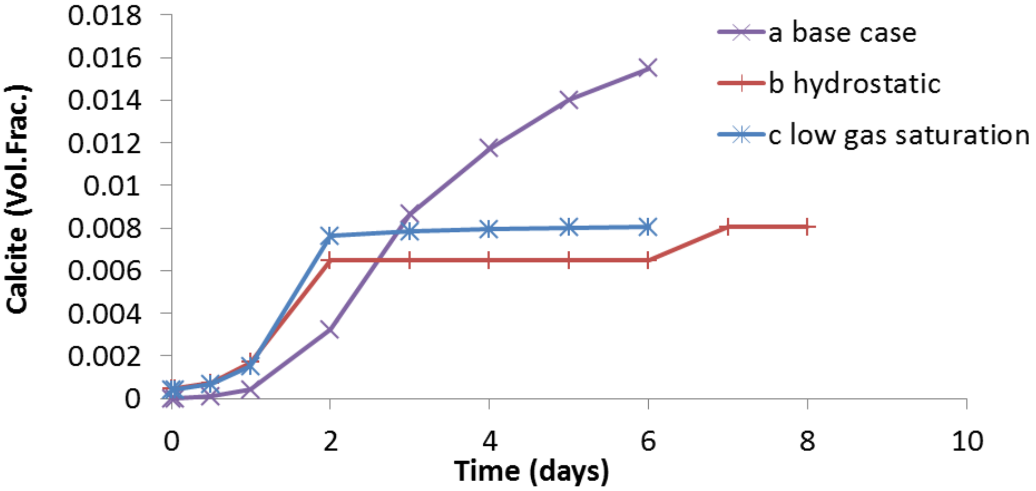

Figure 8. The calcite content in the cell above the leak for three reservoir scenarios. Scenario b and c first show an increase in calcite similar to scenario a, but calcite precipitation roughly stops after 2 days of injection.

4.2.3 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*. In addition, two other porosity-permeability relationships available for TOUGHREACT were checked, Cubic Law (CL) and Simplified Carmen-Kozeny (SCK). All porosity permeability relationships were tested for the scenario of 200 mD permeability with 3m distance and 1 kg/s/cell injection.

With a higher power law exponent, the permeability change is larger when porosity changes. 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 11).

Table 11. 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 (Vol.Frac)	Permeability (m2)
12-8	-100.0	1.79E-02	1.38E-16
12-6	-79.1	1.86E-02	6.03E-16
12-10	-100.0	1.77E-02	2.61E-17
11-8	-76.0	2.02E-02	7.33E-16
13-8	-100.0	1.45E-02	6.42E-18
CL	-24.3	8.75E-02	1.45E-14
SKC	-24.8	8.73E-02	1.20E-14

With a lower critical porosity, more calcite needs to precipitate in order 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 11). Interestingly, scenario 12-6 and 11-8 yield quite similar results, showing that a higher power law component can compensate the higher degree of clogging required. The Cubic Law (CL) and Simplified Carmen-Kozeny (SCK) yield comparable results. Both are characterized by high calcite precipitation but still a high permeability resulting in little leakage reduction and hence remediation success.

4.3 Equilibration

For several scenarios the actual success of the remediation method is numerically assessed by running the equilibration phase after injection of the reactive fluid. Since the 19 m injection scenarios resulted in little to no calcite in the remediation stage these were not considered for equilibration. The 37 remaining remediation scenarios were used for subsequent equilibration. For all equilibration scenarios, the leakage re-establishes to a certain degree, as was expected from the injection stage which indicated a lack of complete clogging. Figure 9 shows examples for the development of the leakage rate. Two of the scenarios were able to stop leakage completely during injection, but the new leakage rate that develops during equilibration varies largely (2a 3m 5kgs and 2a 11m 1kgs, Figure 9). In fact the less successful scenario of the two yields the same final leakage rate as the scenario that never achieved full leakage reduction during remediation (2a 11m 1kgs, Figure 9). Note that due to the new leakage and supply of CO_2, the calcite content can even increase during the equilibration stage. It can be concluded that the success of leakage remediation during injection is very different from the actual success after equilibration.

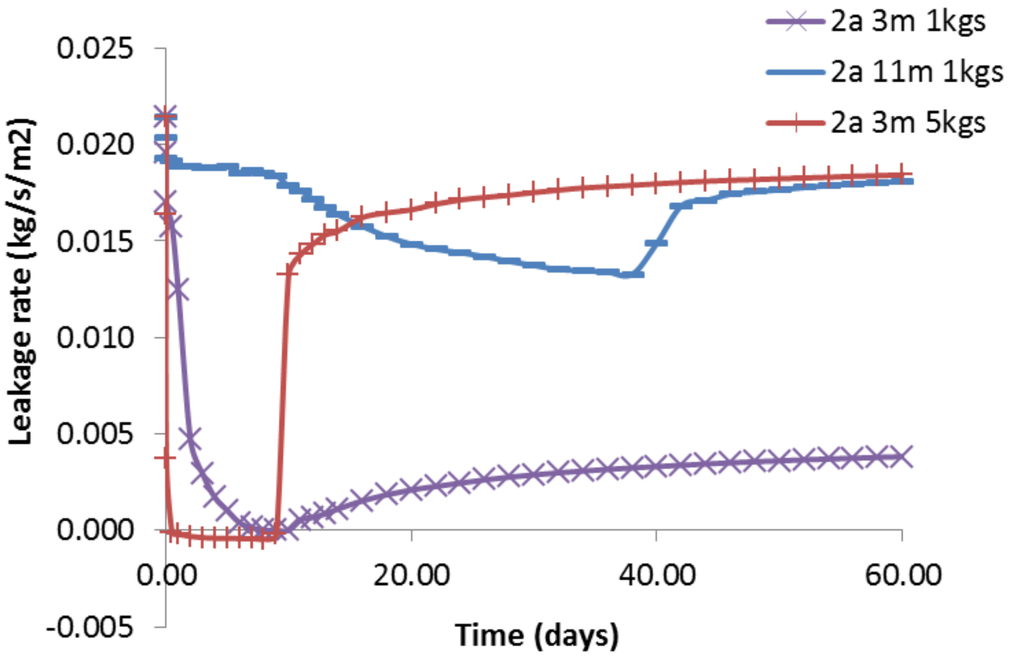

Figure 9. The leakage rate during remediation and equilibration.

The success of remediation after the equilibration phase for scenarios with different permeabilities, injection rates and injection distances are reported in Table 12. The fastest injection rate and the lowest permeability (initial leakage rate) yield little success in remediation. 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 10 compared to Table 12).

Table 12. Overview of the change in leakage rate for the different scenarios indicating the remediation success. Scenarios in grey failed to run. The colours show the relative ranking from the best (green) to the worst results (red).

Injection	Permeability	Injection rate			
distance (m)	kh, kv (mD)	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

4.4 Remediation efficiency

It takes increasingly more time for the reactive solution to reach the leak with injection at larger distance. Considering the radial distribution of injected solution, the method becomes less efficient with distance as more volume is required. Flow will not remain radial since it is affected by the clogging process. The extent of the clogging zone varies largely between scenarios (Figure 7), showing that besides the *effectivity* of clogging the *efficiency* of clogging may be very different from one scenario to another. The efficiency of scenarios can be expressed as the total volume of reactive solution injected during the remediation procedure, i.e. until permeability and pressure hamper further injection.

Table 13 shows that the volume injected varies by three orders of magnitude. The most effective scenarios with 45% or more leakage reduction remaining after equilibration are indicated by bold numbers. The variation is significant, even for the best scenarios, indicating that efficiency and effectivity are not well correlated. The volume of the injected fluid and injection time will govern the cost of the remediation method and are therefore of utmost importance for feasibility of this technique.

Table 13. The volume of remediation solution injected for the different scenarios. The volume (kg) is calculated by multiplying the injection rate (kg/s/cell) with the injection time (s).

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	8.8E+06			
3	200, 20	**2.3E+06**	1.2E+07	1.6E+07	2.2E+05
3	400, 40	**1.6E+07**	**1.2E+07**	1.0E+07	2.6E+06
3	800, 80	1.9E+07	**2.6E+06**	**5.2E+06**	2.6E+06
11	20, 2	9.3E+06	7.8E+06		
11	200, 20	1.1E+07	**1.2E+07**	5.2E+06	1.6E+07
11	400, 40	9.8E+06	2.1E+07	5.2E+06	5.2E+06
11	800, 80	1.6E+07	2.3E+07	1.8E+07	5.2E+06
19	20, 2	3.4E+06	2.6E+06		
19	200, 20	1.1E+07	1.2E+07	1.6E+07	2.6E+06
19	400, 40	1.2E+07	3.9E+06	7.8E+06	2.6E+06
19	800, 80	8.8E+06	1.6E+07	5.2E+06	1.3E+06

5 DISCUSSION

This study shows that remediation of unwanted CO_2 flow 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 formation of any other solid reactant. The actual volume of solid reactant required for full clogging depends heavily on the porosity-permeability relationship. As mentioned by Druhan et al. (2015) and Ito et al. (2014), 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 chosen parameters. In the case of intentional salt clogging (Wasch et al., 2013), the same challenge was encountered. It remains a question of debate 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 studies.

The simulation results also showed that the requirement of CO_2 supply from the leak for calcite formation – in addition to the CO_2 present in the plume – is the main disadvantage of the proposed technique. It requires a delicate balance between injection rate, leakage rate and location of injection in order to achieve sufficient pore blockage. The work of Druhan et al. (2015) also identified the balance between the flow rate through the leak and fluid injection rate as a major influence in the successful placement of the sealant. Delivering 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. (2015) would benefit the method in the sense that less reactant is required to be put in place. However, the stability of such a polymer on the long term is currently not proven. Amorphous silica may become more crystalline over time, a process which is faster at higher temperatures, causing mineral shrinkage and possibly re-established leakage. Besides swelling, delayed precipitation of the solid reactant might take away some difficulties of the remediation method proposed in this report. Instead of the reactivity according to the equilibrium constant and kinetic parameters, engineered solutions with delaying additives could open opportunities for injection further from the leak point as the solid reactant will not precipitate directly upon contact with CO_2. This would reduce the level of detail of knowledge required of the flow properties of the aquifer and the leak characteristics, properties which are not easily measured. For this reason, the use of substances that increase in volume with some delay would benefit the method, since injection would not be restrained and the solution has time to reach the leak where it can subsequently react to form solids and clog the leakage pathway.

6 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. This enables the formation of a strong and long-lived barrier against unwanted migration of CO_2. TOUGHREACT was successfully applied to inject a lime-saturated solution in the vicinity of a CO_2 leak. The reaction of the injected calcium solution with CO_2 caused calcite precipitation blocking the pore space and reducing CO_2 leakage. The method proved to have both a hydraulic and a chemical component, meaning that leakage was partially remediated by chemical precipitation and partially by the pressure of injected water. Since part of the remediation is attributed to water injection which is only a temporary process, stopping injection at the end of the remediation procedure leaves only the chemical clogging. As a result, leakage can partially be re-established. The scenario analyses showed a large variation in the resulting leakage reduction during remediation and afterwards during equilibration. The key parameters including leakage rate, permeability, injection rate and injection distance should be well attuned to achieve a high degree of leakage remediation. In general, fast leakage may contribute to clogging by supplying additional reactive CO_2. Fast injection of the solution on the other hand may push all the CO_2 away – even causing flow into the leak – thus limiting the reaction with CO_2 and hence clogging with the solid reactant.

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