

Results from final numerical modelling to enable risk and safety assessment, development of monitoring program and cost analysis

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Executive summary

The goal of the present deliverable D4.4 of the ConsenCUS project's Work Package 4 is to evaluate the impact of the new experimental and numerical data, obtained in the deliverable D4.3 on the efficiency and safety of CO₂ storage for the potential site at Stenlille, Denmark.

To this end, the following main results were obtained:

1. An improved estimate of the CO₂ recovery factor during temporary storage at Stenlille, using the relative permeability functions, numerically fitted to experimental core-flooding results.
2. An estimate of salt precipitation effects on CO₂ injectivity at Stenlille.
3. A validation of the fluid properties input to a fast simplified model at reservoir scale (Eclipse reservoir simulator) using a comprehensive but computationally expensive model at a sector scale (GEM reservoir simulator).
4. A detailed geochemical model to understand the impact of injecting CO₂ containing small amounts of acid gases at Stenlille.

The reduced uncertainty in saturation functions leads to a more accurate estimation of the mass of injected CO₂ during both permanent and temporary storage. This improved estimate can be used for cost analysis within Work Package 8 of the ConsenCUS project. Also, it allows for a more precise prediction of CO₂ plume migration in the reservoir, facilitating the development of a site-specific monitoring program (to be detailed in the upcoming deliverable D4.5).

1 Introduction

Permanent and temporary CO₂ storage in saline aquifers is associated with uncertainties that can affect the efficiency and safety of storage operations. For the potential CO₂ storage site at Stenlille, the results from deliverable D4.2 indicate that the recovery factor (i.e., the ratio of produced amount of CO₂ to injected) strongly depends on the choice of the saturation functions (i.e., the relative permeability and capillary pressure functions). In deliverable D4.3, the experimental results were history-matched to restrict the potential choices of the saturation functions.

Here, we investigate the impact of reduced uncertainties in saturation functions on the CO₂ recovery factor at the reservoir scale (Section 2). Specifically, we consider the Brooks and Corey (1964) parametrization of CO₂-water relative permeabilities and capillary pressures and characterize the behavior of the CO₂ recovery factor with respect to changes in the Brooks-Corey parameters using the design of experiments (DOE) approach (Montgomery, 2012). The ranges of the Brooks-Corey parameters are constrained with the experimental results from deliverable D4.3.

The experimental and numerical results of the deliverable D4.3 indicate that Stenlille rock properties are not significantly affected by CO₂ injection. However, the effects of salt precipitation are non-negligible. In Section 3, we investigate how these effects manifest at the reservoir scale and assess their implications for CO₂ storage efficiency and safety at Stenlille.

In this work, numerical results at the reservoir scale are obtained using the Eclipse 100 reservoir simulator (Schlumberger, 2017), which employs a simplified description of the fluids in the reservoir, allowing for relatively fast simulation times. Conversely, the GEM reservoir simulator (CMG, 2022) includes a comprehensive thermodynamic description of fluids and fluid-rock interactions, albeit at the cost of slower simulation times. In Section 4, we validate the fluid model input in Eclipse through modeling in GEM.

When captured, the CO₂ will contain impurities, the types and concentration of which depending on the CO₂ source and capture technique. In CO₂ stemming from combustion or cement production, high temperature reactions result in production of acid gasses that are highly reactive in hydrous environments. To understand the impact of injection of CO₂ containing small amounts

of these acid gasses, a theoretical and numerical model for the reactions occurring between NOX, SO₂, and O₂ at reservoir conditions is developed; see Section 5.

2 Efficiency of temporary CO₂ storage

As in deliverables D4.2 and D4.3, we consider the Brooks and Corey (1964) parametrization of the CO₂-water relative permeabilities and capillary pressures, which have the form

$$k_{rw} = K_w \left(\frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}} \right)^{n_w} \quad k_{rn} = K_n \left(\frac{S_n - S_{nr}}{1 - S_{wr} - S_{nr}} \right)^{n_n}, \quad (1)$$

$$p_c = P_e \left(\frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}} \right)^{-1/\lambda}, \quad (2)$$

where S denote the saturations, S_{wr} is the residual water saturation, S_{nr} is the residual CO₂ saturation, n_α is the Brooks-Corey exponent for the wetting and non-wetting phase $\alpha = w, n$, respectively, K are the corresponding endpoint permeabilities, P_e is the entry pressure and λ is a Corey exponent.

In deliverable D4.2 (Tables 2 and 3), the ranges of the Brooks-Corey parameters from literature data are identified for both drainage (subscript d) and imbibition (subscript i). In deliverable D4.3 (Tables 15), the Brooks-Corey parameters for the drainage branch of relative permeability functions were identified, which yield the best fit to the core flooding results. For convenience, these data are reproduced in Table 1 and Table 2.

Table 1. The literature data for Brooks-Corey parameter ranges for relative permeabilities, and the parameters which yield the best fit experimental results from D4.3.

	S_{wr}	S_{nrd}	S_{nri}	K_{wd}	K_{wi}	K_n	n_{wd}	n_{wi}	n_{nd}	n_{ni}
Lower bound (literature data)	0.29	0	0.2	0.7	0.05	0.05	1.4	1.7	0.47	0.4
Experimental fit	0.35	0.1	-	1	-	0.33	4	-	2	-

Upper bound (literature data)	0.67	0.05	0.36	1	0.55	0.55	53	5.5	5.2	4.3
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Table 2. Brooks-Corey parameter ranges for capillary pressures.

Range	P_{ei} (bar)	$P_{ed}-P_{ei}$ (bar)	λ_i	$\lambda_d - \lambda_i$
min	8E-03	0	0.5	0
max	5E-02	1E-02	0.8	0.15

Note that only the drainage parameters can be determined from the data in deliverable D4.3 because the experiment consists in injecting the non-wetting phase (supercritical CO₂) in a rock sample, saturated with brine (wetting phase). The fitted Brooks-Corey parameters lie within their respective bounds from the literature with an exception of unusually high irreducible CO₂ saturation S_{nrd} .

To account for reduced uncertainty in Brooks-Corey parameters, we set the parameters

$$S_{wr}, S_{nrd}, K_{wd}, K_n, n_{wd}, n_{nd} \quad (3)$$

assuming that other Brooks-Corey parameters are uniformly distributed within the corresponding ranges and generate 100 quasi-random samples for each of these parameters using the Latin hypercube sampling (LHS) approach (McKay, Beckman, & Conover, 1979). The resulting relative permeability and capillary pressure curves are presented in Figure 1 and Figure 2, respectively.

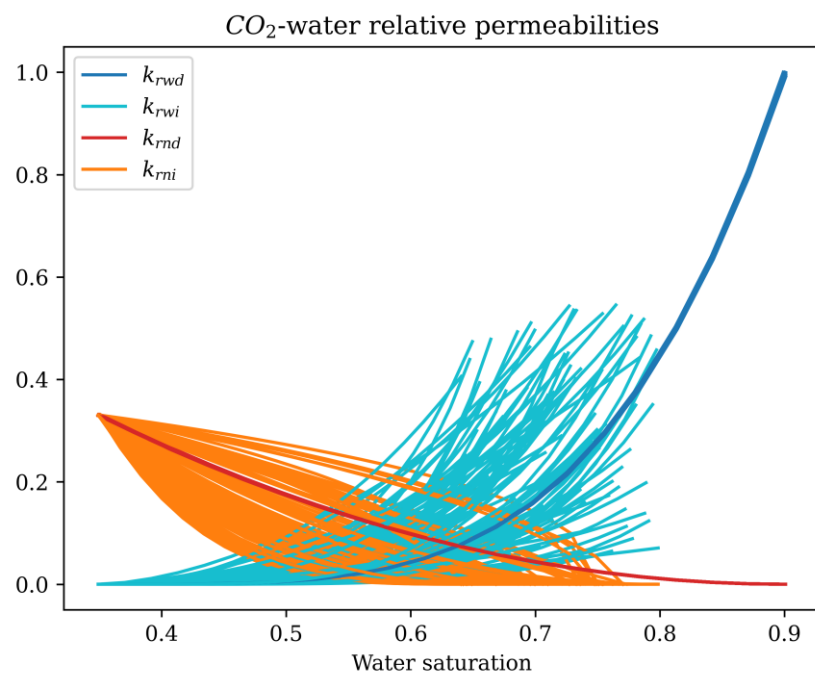


Figure 1. Hundred realizations of Brooks-Corey relative permeability curves.

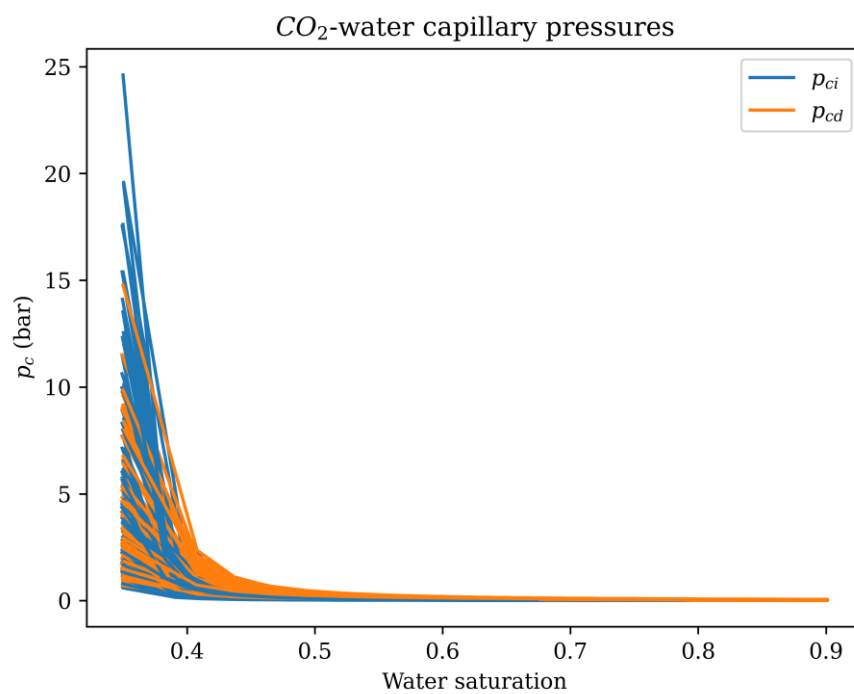


Figure 2. Hundred realizations of Brooks-Corey capillary pressure curves.

Since the Brooks-Corey parameters for the drainage (3) are fixed, the drainage branches of the relative permeability functions do not vary from one realization. Still, similar to the results in D4.3, there is a large variation in imbibition relative permeabilities.

The numerical results at the reservoir scale are obtained using the Eclipse 100 reservoir simulator (Schlumberger, 2017). The model represents the two fluid phases in the reservoir – formation brine and supercritical CO₂ – as two pseudo-components. At reservoir conditions, CO₂ can dissolve in water, but water cannot dissolve in CO₂. Parameters and correlations for specific fluids are provided via numerical values and tables, offering flexibility in fluid descriptions. In Section 4, we validate the fluid model input in Eclipse using a comprehensive thermodynamic modeling in GEM (CMG, 2022).

The Eclipse model does not handle different chemical components in the formation brine, different rock minerals, and geochemical reactions. Consequently, several important physical effects (such as salt precipitation) cannot be modelled using Eclipse. However, this simplification results in relatively fast simulation times, making reservoir-scale modeling feasible within affordable time frames (each forward simulation run below takes few minutes using the available computational setup¹).

Analogous to the approach in deliverable D4.2 (Section 4.2), we consider a scenario, when CO₂ is injected in a well ST-11 located at the top of the structure for 10 years with the bottomhole pressure control of 257 bars, followed by 10 years production with the topside pressure control of 1 bar. Depending on a specific set of relative permeabilities and capillary pressures in Figure 1 and Figure 2, the mass of injected and produced CO₂ varies as indicated in Figure 3.

¹ A 16-core Eclipse license on a workstation with 40 cores and 128 Gb RAM.

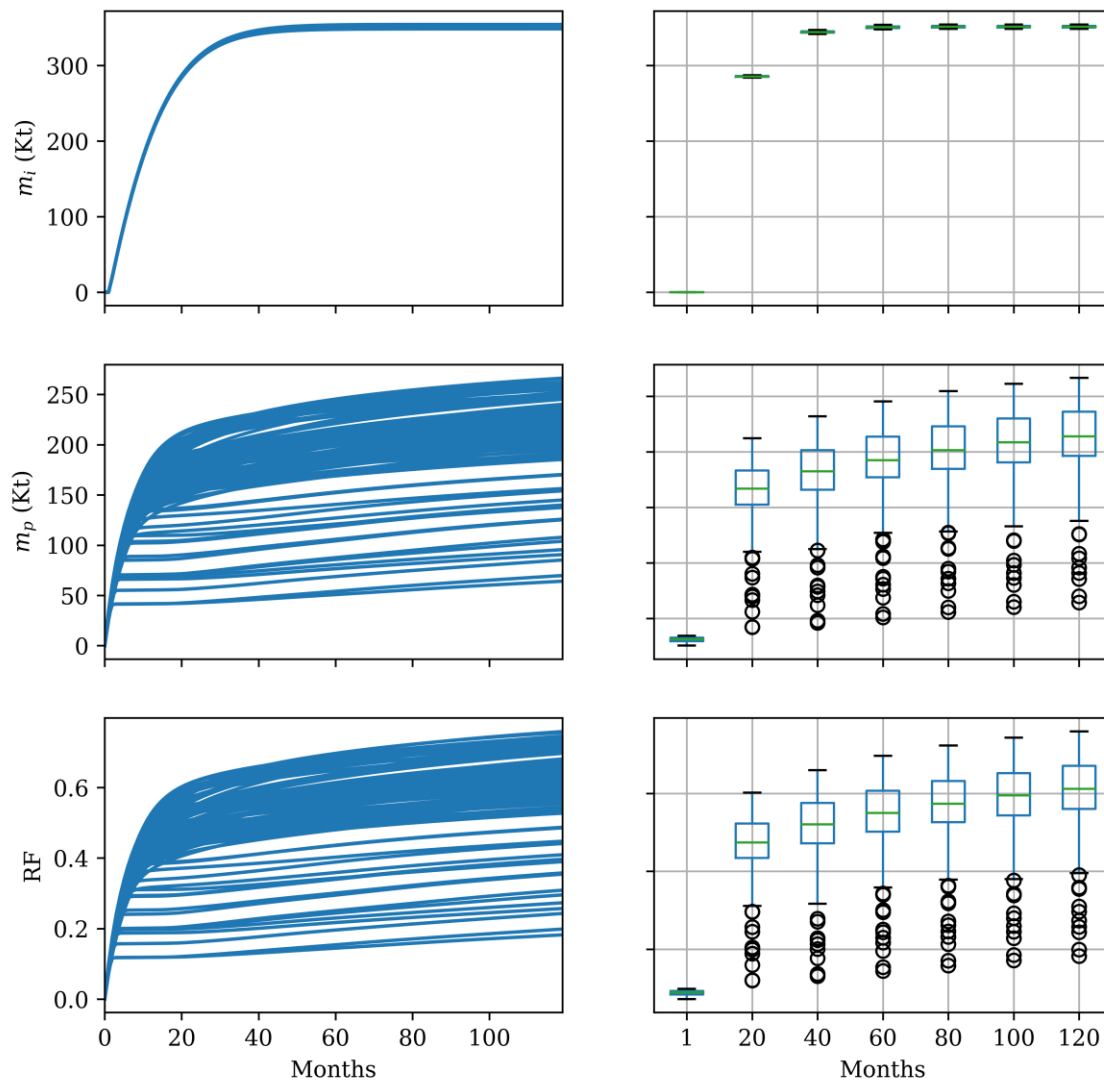


Figure 3. Efficiency of temporary CO₂ storage at Stenlille well ST-11 using an ensemble of saturation functions.

In the left graphs of Figure 3, the ensemble of injected CO₂ mass in kilotons is plotted as a function of time after injection start, and the ensemble of produced CO₂ mass in kilotons, as well as the corresponding recovery factors, are plotted as a function of time after production start.

The distributions of injected and produced amounts and the CO₂ recovery factors are visualized using box plots in the right column of Figure 3. The boxes extend from the first quartile (Q₁; 25% of the data is below this point) to the third quartile (Q₃; 75% of the data is below this point) values of the data, with a line at the median (Q₂; green line; 50% of the data is below this point). The outliers (denoted with circles) are defined as the data points, lying farther than 1.5 * (Q₃ - Q₁) from the edges of the box.

Observe that there is a very small variation in the injected amounts of CO₂, which is a direct consequence of fixed drainage relative permeability functions (cf. Figure 1). After 10 years of injection in ST-11, the median injected mass is 351 Kt, with the first and third quartiles are 350 and 352 Kt, respectively. This is in stark contrast to the unconstrained results in D4.2, where the median injected mass was 135 Kt, and the first and third quartiles were 96 and 171 Kt, respectively. This drastic reduction in uncertainty clearly demonstrates the value of experimental data and numerical modeling in D4.3.

The box plots in Figure 3 highlight the significant variation in produced amounts and in CO₂ recovery factors, depending on the specific choice of imbibition saturation functions. The fact that the amount of recovered CO₂ is always less than the amount of injected CO₂ (recovery factor, $RF < 1$) is due to capillary and solubility trapping. In the scenario shown in Figure 3, the median recovery factor is 0.61. This number is notably different from the corresponding estimate from D4.3 ($RF=0.25$), once again underscoring the importance of constraining simulation results with laboratory data and modeling.

3 Impact of salt precipitation on CO₂ injectivity

Deliverable D4.3 contains the results of laboratory experiments, which indicate that there is a possibility of salt precipitation due to CO₂ injection into brine-saturated rock from Stenlille. A core-scale reactive fluid flow numerical model was developed for the numerical simulation of a laboratory experiment where CO₂ has been injected into a brine-saturated rock sample from Stenlille. The model is implemented in the format of CMG GEM (CMG, 2022).

The model describes both brine and CO₂ using the Peng-Robinson equation of state (Peng & Robinson, 1976), allowing for CO₂ to dissolve in water and water to dissolve in CO₂. Additionally, the modelled brine and rock compositions are set to match the actual values for Stenlille rocks. This provides a comprehensive numerical model used to assess the influence of geochemical reactions, salt precipitation, and water vaporization on the rock sample's porosity and permeability.

The detailed description of fluid-rock interaction in the GEM model comes with a trade-off – even for a one-dimensional (1D) core flood simulation, the model runs in approximately one hour. For a realistic three-dimensional (3D) geometry, this computational burden is prohibitively expensive. In what follows, we describe the steps to simplify the model so that the resulting simplified model can be used at a sector scale without significantly compromising accuracy.

3.1 Radial model

Let us set up a radial model that represents a sector near an injection well at the flank of the Stenlille structure, as illustrated in Figure 4 and Figure 5. The model with 13 cells in radial direction and nine cells in vertical direction has a radius of approximately 770 m and a depth of 45 m. The grid cells are refined towards the wellbore, which has the radius of 10 cm. The smallest radial cell has a radius of 10 cm, while the largest cell has a radius of 400 m. Vertically, the model is partitioned into uniform cells with a height of five meters. For comparison, the Eclipse grid cells near the well have dimensions of approximately 100 x 100 x 3 meters. All grid cells are assigned a uniform porosity of 0.2487 and permeability of 134.05 mD. The reservoir pressure is calculated using hydrostatic equilibrium, and the reservoir temperature is maintained at 50°C.

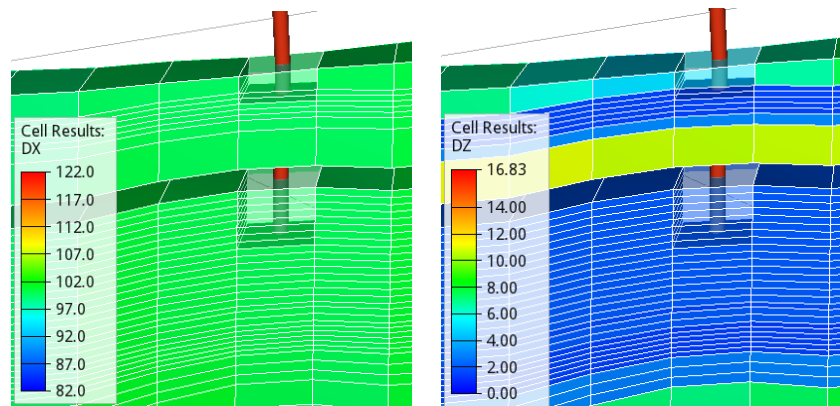


Figure 4. Grid cell sizes near an injection well at Stenlille.

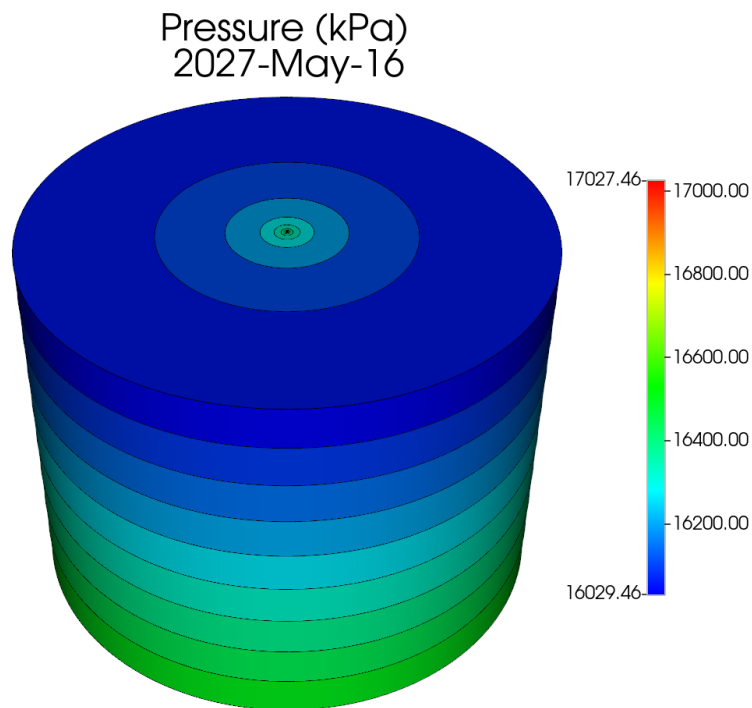


Figure 5. Pressure distribution after CO₂ injection in a radial model for a sector near an injection well at Stenlille.

The simulation scenario involves the injection of supercritical CO₂ into brine-saturated rock at a rate of 100 Kt/year. As a result of water dissolution in the CO₂, salt precipitates, resulting in a decrease in both rock porosity and permeability.

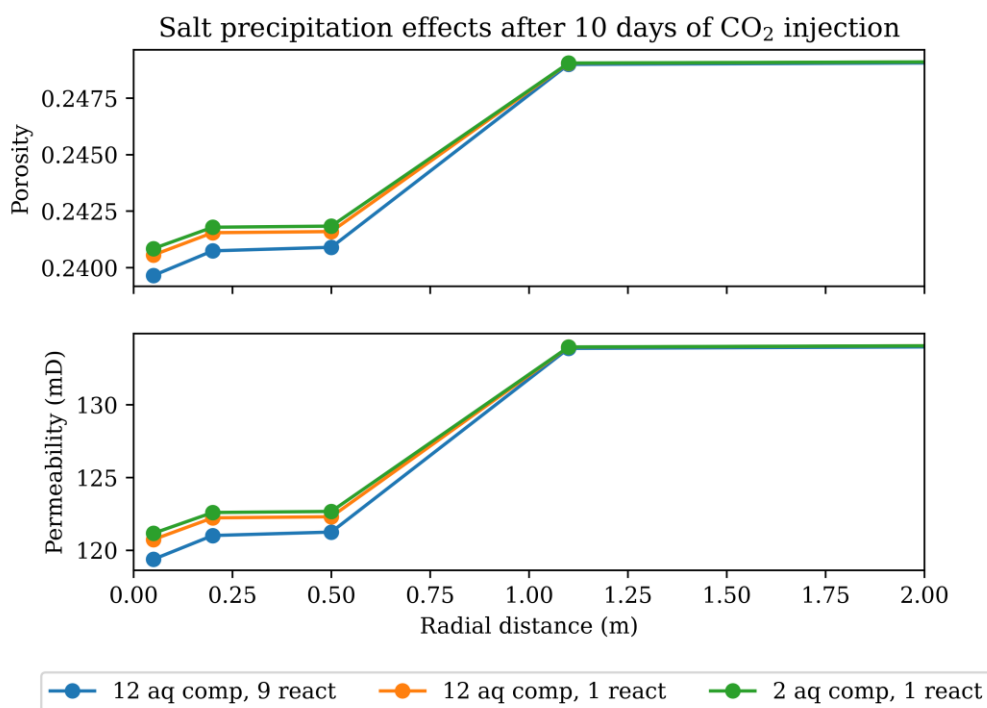


Figure 6. Impact of CO₂ injection on rock porosity and permeability using 3 different GEM models (see text). Markers denote cell centroids.

Figure 6 presents the impact of salt precipitation on rock porosity and permeability using three different GEM models. The original model, presented in D4.3, represents Stenlille brine as an aqueous solution with 12 components (see Table 12 in D4.3), involves six rock minerals (see Table 11 in D4.3), and nine geochemical reactions (see Table 15 in D4.3). Using the available computational setup² it takes approximately two hours (wall time) to obtain the results in Figure 6. The run time mentioned is primarily for comparative purposes to evaluate the numerical performance of the original model against the simplified models below. Note that the actual run time can be optimized by manually tuning the numerical solver parameters.

Since the experimental results in deliverable D4.3 suggest that Stenlille rock properties are not significantly affected by CO₂ injection, certain geochemical reactions and rock minerals can potentially be removed from the original model without significantly impacting accuracy. Numerical results from an intermediate model that only contains the salt (halite) precipitation

² A single-core license of CMG GEM on a workstation with 40 cores and 128 Gb RAM.

reaction and halite as the sole reactive rock mineral are presented in Figure 6 (orange line). The corresponding run time for this model, using the same numerical setup, is 42 minutes.

Finally, the results from a model which reduces the number of aqueous components to just Na^+ and Cl^- and contains the halite precipitation reaction are presented in Figure 6 (green line). The corresponding run time for this model, using the same numerical setup, is 19 minutes.

The numerical results from all three models shown in Figure 6 agree with each other qualitatively. The original model from D4.3 predicts a slightly larger decrease in porosity and permeability due to salt precipitation compared to the two simplified models. However, the difference in predictions does not exceed 1%. Notably, the computational gain from using the reduced model over the original model is more than six-fold.

Using the reduced model presented above, let us evaluate the impact of different grid resolution on the accuracy of the simulation results. To this end, we compare in Figure 7 the corresponding results in Figure 6 with the results for a refined grid with the smallest cell size of 0.03 m, and with the results for a coarsened model with the smallest cell size of 1 m.

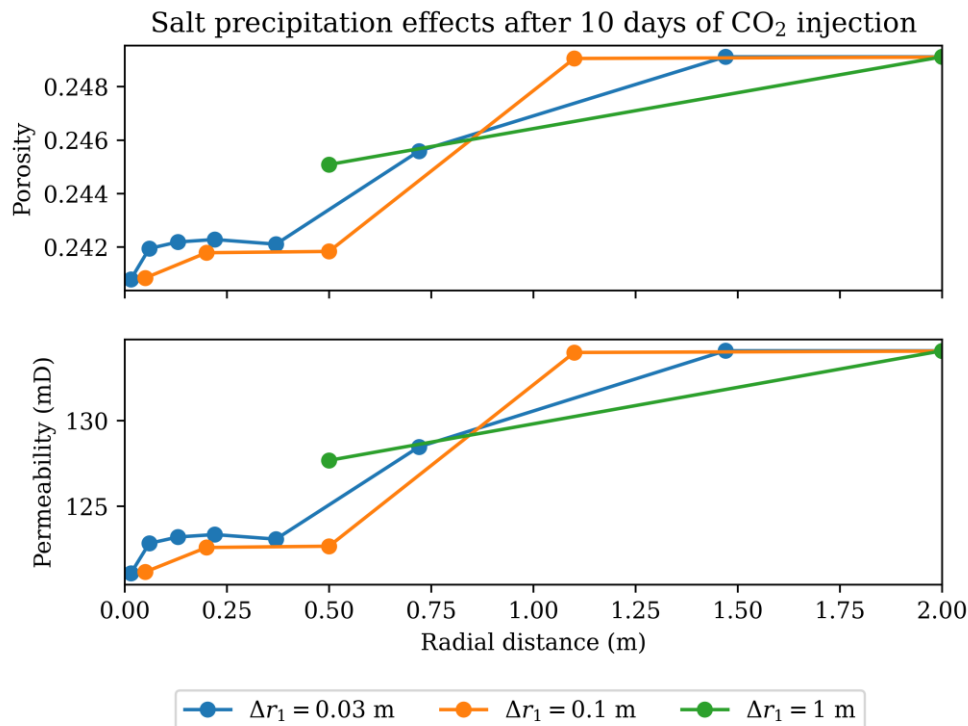


Figure 7. Grid refinement results for the reduced model. Markers denote cell centroids.

Since the results for the finest grid with $\Delta r_1 = 0.03$ m are similar to those for the grid with $\Delta r_1 = 0.1$ m, we conclude that 0.1 m is sufficient for numerical resolution of salt precipitation. In contrast, the grid with $\Delta r_1 = 1$ is too coarse to ensure adequate accuracy.

While all numerical results in Figure 6 and Figure 7 predict a decrease in porosity and permeability due to salt precipitation, the amount of this decrease is relatively small: porosity is decreased by a maximum of 3% and permeability by a maximum of 11%. The maximum amount of precipitated salt in the porous rock depends on the amount of brine accessible to the injected CO_2 . This corresponding number is an input parameter in GEM modelling.

3.2 Sector model

To evaluate the impact of salt precipitation on CO_2 injectivity at Stenlille, we conduct an analysis on a sector of the reservoir model located near an injection well at the flank of the reservoir structure (see Figure 8).

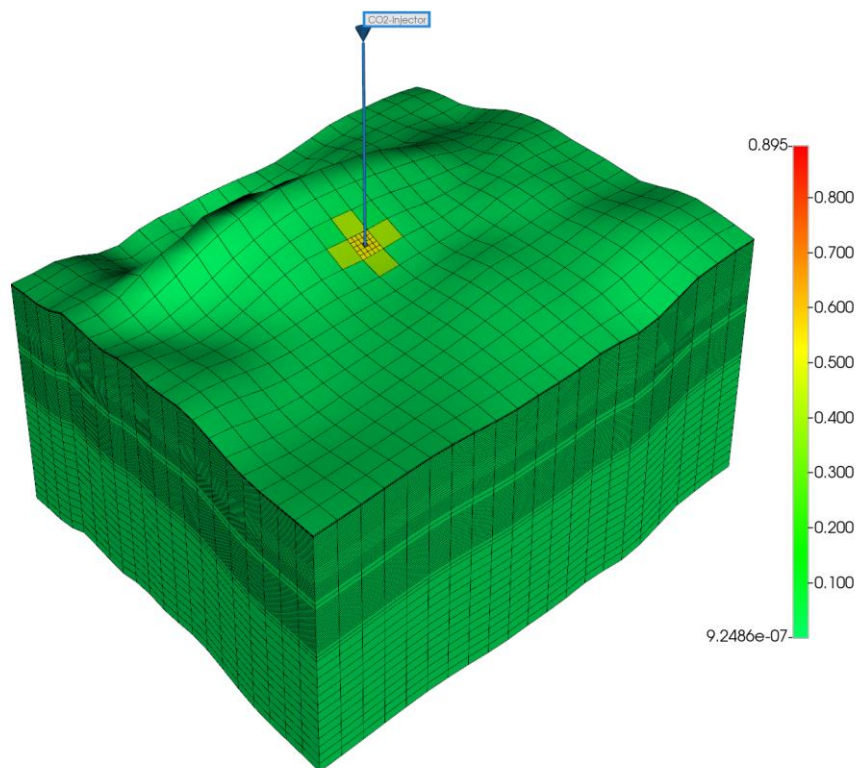


Figure 8. CO_2 saturation observed after 160 days of CO_2 injection.

The GEM model contains 38,000 active cells, populated with a distribution of porosities and permeabilities specific for Stenlille. Local grid refinement is applied near the injection well, resulting in the smallest grid cells having the lateral dimensions of approximately 26 cm. This cell size is chosen based on the grid convergence analysis of the radial model (Figure 7).

The effects of salt precipitation at the sector scale are visualized in Figure 9 using the ratio of grid cell permeabilities at consecutive time steps, referred to as the resistance factor in GEM terminology (see Section 5.1 in D4.3). A resistance factor greater than unity indicates a decrease in permeability. The results in Figure 9 predict a near-well permeability decrease of approximately 10%, which matches the results from the radial model.

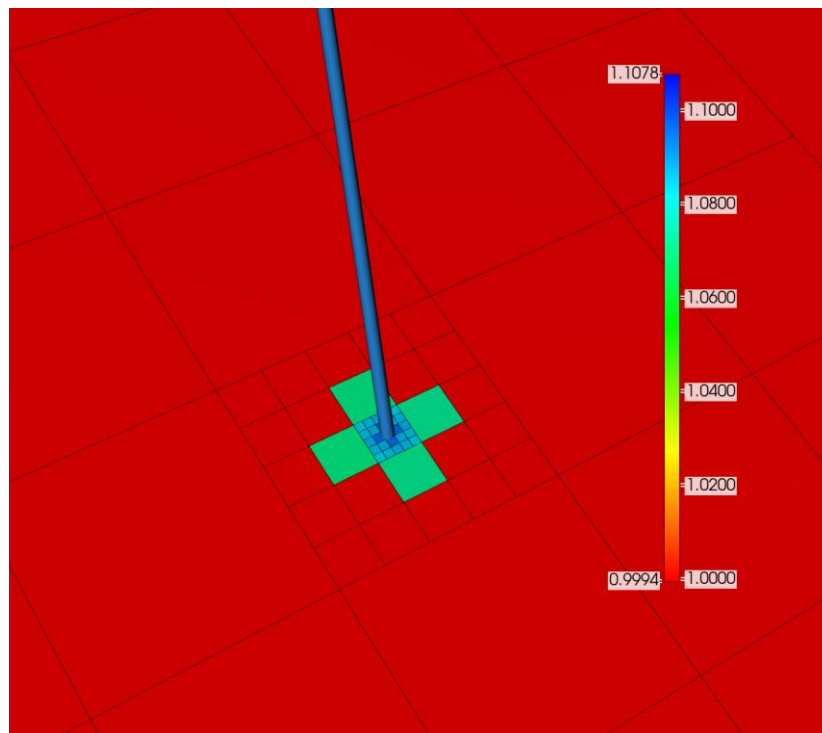


Figure 9. The resistance factor for the locally refined grid cells near the injection well in the Stenlille sector model after 160 days of CO₂ injection.

The simulation run time for the sector model is approximately 40 minutes, making it feasible, in principle, for reservoir-scale modeling (e.g. using the Stenlille model in D4.3, converted into GEM format). Still, the computational effort required is prohibitively large for using the GEM model in an uncertainty analysis as described in Section 2.

4 Fluid properties input to a reservoir scale model

In this work, the numerical results at the reservoir scale are obtained using the Eclipse 100 reservoir simulator (Schlumberger, 2017), which employs a simplified description of the fluids in the reservoir. In what follows, we validate the fluid model input in Eclipse using a comprehensive thermodynamic modeling in GEM (CMG, 2022).

4.1 CO₂ density and viscosity

The Bahadori et al. (2009) correlation is used to determine the dependency of CO₂ density on pressure for input into the Eclipse model from D4.2, while GEM uses the Peng-Robinson (1978) equation of state for the same purpose.

The viscosities are provided as input to both Eclipse and GEM models. For the Eclipse model, the Fenghour et al. (1998) correlation is used, while the Jossi, Stiel, and Thodos (1962) correlation is used for the GEM model.

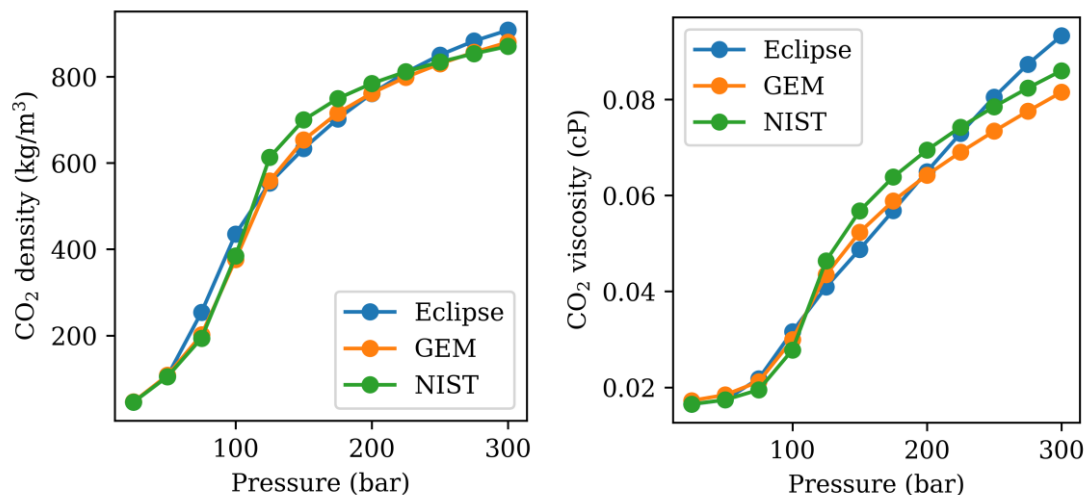


Figure 10. A comparison of the CO₂ density and viscosity from the Eclipse and GEM models with NIST data at 50°C.

A comparison of the CO₂ densities and viscosities for the Eclipse and GEM models with the NIST data (NIST Chemistry Webbook: National Institute of Standards and Technology, 2023) for a temperature of 50°C – corresponding to the reservoir temperature at Stenlille – is provided in Figure 10. Overall, the results from both Eclipse and GEM match the NIST data well, although an increased discrepancy can be observed for viscosities at high pressures.

4.2 Brine density

The Batzle & Wang (1992) correlation is used to determine the dependency of brine density on pressure for input into the Eclipse model from D4.2, while GEM uses the Rowe & Chou (1970) correlation for the same purpose. For a specific pressure and temperature, these correlations estimate brine density as a function of equivalent NaCl molality, which needs to be calculated from the composition of aqueous components in a specific brine. According to the data in deliverable D4.3 (Table 2), the equivalent NaCl molality of Stenlille brine is 3.41.

In Figure 11, a comparison of the brine density correlations for the Eclipse and GEM models is presented for two cases: a brine with NaCl molality of 5, and the Stenlille brine with an equivalent NaCl molality of 3.41. The accuracy of the correlations for the brine with an NaCl molality of 5 is compared with the experimental data of Yan et al. (2011). All data are for a temperature of 50°C. The results indicate that both models can predict brine density with a relative error of less than 0.6%. For the brine with NaCl molality of 5, the correlation in the CMG model yields lower brine densities as compared to the correlation in the Eclipse model for a wide range of pressures. The same behavior can be observed in the model predictions for the Stenlille brine.

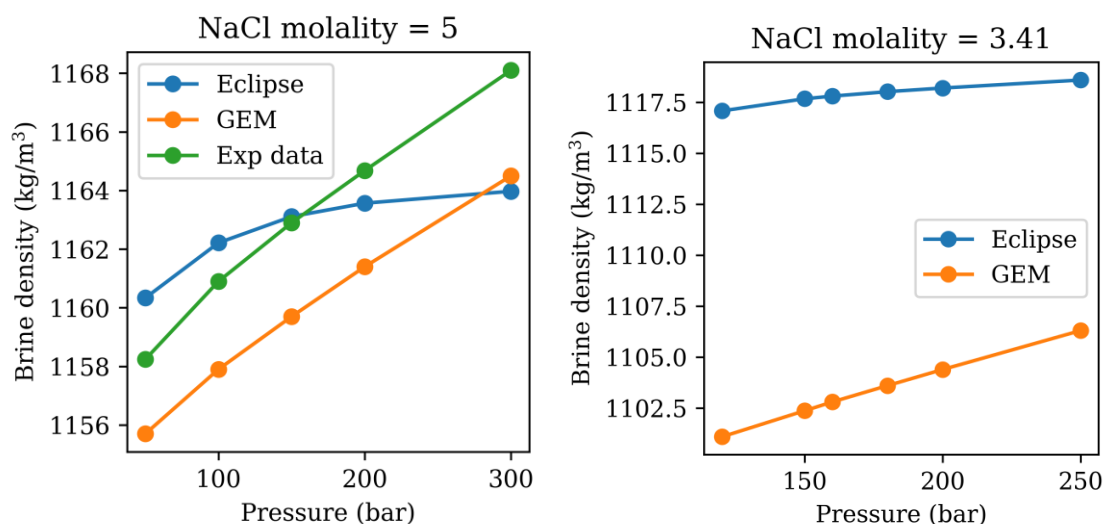


Figure 11. A comparison of the brine density from the Eclipse and GEM models at 50°C. The results for an NaCl molality of 5 are compared with the experimental data of Yan et al. (2011).

4.3 Brine viscosity

The Kestin et al. (1981) correlation is used to determine the dependency of brine density on pressure for input into the GEM model, see Figure 12. The same dependency is used in the Eclipse model.

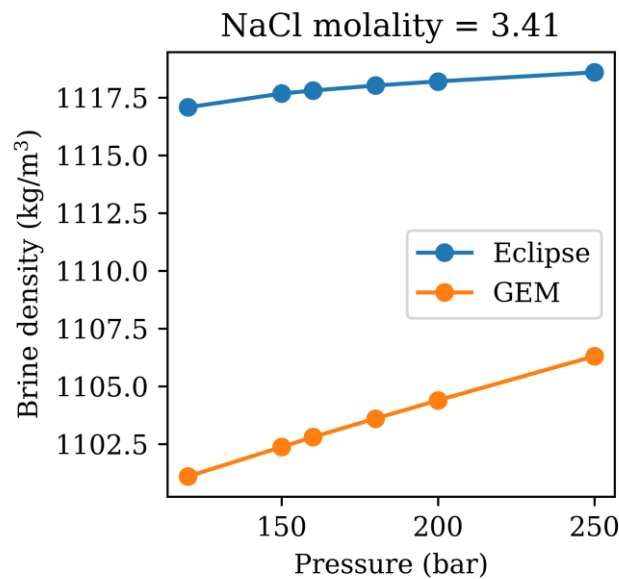


Figure 12. A comparison of the brine viscosity from the Eclipse and GEM models at 50°C.

4.4 CO₂ solubility in brine

The approach used in the Eclipse model consists in specifying the dependency of the volume fraction of CO₂ dissolved in brine using the Chang et al. (1998) correlation. In the GEM model, the CO₂ solubility in brine is calculated using Harvey's method (Harvey, 1996), which accounts for the effects of pressure, temperature, and salinity on Henry's constant.

In Figure 13, a comparison of the CO₂ solubility correlations for the Eclipse and GEM models is presented for two cases: a brine with NaCl molality of 5, and the Stenlille brine with an equivalent NaCl molality of 3.41. The accuracy of the correlations for the brine with an NaCl molality of 5 is compared with the experimental data of Yan et al. (2011). All data are for a temperature of 50°C. Note that the Eclipse model overpredicts the experimentally measured CO₂ solubility while the

CMG model underpredicts it. On average, the prediction error is approximately 20% for each method.

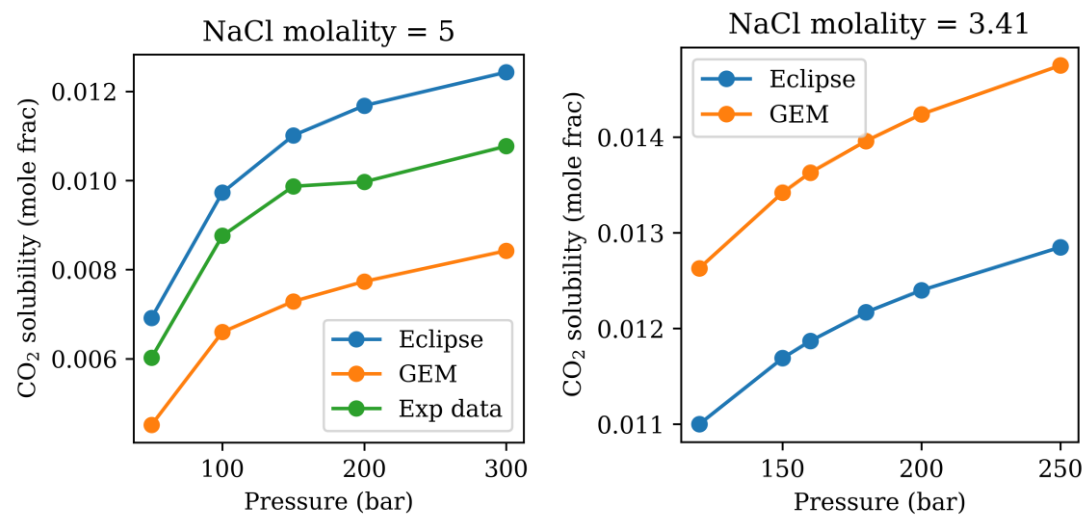


Figure 13. A comparison of the CO₂ solubility from the Eclipse and GEM models at 50°C. The results for an NaCl molality of 5 are compared with the experimental data of Yan et al. (2011).

5 Geochemical modeling

When captured, the CO₂ will contain impurities, the types and concentration of which depends on the CO₂ source and capture technique. In CO₂ stemming from combustion or cement production, high temperature reactions result in production of acid gasses that are highly reactive in hydrous environments. The most important ones are NO_x, SO_x, and O₂. Based on published estimates in the scientific literature, NO_x and SO_x are expected to occur at maximum levels of 50 to 100 ppm mole fraction (Rütters et al., 2022; Luna-Ortiz et al., 2022) whereas O₂ maximum levels range from 10 to ~7500 ppm. Two projects have defined specifications for the gas they will accept. Here, concentrations are 10 ppm for all three gases (Northern Lights project) and 5, 20 and 40 ppm for NO_x, SO_x and O₂ (Porthos project). However, it is unknown if the capture techniques will be able to comply with these specifications. The impact of the impurities during CO₂ injection in geological formations has been the subject of some studies, which indicate that critical reactions are fast and likely to occur near the injection well (e.g., Spycher et al., 2019). Much is yet to be understood since the concentration of impurities is currently unknown and published studies have not considered all pertinent major reactions that can occur.

To understand the impact of injection of CO₂ containing small amounts of the acid gasses in previous and ongoing projects, we have developed a theoretical model for the reactions occurring between NO_x, SO₂, and O₂ at reservoir conditions. The first version of this model was reported in ConcenCUS deliverable D4.2. It was later expanded to also include reactions with NO and refined to account for diffusion limited reaction kinetics (ConcenCUS deliverable D4.3; Kazmierczak et al., 2023). The model is assembled from information on thermodynamic and kinetics properties reported in a range of scientific publications. A core flooding experiment performed in the project GreenSand Phase 2 yielded results that were not inconsistent with those predicted by the model. However, several artefacts operated during the experiments, meaning that the results could not firmly establish the validity of the model. Consequently, the simulated outcome is uncertain even though we have critically reviewed all aspects of the model.

In Part 1 of this chapter, we briefly introduce the model for impurity reactions and present a parametric study based on 1D reactive transport simulations to probe the influence of concentration variability of the impurities. The aim of this work is to define what reactions will occur and what products may form at a range of condition. To a smaller extent, the work builds on simulations for carbonate reservoir rock performed in the project DisCO₂. In Part 2, we report

the results of 1D and 2D simulations of cyclic injection of pure and impure CO₂ in sandstone with the aim of probing where the presence of impurities might influence storage operation.

In both parts, we have performed reactive transport modelling of two-phase flow with the code TOUGHREACT v4.13 (Sonnenthal et al., 2021; Spycher et al., 2021) using the ECO2N module for the properties of CO₂, water and NaCl (Pruess, 2005). Details of the methods are given in Deliverable D.4.2. Briefly, fluid flow was calculated with the van Genuchten-Mualem formulation (van Genuchten, 1980; Mualem, 1976):

$$k_{rw} = \left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{1/2} \left(1 - \left(1 - \left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{1/\lambda} \right)^\lambda \right)^2, \quad \text{Eq. 1}$$

$$k_{rCO_2} = \left(1 - \frac{S_w - S_{wr}}{1 - S_{wr} - S_{CO_2r}} \right)^2 \left(1 - \left(\frac{S_w - S_{wr}}{1 - S_{wr} - S_{CO_2r}} \right)^\lambda \right)^2, \quad \text{Eq. 2}$$

$$p_c = -p_{c0} \left(\left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{-1/\lambda} - 1 \right)^{1-\lambda}, \text{ with } p_c > -p_{c,max}. \quad \text{Eq. 3}$$

Here, k_x represents the relative permeability of fluid x ; S_x , its saturation; S_{xr} , its residual saturation. The subscripts w and CO_2 refers to water and CO_2 ; λ , to a parameter describing the slope of curves; p_c , to the capillary pressure; p_{c0} , to a factor acting on p_c ; and $p_{c,max}$, to the maximum attainable capillary pressure.

In the simulations, it is assumed that equilibrium conditions govern the solubility of CO₂ in water, water in CO₂, and NaCl in water. Dissolution rates at far-from-equilibrium were expressed as:

$$r_+ = k_a e^{\frac{-E_{a(a)}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right)} (a_{H^+})^m + k_n e^{\frac{-E_{a(n)}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right)}. \quad \text{Eq. 4}$$

Here, r_+ is the surface normalized dissolution rate at far from equilibrium (mol/m²/s); k_a and k_n are rate constants at 25 °C for the reactions at acidic and the neutral conditions (mol/m²/s), $E_{a(a)}$ and $E_{a(n)}$, the corresponding activation energies of the reactions (kJ/mol); R is the gas constant (8.314 × 10⁻³ kJ/mol/K); T , the absolute temperature (K). a_{H^+} represents the activity of the proton; and m , the reaction order with respect to a_{H^+} . The parameter values used for calcite were $k_a = 5 \cdot 10^{-3}$ mol/m²/s, $k_n = 1.55 \cdot 10^{-8}$ mol/m²/s, $E_{a(a)} = 14.4$ kJ/mol and $E_{a(n)} = 23.5$ kJ/mol, based on Palandri and Kharaka (2004).

In our simulations, the net dissolution rate, r_{net} , as a function of calcite saturation was approximated by:

$$r_{net} = r_+ (1 - \Omega), \quad \text{Eq. 5}$$

where Ω refers to the saturation ratio, which is given by:

$$\Omega = \frac{IAP}{Ksp}, \text{ where: } IAP = a_{Ca^{2+}}a_{CO_3^{2-}} \text{ and } Ksp = a_{Ca^{2+}}^{eq}a_{CO_3^{2-}}^{eq}. \quad \text{Eq. 6}$$

Finally, the net rate is multiplied by the reactive surface area, SA, to calculate release rates. In simulations with anhydrite, precipitation or dissolution were assumed to be instantaneous to provide equilibrium.

Upon dissolution in water, the impurity species undergo reactions subject to kinetic constraint. The rate of a given aqueous reaction is given by:

$$r_{aq} = k \prod_{j=1}^{j=n} C_j^{v_j}, \quad \text{Eq. 7}$$

where r_{aq} represents the rate of an aqueous reaction; k , the rate constant of the reaction (in moles/L/s); C_1 to C_n , the concentration of species affecting the reaction rate (mol/L) and v_1 to v_n , their exponent in the rate expression.

5.1 Parametric study on the geochemical impact of the impurity variability of CO₂

Capturing and purifying CO₂ is the first step in carbon capture, storage, and utilization (CCUS). However, this process is highly costly, potentially jeopardizing the financial viability of CCUS projects and impurities in capture CO₂ can cause negative impacts on the projects (A. Razak et al., 2023; Talman, 2015). Therefore, optimizing and standardizing the purity of captured CO₂ is necessary. The types and concentration of impurities in captured CO₂ vary depending on the origins of the CO₂ and the capture methods employed (Talman, 2015). In this work, we focus on oxidizing impurity gases i.e., SO₂, NO₂, and O₂ which are common in post-combustion CO₂ capture methods (A. Razak et al., 2023; Talman, 2015). These impurities can produce strong acids such as sulfuric or nitric acids, leading to harsh corrosive conditions that might damage injection wells, dissolve caprocks, and alter the properties of the storage formations, affecting CO₂ injectivity.

The fastest interactions among SO_2 , NO_x , and O_2 are depicted schematically in Figure 14. The reaction pathway is kinetically controlled; thus, information of the reaction rates is crucial for assessing the geochemical impact of these impurities in deep brine aquifers. Kazmierczak et al., (2023) reviewed literature and compiled major interactions among these impurities and recalculated reaction rates to reflect conditions during CO_2 injection i.e., diffusion-limited cases with temperature and pressure corrections (Figure 14 and Table 3).

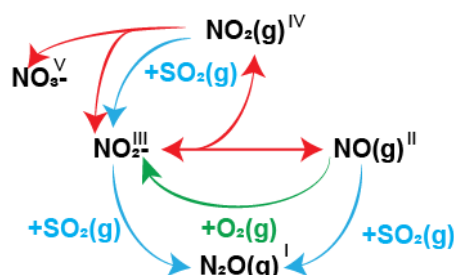


Figure 14. Schematic diagram of interactions among impurities. The superscript roman numbers of N species indicate the redox status of N.

They identified six kinetically controlled reactions. When $\text{NO}_2(\text{g})$ dissolves in water, it can disproportionate to nitrite (NO_2^- , N(III)) and nitrate (NO_3^- , N(V); Figure 14; Reaction 1 in *Table 3*), generating H^+ in the processes. Nitrous acid can then disproportionate further to produce $\text{NO}_2(\text{aq})$ and $\text{NO}(\text{aq})$ in a reversible reaction (Reaction 2f and 2r in *Table 3*). This will either consume or produce H^+ . Nitrogen monoxide (NO , N(II)) undergoes oxidation, consuming oxygen and producing NO_2^- (Reaction 3). Sulfur dioxide interacts with NO_2 (Reaction 4), NO_2^- (Reaction 5), and NO (aq; Reaction 6), with nitrous oxide (N_2O , N(I)), H^+ and SO_4^{2-} being the main products. In addition to the six reactions included here, SO_2 and O_2 can also react to produce H_2SO_4 . However, preliminary simulations showed that this reaction occurs so slowly that it has no influence within the timeframe reported here. Hence, we have excluded this reaction.

Table 3. Kinetic reactions included in the study.

Nr.	Reaction	Reaction rate (mol ⁻¹ L S ⁻¹)	Power terms
1	2NO ₂ (aq) + H ₂ O → NO ₂ ⁻ + NO ₃ ⁻ + 2H ⁺ + TC1	5.47 × 10 ⁴	[NO ₂ (aq)] ^{1.5}
2f	2NO ₂ ⁻ + 2H ⁺ → NO ₂ (aq) + NO(aq) + H ₂ O + TC2f	4.36 × 10 ²	[HNO ₂ (aq)] ²
2r	NO ₂ (aq) + NO(aq) + H ₂ O → 2NO ₂ ⁻ + 2H ⁺ TC2r	1.74 × 10 ⁸	[NO ₂ (aq)][NO(aq)]

3	$4\text{NO}(\text{aq}) + \text{O}_2(\text{aq}) + 2\text{H}_2\text{O} \rightarrow 4\text{NO}_2^- + 4\text{H}^+ + \text{TC3}$	2.1×10^6	$[\text{NO}(\text{aq})][\text{O}_2(\text{aq})]$
4	$\text{SO}_2(\text{aq}) + 2\text{NO}_2(\text{aq}) + 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{NO}_2^- + \text{TC4}$	1.06×10^5	$[\text{NO}_2(\text{aq})][\text{S}(\text{IV})]$
5	$2\text{SO}_2(\text{aq}) + 2\text{NO}_2^- + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{SO}_4^{2-} + \text{N}_2\text{O}(\text{aq}) + \text{TC5}$	78.85	$[\text{H}^+]^{0.5}[\text{N}(\text{III})][\text{S}(\text{IV})]$
6	$2.0\text{NO}(\text{aq}) + \text{SO}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{N}_2\text{O}(\text{aq}) + \text{SO}_4^{2-} + 2\text{H}^+ + \text{TC6}$	32	$[\text{NO}][\text{S}(\text{IV})]$

The six reactions unfold at rates depending on the gas composition and the concentration of reaction products, the latter of which will change with time. In addition, Reaction 2f and 3 are capable of producing species that are reactants in upstream reactions. Thus, the manner by which the reactions unfold is not obvious. We conducted a parametric study to evaluate the geochemical impact of varying impurity compositions in the injected CO₂ on the brine composition using a reactive transport model (Table 4). We tested eight different compositions, where the partial pressure of NO₂, SO₂, and O₂ were set at either 50 or 10 ppm (Table 4) based on the consultation with operators. All six reactions were traced using hypothetical neutrally charged tracers (TC1, TC2f, TC2r, TC3, TC4, TC5, and TC6; Table 3), allowing us to quantify to what the extent the individual reactions contributed to the net outcome. The reversible reaction, Reaction 2, was treated separately as Reaction2f (forward reaction) and 2r (reverse reaction) to trace them without affecting the equilibrium between two reactions. Given that Reaction 2f and 5 are pH dependent, we compared two scenarios: one without mineral buffering (Case I) and one with pH buffering by chalk (Case II).

Table 4. Impurity gas concentrations (ppm mole fraction) evaluated in this study.

Scenario	NO ₂	SO ₂	O ₂
1. N-50	50	10	10
2. S-50	10	50	10
3. O-50	10	10	50
4. N×S-50	50	50	10
5. S×O-50	10	50	50
6. N×O-50	50	10	50
7. All-50	50	50	50
8. All-10	10	10	10

5.1.1 Methods

5.1.1.1 Basic model setup

We employed TOUGHREACT v4.13-ECO2N with the Pitzer database with modifications to accommodate 1) the kinetic reactions defined by Kazmierczak et al. (2023); 2) equilibrium parameters for gas-liquid reactions under the simulation conditions of 60 °C and 200 bar; and 3) solubility parameters for salts such as $\text{NaHSO}_4\text{-H}_2\text{O}$ and $\text{Na}_3\text{H}(\text{SO}_4)_2$ (Christov and Moller, 2004). The model employed a 2 km long x 100 m thick 1-D radial grid (Table 5), comprising 250 in total grid blocks, excluding the last block which was boundary conditions. The first 5 m from the well borehole (radius 0.1 m) was finely grided with an increment of 0.05 m. Beyond this, up to 50 m from the well borehole, grid block size increased logarithmically with a factor of 1.0350. Grid spacing became coarser up to 2 km from the well borehole.

Table 5. Grid set-up for the simulations.

Cumulative radial distance (m)	Space discretization
0.1	Well borehole radius
5.1	100 of an increment with 0.05m
50	100 of logarithmic increments
100	30 of logarithmic increments
2000	20 of logarithmic increments
10^{30}	One cell to provide open boundary condition

Formation parameters such as porosity (0.30), absolute permeability ($10 \times 10^{-14} \text{ m}^2$), relative permeability ($S_{lr} = 0.30$, $m = 0.457$, $S_{gr} = 0.05$) and capillary pressure ($P_0 = 19.61 \text{ kPa}$, $S_{lr} = 0.0$, $S_{ls} = 0.999$, $\lambda = 0.457$) were followed Pruess and Müller (2009).

5.1.1.2 Scenarios

Case I: Na-Cl brine

Supercritical CO_2 with the eight different impurity compositions (Table 6) was injected into brine with a dissolved NaCl mass fraction (X_s) of 20%, corresponding to 4.31 mol/kg of water of Na^+ and Cl^- (Table 6). The injection rate of CO_2 was 0.1 kg/s for 100 days, during which complete dry-out did not occur. In Case I, the initial mineral composition was undefined (no mineral

reaction), and a set of salts e.g., halite, thenardite (Na_2SO_4), calcite, $\text{NaHSO}_4\text{-H}_2\text{O}$, and anhydrite were allowed to precipitate.

Table 6. Summary of initial brine chemistry and mineral condition of Case I and Case II.

	Case I	Case II
	Na-Cl brine in 1D	Na-Cl brine with chalk in 1D
Brine chemistry (mol/kg of water)		
Na^+	4.310	4.310
Cl^-	4.310	4.310
Ca^{2+}	5×10^{-05}	6.1×10^{-04}
HCO_3^-	4×10^{-04}	6.1×10^{-04}
SO_4^{2-}	1×10^{-20}	1×10^{-20}
X_s	20	20
pH	7.12	9.00
Initial mineral conditions		
Mineral composition	Not defined	90 % Calcite (kinetic)

Case II: Na-Cl brine in chalk

In Case II, supercritical CO_2 with the same eight impurity compositions was injected in brine with an X_s of 20% and saturated with calcite (Table 6). The initial brine composition of Case II was obtained by reacting Case I's brine with chalk until the water chemistry stabilized. The initial mineral composition in Case II was 90% of calcite with remaining 10% undefined. Calcite dissolution and precipitation was kinetically controlled following Palandri and Kharaka (2004) as described in the earlier section. Except for calcite, all other settings in Case II were identical to those in Case I.

5.1.2 Results

Figure 15 and Figure 16 present the results for the scenarios N-50, S-50, O-50, All-50 and All-10 in Case I and Case II, respectively. In the upper part, the figures show the temporal evolution (y-axis) of gas saturation in the pore space and the partial pressure of the impurity gases, normalized to their respective input amounts. In the lower part, the concentration of tracers (mol/m^3 grid cell) of Case I and Case II are shown. The results of Reaction 2f are displayed as net tracer mass by subtracting TC2r from TC2f (TC2f* in Figure 15 and Figure 16). When TC2r exceeds TC2f,

indicating a net reverse reaction, a net TC2r (TC2r-TC2f) is shown as TC2r* (Figure 15 and Figure 16).

Across all the scenarios, pressure (up to 200.3 bar), and saturation of water (0.52 at the injection well) and gas (0.25 at the injection well) remained the same (Figure 15 and Figure 16). The temporal evolution patterns of NxO-50 were closely resembled those of N-50, SxO-50 mirrored S-50, and NxS-50 aligned with All-50 in both Case I and Case II; thus, these results are not shown individually as figure. Instead, the mass balance and pH profiles for these cases are included with the other five compositions in Figure 17 and Figure 18.

5.1.2.1 Reaction pathways

Case I (without mineral reactions)

Without pH buffering by mineral weathering (Case I), when supercritical CO₂ was co-injected with 50 ppm of NO₂, 10 ppm of SO₂, and 10 ppm of O₂ (N-50) over 100 days, SO₂(g) was completely consumed near the injection well, and NO₂(g) was consumed slightly slower (Figure 15). O₂ (g) consumption was about 32 %, and its normalized partial pressure progressively decreased toward the CO₂ front (Figure 15). The tracers revealed that both NO₂(g) and SO₂(g) were rapidly consumed near the injection well via Reaction 1 ($\text{NO}_2 \rightarrow \text{NO}_3^- + \text{NO}_2^-$), 4 ($\text{SO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}$) and 5 ($\text{SO}_2 + \text{NO}_2^- \rightarrow \text{N}_2\text{O}$; Figure 2). Reaction 2f, producing NO and NO₂, also intensively occurred, leading to a secondary reaction zone of Reaction 1 and 3 ($\text{NO} + \text{O}_2 \rightarrow \text{NO}_2^-$), nearer the CO₂ front (Figure 15). The reaction intensities of the secondary reaction zone were about 2-4 orders of magnitude lower than those near the injection well (Figure 15). Reaction 6 ($\text{SO}_2 + \text{NO} \rightarrow \text{N}_2\text{O}$) occurred at a significantly lower rate than other SO₂ consuming reactions (i.e., Reaction 4 and 5; Figure 15).

In contrast, when supercritical CO₂ was co-injected with the higher SO₂ concentration (50 ppm; S-50; Table 4), approximately 30 % of SO₂(g) remained in the gas phase, and O₂(g) consumption was negligible (Figure 15), while NO₂(g) was completely consumed. In S-50, a sequence of Reaction 4 ($\text{SO}_2 + \text{NO}_2 \rightarrow \text{NO}_2^-$) and 5 ($\text{SO}_2 + \text{NO}_2^- \rightarrow \text{N}_2\text{O}$), where NO₂ and SO₂ interacted and converted to SO₄²⁻ and N₂O, were dominant (Figure 15). About 20 % of the nitrite produced in Reaction 4 went through reaction 2f, producing NO₂ and NO. These products were further interacted with SO₂ via Reaction 4 and Reaction 6. In S-50, Reaction 1 ($\text{NO}_2 \rightarrow \text{NO}_3^- + \text{NO}_2^-$) and Reaction 3 ($\text{NO} + \text{O}_2 \rightarrow \text{NO}_2^-$) did occur negligibly, and no secondary reaction zone developed (Figure 15).

For scenarios O-50, All-50 and All-10, the dominance of reaction pathways was similar to those of N-50 (Figure 15), albeit some N_2O was produced. Reaction 1, 2, 4, and 5 were the primary pathways to consume $\text{NO}_2(\text{g})$ and $\text{SO}_2(\text{g})$. In these three scenarios, a secondary reaction zone near the CO_2 front also developed. The normalized partial pressure of O_2 in O-50 and All-10 were close to the input amount. In these scenarios, with NO_2 at 10 ppm, NO production was lower than in All-50 or N-50, resulting in a significantly lower intensity of Reaction 3.

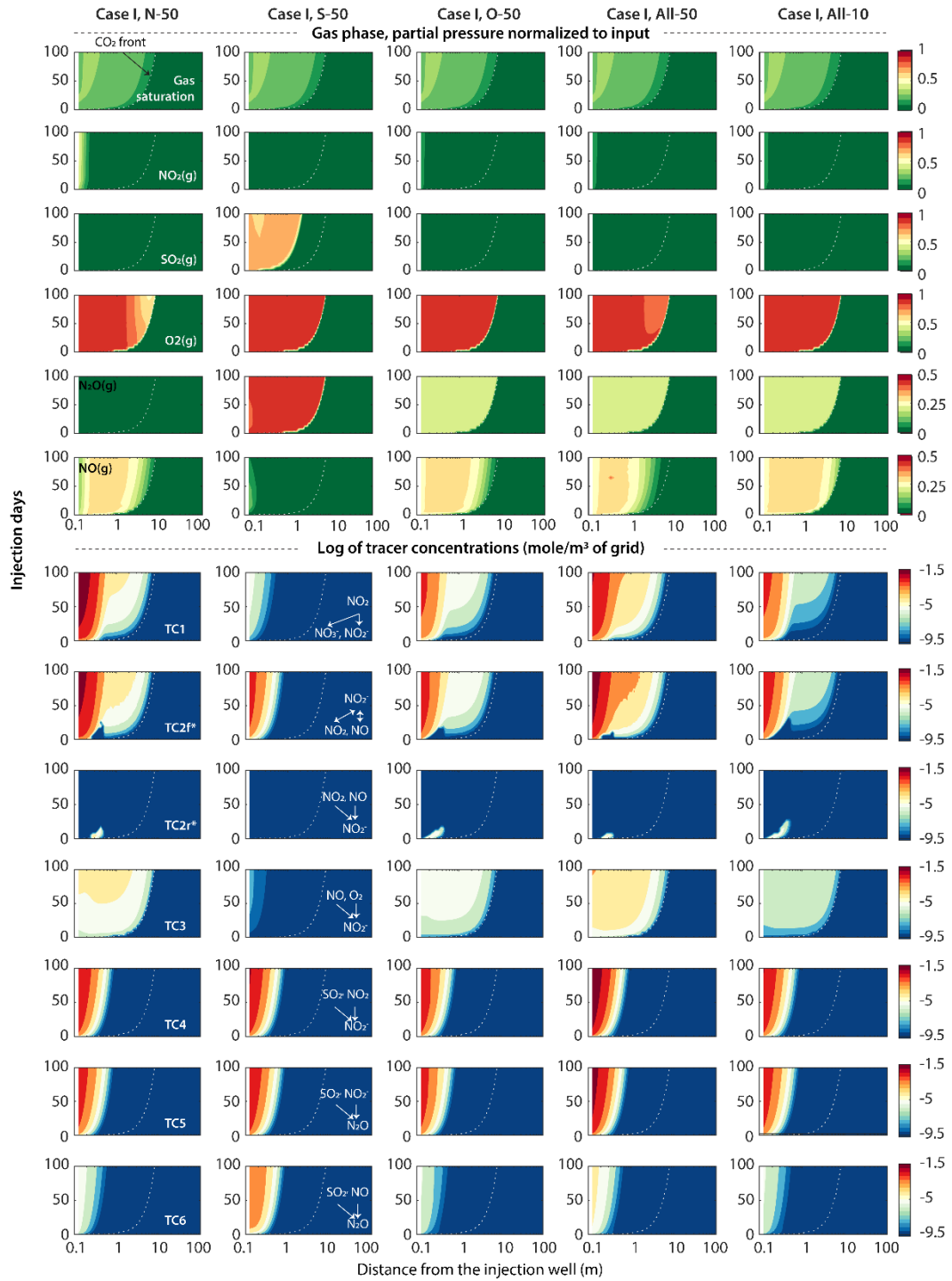


Figure 15. Temporal evolution of gas saturation and partial pressure of gas normalized to their respective input amounts and the mass of tracers of Case I without rock buffering of pH. The X-axis represents the distance from the injection well (log-scale) and the y-axis represents the injection days (from bottom to up). The white dotted line represents the CO₂ front.

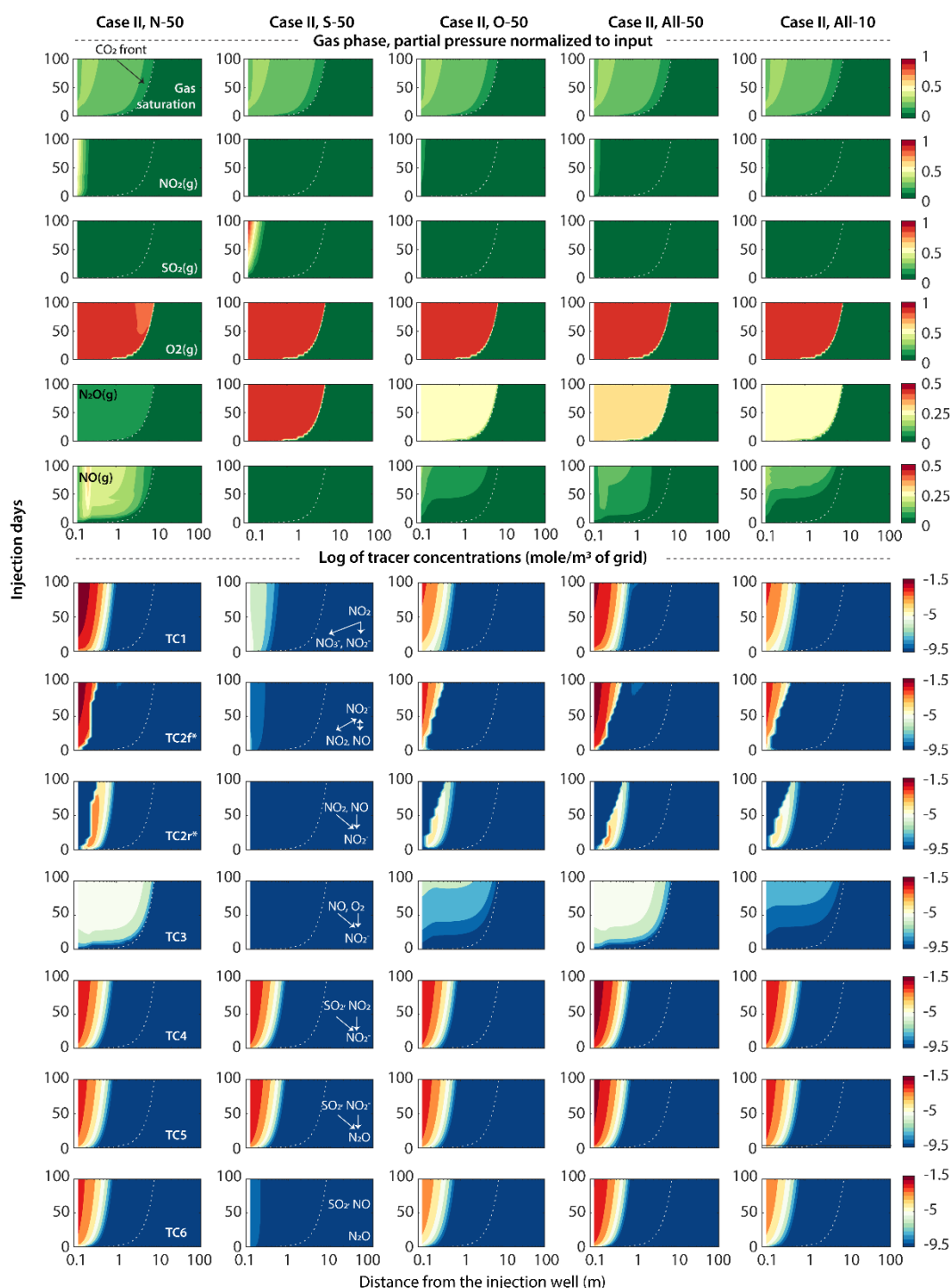


Figure 16. Temporal evolution of gas saturation and partial pressure of gases normalized to their respective input amounts and mass of tracers as a function of distance from the injection well for Case II with buffering of pH by calcite dissolution. The y-axis represents the injection time (bottom to top). The white dotted line represents the CO_2 front.

Case II (with chalk)

With pH buffering by chalk (i.e., Case II), impurities injected with supercritical CO₂ reacted through different pathways compared to those without pH buffering (i.e., Case I). In N-50, as in N-50 of Case I, Reaction 1, 2, 4 and 5 were dominant (Figure 16). However, in Case II, N-50 showed a significant net Reaction 2r, converting NO and NO₂ back to NO₂⁻ at the reaction front, reflecting a pH dependent decrease in HNO₂(aq) concentration, which substantially lowered the rate of Reaction 2f. In addition, Reaction 6 (SO₂ + NO → N₂O) had higher intensity than in Case I (Figure 15 and Figure 16). Reaction 3 in Case II occurred at a lower rate likely due to the higher intensities of Reaction 2r and 6, which consume NO. Consequently, the normalized partial pressure of O₂ remained close to the input amount (Figure 16).

In S-50 of Case II, Reaction 4 and 5 were the predominant dominant processes, while the other reactions were negligible (Figure 16). Compared to Case I's S-50, the intensity of Reaction 2f was significantly lower (Figure 16). The normalized partial pressure of SO₂ was close to the input amount at the injection well and rapidly decreased with increasing distance from the injection well (Figure 16).

For scenarios O-50, All-50, and All-10 in Case II, the dominant reaction pathways were similar to those of N-50 (Figure 16). NO₂(g) and SO₂(g) were completely converted via Reaction 1, 2, 4, and 5. In addition, there was no secondary reaction zone in these three scenarios, and O₂(g) was remained close to the input amount.

5.1.2.2 Mass balance of N, S and O at the end of 100-day injection

Different dominance of reaction pathways, depending on the gas and brine compositions, resulted in different end products of N, S and O (Figure 15). In N-50 of Case I, NO₂(g) was predominantly converted to NO₃⁻ (61%), and the remainder distributed among NO₂⁻ (12%), NO (15%), and N₂O (9%), consistent with the dominance of Reaction 1. Its SO₂ input was converted to SO₄²⁻. O₂ recovery was only 88 % of the input: 58 % as O₂ and 32 % as TC3 (consumed). N-50 in Case II (with chalk) showed the similar results to Case I except for a higher fraction of NO₂⁻ (22 %) and lower NO (9%), consistent with low intensity of Reaction 2f (NO₂⁻ → NO + NO₂) due to higher pH. The lower production of NO led to a lower O₂ consumption, which was 12 % of the input amount (recovery:86%). Its SO₂ was predominantly present as anhydrite (91%), with the rest as SO₄²⁻.

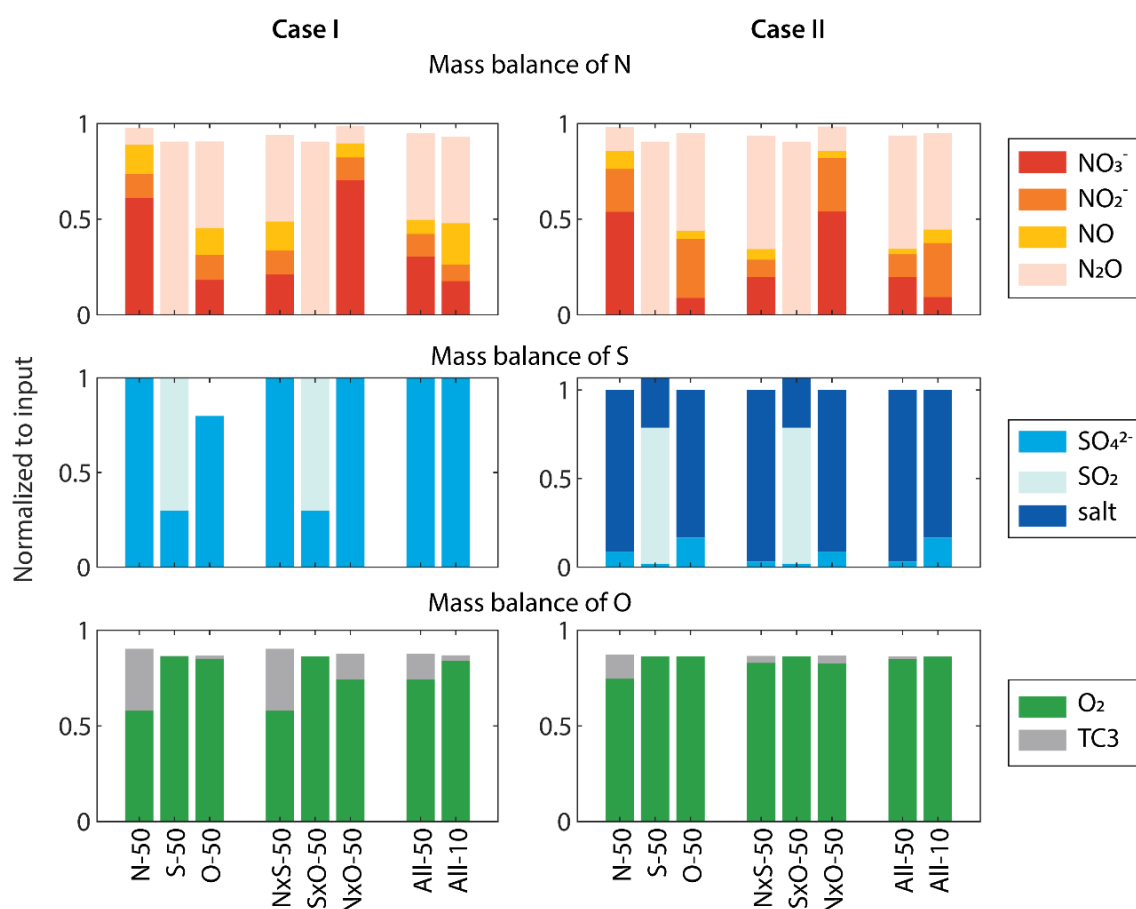


Figure 17. Mass balance of N, S and O after 100-days of injection for Case I and Case II

For S-50 (and SxO-50) in both cases, $\text{NO}_2(\text{g})$ was all converted to N_2O (Figure 17), which can be explained by the dominance of Reaction 4 ($\text{SO}_2 + \text{NO}_2 \rightarrow \text{NO}_2^-$) and 5 ($\text{SO}_2 + \text{NO}_2^- \rightarrow \text{N}_2\text{O}$). In both cases, about ~70 % of SO_2 remained as SO_2 , and the rest was either SO_4^{2-} (Case I) or anhydrite (Case II). Oxygen in S-50 (and SxO-50) was negligibly consumed.

In O-50, All-50 and All-10 of Case I and Case II, $\text{NO}_2(\text{g})$ were mainly converted to N_2O (~45% to 59%), with the remainder differently distributed among NO_3^- , NO_2^- , and NO (Figure 17). In All-50, the NO_3^- fractions were higher (30% in Case I and 20 % Case II) than those of NO_2^- (12% in Case I and 11 in Case II) and NO (7% in Case I and 2 % in Case II), due to higher contributions from Reaction 1. $\text{SO}_2(\text{g})$ of these three impurity scenarios in Case I were converted to SO_4^{2-} , while in Case II it predominantly formed anhydrite (83~96%) with a trace SO_4^{2-} (Figure 17).

NxO-50 in both cases showed the similar mass balances as N-50, and SxO-50 as S-50, respectively. Similarly, NxS-50 results were similar to those of All-50 in both cases (Figure 17).

5.1.2.3 pH profile development

The overall pH profiles of different impurity scenarios in Case I were similar to each other: extremely low pH (from about -1 to 0) near the injection well and increasing rapidly with distance up to 0.5 m then stabilizing at pH ~2.8 up to the CO₂ front (Figure 18). Among the five impurity scenarios, All-50 (and NxS-50) showed the lowest pH (~ -1) near the injection well, which can be attributed to higher input of strong acid sources (i.e., NO₂ = 50ppm, SO₂ = 50 ppm, O₂ = 50 ppm). N-50 (and NxO-50) had similar pH profile as that of All-50 (Figure 18). Conversely, higher pH in O-50 and All-10 was attributed to the lower concentrations of NO₂ and SO₂.

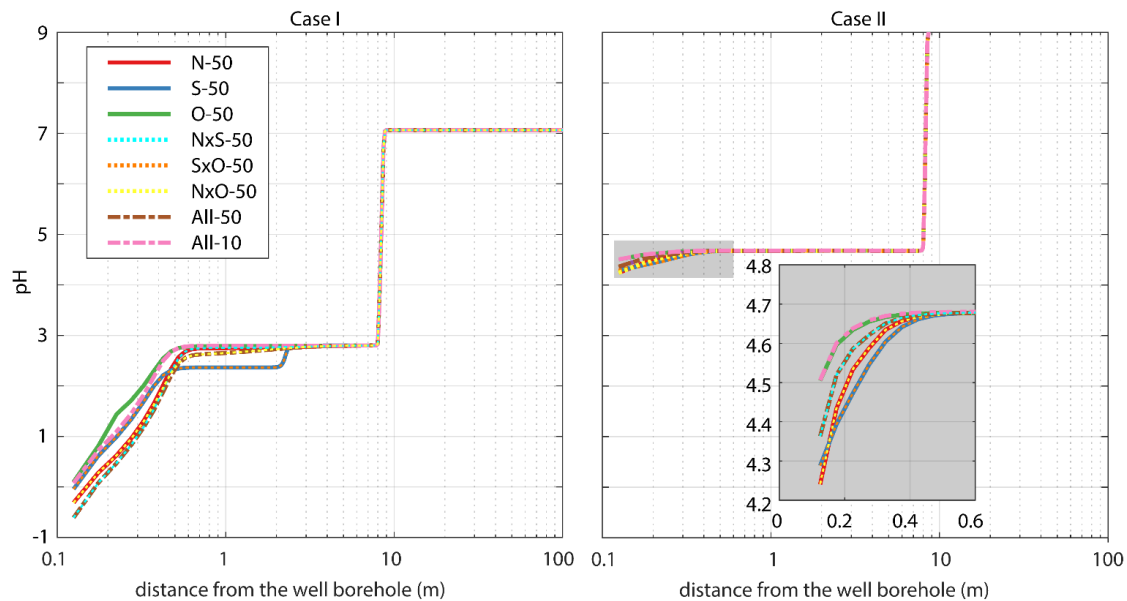
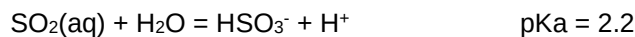


Figure 18. pH profiles of Case I (left) and Case II (right) of all impurity composition scenarios. For Case II, pH near the injection well (0.6 m from the well) was zoomed in a gray box.

In S-50 (and SxO-50) of Case I, pH was about half a unit lower than other impurity scenarios between 0.3 to 2 m (Figure 18) likely because the remaining SO₂ dissolved into water and dissociated into HSO₃⁻ and H⁺:



In Case II, where calcite buffers the pH of the brine, pH profiles of all the impurity scenarios were well-buffered between 4.2 to 4.7. Differences among the impurity scenarios were relatively small

compared to Case I. The lowest pH right at the injection well was simulated under N-50 (and NxO-50), while further from the injection well, S-50 (and SxO-50) showed slightly lower pH. All-50 (and NxS-50) and All-10 (and O-50) showed the second and the highest pH profiles, respectively (Figure 18).

5.1.3 Discussion and conclusions

This parametric study demonstrates that the impurity compositions and brine pH significantly influence the dominant reaction pathways and the development of geochemical conditions (i.e., pH). Here we have summarized our results into five discussion points.

5.1.3.1 Role of impurity composition on dominant pathways

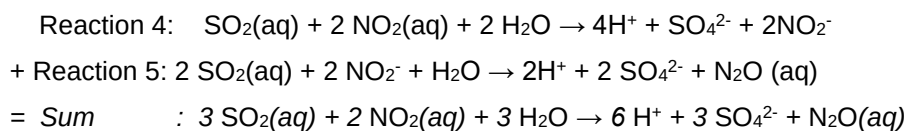
The simulations highlight distinctive patterns for S-dominant scenarios (S-50 and SxO-50) compared to others. SO₂, being the most soluble gas among those in the simulation (Table 7), dissolves extensively in brine and then convert quickly to SO₄²⁻.

Table 7. Equilibrium constants between gas and liquid phases of gases considered in this study.

Reaction	Equilibrium constant (log K)
SO ₂ (g) ↔ SO ₂ (aq)	-1.2111*
NO ₂ (g) ↔ NO ₂ (aq)	-3.2768*
O ₂ (g) ↔ O ₂ (aq)	-3.1076
N ₂ O(g) ↔ N ₂ O(aq)	-2.3999*
NO(g) ↔ NO(aq)	-2.5898*

* Corrected for fugacity at 60 °C and 200 bar.

Consequently, Reaction 4 and 5 become dominant, converting all NO₂ to N₂O. These results suggest that the reaction pathways for S-dominant scenarios can be simplified by combining Reaction 4 and Reaction 5:



This simplified reaction equation indicates that as long as the amount of NO₂ is lower than 2/3 of SO₂, this reaction may be the predominant one; thus, other reactions (Reaction 1,2,3 and 6) can

be ignored, greatly decreasing computational time. For such scenarios, the slower reaction between SO₂ and O₂ would have to be included to correctly predict long term evolution of the gas composition. For other cases, however, all six reactions must be considered to evaluate the impact of impurities.

5.1.3.2 Role of brine pH in determining dominant pathway

The role of brine's pH on determining dominant reaction pathways is appreciable mostly for the N species. For instance, reaction 2f, which plays a central role in the NO₂ reaction cycle by converting NO₂⁻ back to NO₂ and NO, occur at a rate depending on [HNO₂(aq)]² (Table 7). HNO₂(aq) can dissociate to NO₂⁻ and H⁺ with a pKa value of 3.006:



In the pH range of Case II (4.2-4.8), the HNO₂(aq) fraction will be small (Figure 19).

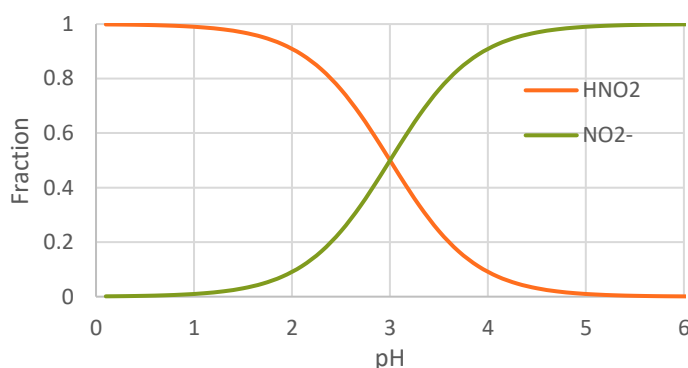


Figure 19. HNO₂(aq) and NO₂⁻ fractions as a function of pH.

However, the reaction intensity of Reaction 2f in Case II was still about half that of Case I (Figure 20). These results may be because Reaction 1 (NO₂ → NO₃⁻ + NO₂⁻) and Reaction 4 (NO₂ + SO₂ → NO₂⁻), which are the most intensive, continuously produced NO₂⁻, allowing Reaction 2f to proceed even with trace amounts of [HNO₂]. Note that Figure 7 also indicates to what degree reactions lead to recycling of nitrogen through NO₂ production by downstream Reactions 2f and 3. This is most notable for the NxO-50 scenario, where approximately 50 % of the NO₂ becomes temporarily regenerated.

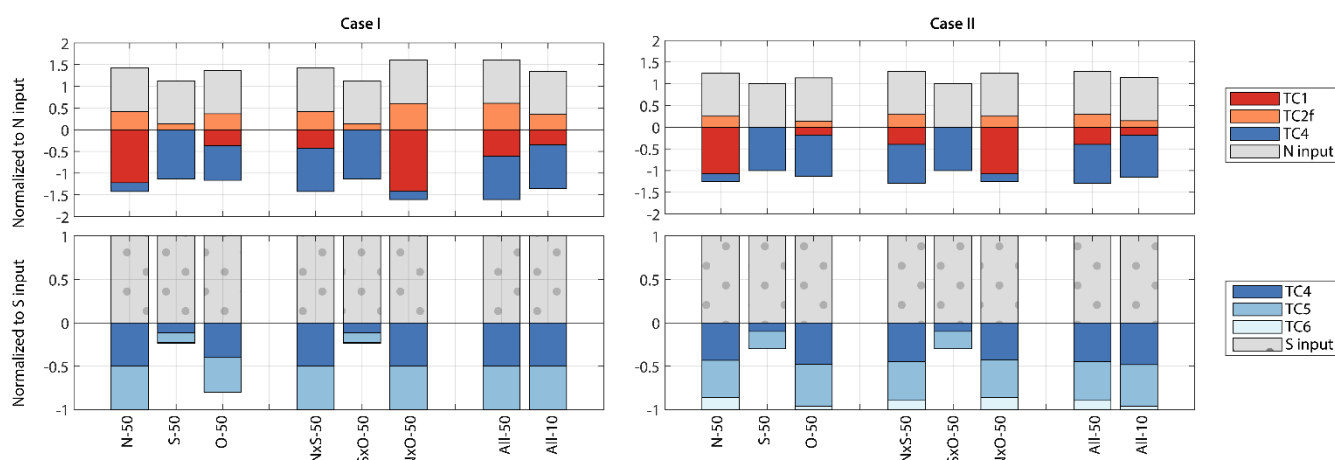


Figure 20. N and S consumption by reaction. The contribution of each reaction is shown by tracer. The contributions were normalized to the respective input.

5.1.3.3 Chromatographic separation of reaction fronts

The simulation results show that the reaction fronts of different impurities separated, likely based on gas solubility. SO_2 , being the most soluble gas (Table 7), reacts right at the injection well. NO_2 is much less soluble than SO_2 (Table 7), and its reactions (Reaction 1, 2f and 3) occur at a wider zone. In addition, the reproduction of NO_2 by Reaction 2f may contribute to the wider NO_2 reaction front. The O_2 reaction front was also wide mainly because O_2 is consumed with NO , which was internally produced only by Reaction 2f. This separation was not prominent in Case II, where Reaction 2f was relatively slower. Thus, we concluded that while brine pH may play a smaller role in determining dominant pathways, it may be critical in developing reaction zones by producing intermediate products with different solubilities. Such effects may be more prominent in complex grid systems, such as 2D or dual permeability-porosity conditions, where the interplay between transport and kinetic reactions will be more dynamic.

5.1.3.4 Precipitation of solids

In this study, although complete dry-out did not occur, halite was precipitated in Case I, and both halite and anhydrite (CaSO_4) were precipitated in Case II at the injection well (Table 8). Precipitation of anhydrite (or gypsum) or barite has been reported particularly under conditions of co-injection of SO_2 (Talman, 2015). The highest volume increase of anhydrite was obtained in All-50, where produced acid dissolved most calcite, supplying Ca^{2+} . In addition, the higher concentrations of SO_4^{2-} of All-50 led to anhydrite precipitation. Although the effects of mineral

dissolution/precipitation on porosity and permeability changes were not considered, the results imply that the impurity compositions may alter the petrophysical properties of the storage formation, particularly around the injection well, possibly affecting CO₂ injectivity.

Table 8. Mineral abundance changes compared to the initial values in volume percent in the first grid cell in Case II.

Impurity scenario	Halite (%)	Anhydrite (%)	Calcite (%)
N-50	6.10	+0.21	-0.22
S-50	6.12	+0.32	-0.24
O-50	6.07	+0.19	-0.13
All-50	6.08	+1.12	-0.88
All-10	6.07	+0.19	-0.14

This study also considered NaHSO₄-H₂O (sodium bisulfate in Figure 21) and Na₃H(SO₄)₂ (sodium sesquisulfate in Figure 21) as potential salts to precipitate at low pH, where HSO₄⁻ is the predominant species of S(V). However, these salts did not precipitate, likely due to their high solubility compared to other SO₄²⁻ or Na⁺ containing salt such as anhydrite and halite. Therefore, the brine Na⁺ and SO₄²⁻ concentrations were unlikely to build up sufficiently for NaHSO₄-H₂O or Na₃H(SO₄)₂ precipitation. Mirabilite (Na₂SO₄·10H₂O) or thenardite (Na₂SO₄) might precipitate if the molar ratio of Na⁺/Cl⁻ far exceeds that of halite (1:1).

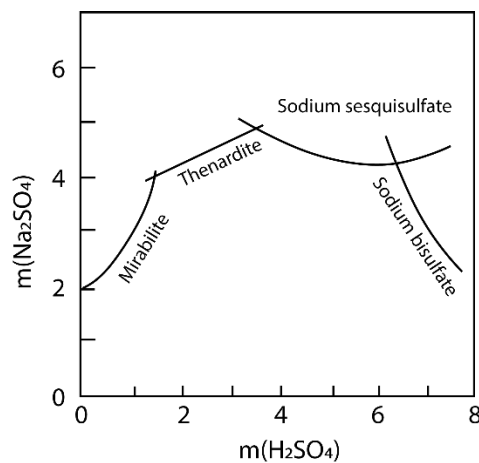


Figure 21. Solubilities of Na₂SO₄-H₂SO₄-H₂O system. (modified Figure 8 of Christov and Moller 2004)

5.1.3.5 Calcite as pH buffer under various impurity conditions

Our study show that even trace amounts of impurities (NO_2 , SO_2 , and $\text{O}_2 = 10$ ppm, All-10) might create corrosive conditions if pH buffering by mineral dissolution is limited (Case I). However, such conditions (no pH or little buffering by mineral dissolution) are rare or would require time to develop. In Case II, with 90% (v/v) calcite, pH was well-buffered between 4.2 to 4.8. These results are expected to be valid for carbonate reservoirs such as chalk.

A set of additional analysis was carried out to evaluate the pH sensitivity to the calcite volume fraction (Figure 22). Results show that even with calcite volume fractions as low as 1 %, pH profiles of N-50 and S-50 were identical to those of Case II (Figure 22). Even at 0.1 % (v/v) calcite, except for the first 0.1 (N-50) to 0.2 (S-50) m, the pH profiles were consistent with those in higher calcite fraction cases. These results suggest that even trace amounts of calcite (~1 % v/v) may sufficiently buffer brine pH - at least for the first 100 days with the injection rate used in these simulations.

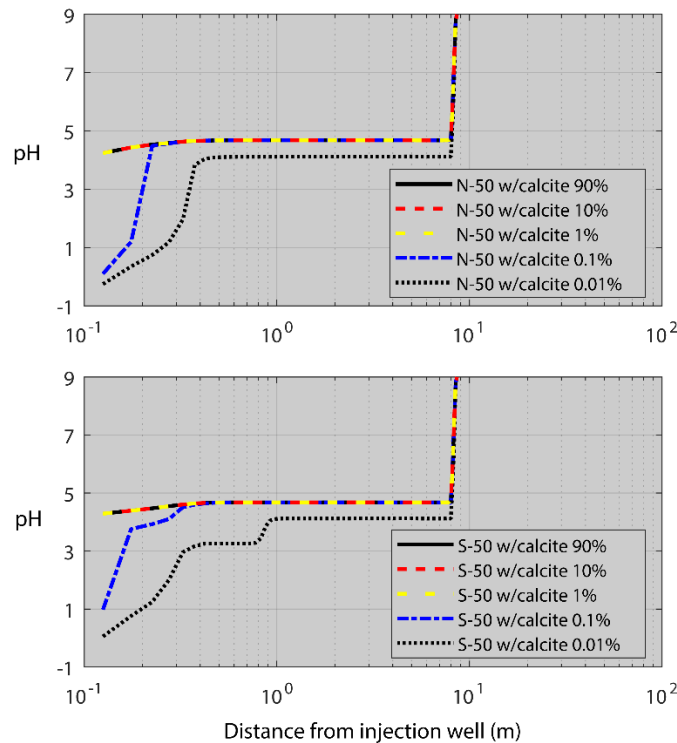


Figure 22. pH profiles of N-50 and S-50 with varying calcite volume fractions

5.2 Part 2 - simulations of cyclic injection of pure and impure CO₂ in siliciclastic rock

Our simulations in the parametric study predict that injection of CO₂ with NO₂, SO₂ and O₂ in siliciclastic rock without carbonate buffering can result in very low pH. In hydrous environments, many of the acid generating reactions are very fast. Thus, they will occur as soon as the injected CO₂ sees formation water. If water exists at the injection well, the volume of water and rock interacting with the impurities would be relatively small and the acidification more intense, meaning that infrastructure could be at high risk from corrosion. Moreover, evaporation of formation water near the well during injection can cause salt precipitation in pore spaces, potentially lowering the permeability to a degree that complicate injection. These aspects hinges on the distribution of water. They can affect any CO₂ storage operation in siliciclastic reservoirs to some extent, but we expect that they would be particularly important to consider for temporary storage, where the CO₂ production could lead to flow of water towards the well.

5.2.1 2D simulations of fluid flow, phase distribution and salt precipitation during cyclic injection of CO₂

To probe the distribution of water in the near-well environment, we first simulated the movement of fluids, evaporation of water and salt precipitation during injection/production of pure CO₂. In the simulations, it was assumed that CO₂ injection/production would be performed from a horizontal well with a 100 m perforated section in contact with a baffled portion of the reservoir with 100 m depth in Y-direction. These assumptions allow the geometry to be simplified to 2D. Additionally, we assumed that the geometry was identical on each side of the horizontal well, so that only one half of the system would have to be simulated. Simulations were conducted with a grid consisting of 140 by 57 cells (X-direction by Z-direction) having sizes increasing with distance from the well, which was located in the upper left corner of the model. Figure 23 provides a schematic overview of the grid geometry and Table 9 provides the parameter values for the fluid flow calculations. The simulations were performed with cycles of injection and production where the length of injection periods equalled those of production. Three cycle periodicities were tested with injection times of 1 week, 1 month and 0.5 year. During the injection period, injection rates were 6.34 kg/s, which correspond to a total injection of ~0.2 Mton CO₂ for the 1 year simulated time. During production, the production rate varied to provide a pressure of 160 bar at the well with a production index of 5×10^{-12} . The parameter values for S_{wr} , P_0 and $P_{c,max}$ in the capillary pressure function were subject to parametric study (Table 9).

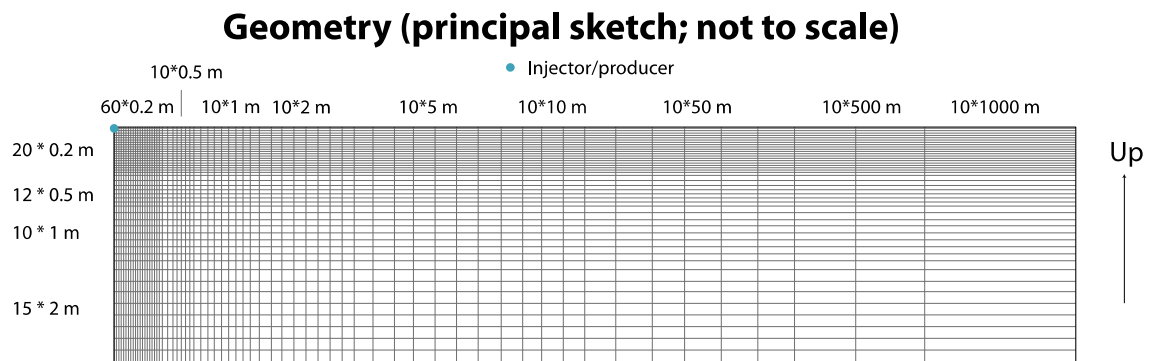


Figure 23. Schematic rendering of the model geometry.

Table 9. Flow parameters used in Part 2 simulations.

Parameter	Value
Porosity	0.245
Horizontal permeability	$5.803 \times 10^{-13} \text{ m}^2$
Vertical permeability	$5.803 \times 10^{-14} \text{ m}^2$
λ	0.457
S_{wr}	0 to 0.3
S_{nr}	0.05
P_0	0.02 to 0.2 bar
$P_{c,max}$	10 to 100 bar

Figure 24 depicts the temporal evolution of injection and production rates for the three scenarios. No fluids other than CO₂ were produced in the simulations. During production, rates initially become unrealistically high, but they quickly decrease to more realistic values which govern the amount of CO₂ extractable. The production rate is below 10 kg/s throughout 87 to 94% of the production time in the three cyclic scenarios. Thus, we interpret that the initial, short spike in rates does not have critical influence on the results. Consistent with this interpretation, simulations with a production index of 10^{-13} , which gave a maximum production rate of 4 kg/s, yielded results that were very similar from those obtained with a production index of 5×10^{-12} in terms of CO₂ and water distribution and salt precipitation, but with slightly lowered production of CO₂.

Figure 25 depicts the reclaimed fraction of injected CO₂, i.e., the fraction of injected CO₂ for a given cycle that can be produced within the same cycle. For the simulation with half-year injection and half-year production, about 60 % of the CO₂ could be produced within 0.5 year. This fraction is higher than predicted by Andrianov et al. (2022). The difference most likely reflects that 1) the earlier simulations were based on 10 years of injection, which allowed much redistribution of CO₂,

and then 10 years of production, 2) that the well production index might differ in the two simulation and 3) that the simulations presented here are based on a simpler model. The reclaimed CO₂ fraction increases with shorter cycle time and reaches up to 0.88 for the weekly injection/production scenario. This change most likely reflects that CO₂ has little time to flow towards an "equilibrium-like" distribution with higher capillary- and solution trapping when cycles are short. After injection, the region that is partially saturated is much larger for the biannual cycling that for the shorter periodicities (Figure 26, note the scale of the x-axes). Finally, the reclaimed fraction depends on the well's production index. For the monthly injection/production scenario, the fraction decreases from ~0.8 to ~0.5 when production index is decreased from 5×10^{-12} to 10^{-13} . Thus, wells capable of high production would be beneficial for a temporary storage operation, provided that consumers of the produced CO₂ exist.

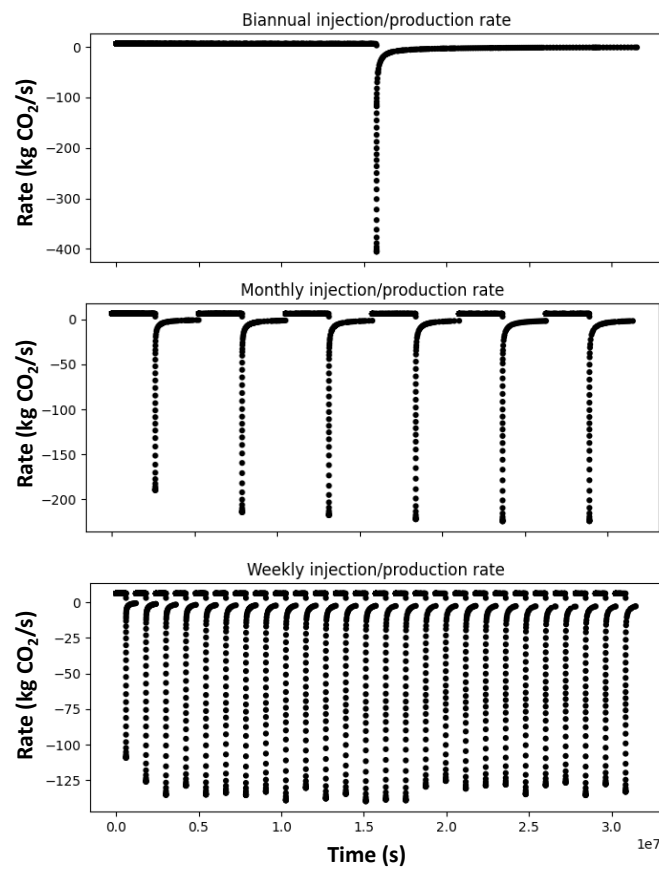


Figure 24. Rate of CO₂ injection (positive) and production (negative) during one cycle of 1 year, 6 cycles of 2 months, and 26 cycles of 2 weeks.

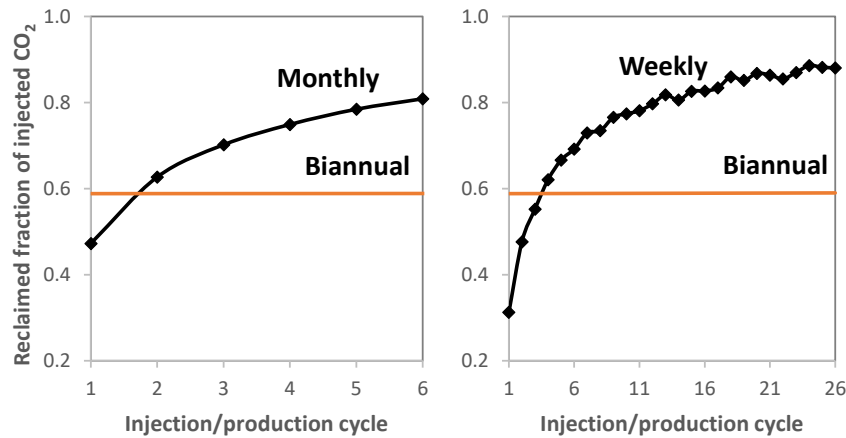


Figure 25. Reclaimed fraction of CO₂ injected per cycle during one cycle of 1 year (biannual), 6 cycles of 2 months (monthly), and 26 cycles of 2 weeks (weekly).

The spatial distribution of pressure and water saturation in the reservoir at the final injection/production cycle for the three scenarios are shown in Figure 26. The final pressure at the injector is the highest during one cycle of 1 year, ~240 bars, which is 80 bars higher than the initial pressure. Andrianov et al. (2022) estimated fracturing pressure of 257 bars at Stenlille wells. Thus, injection of 0.2 Mt CO₂ in one cycle of 1 year might be sustainable. Pressure increase at the injector during weekly injection/production is rather low, and the pressure at the final injection cycle is ~24 bars above the initial pressure of 160 bars. The pressure distribution at the final production cycle after 1 year of the cyclic injection/production is relatively similar for the three cycle periodicities (Figure 26). The highest pressure, ~175 bars, occurs at the bottom of the reservoir, adjacent to the CO₂ front. The CO₂ front at the end of the injection had clearly propagated furthest in the scenario with only one cycle as would be expected. After the final production, however, the CO₂ distribution is fairly similar for all three scenarios with a front that had progressed approximately 400 meters laterally and 40 m vertically from the injection/production well.

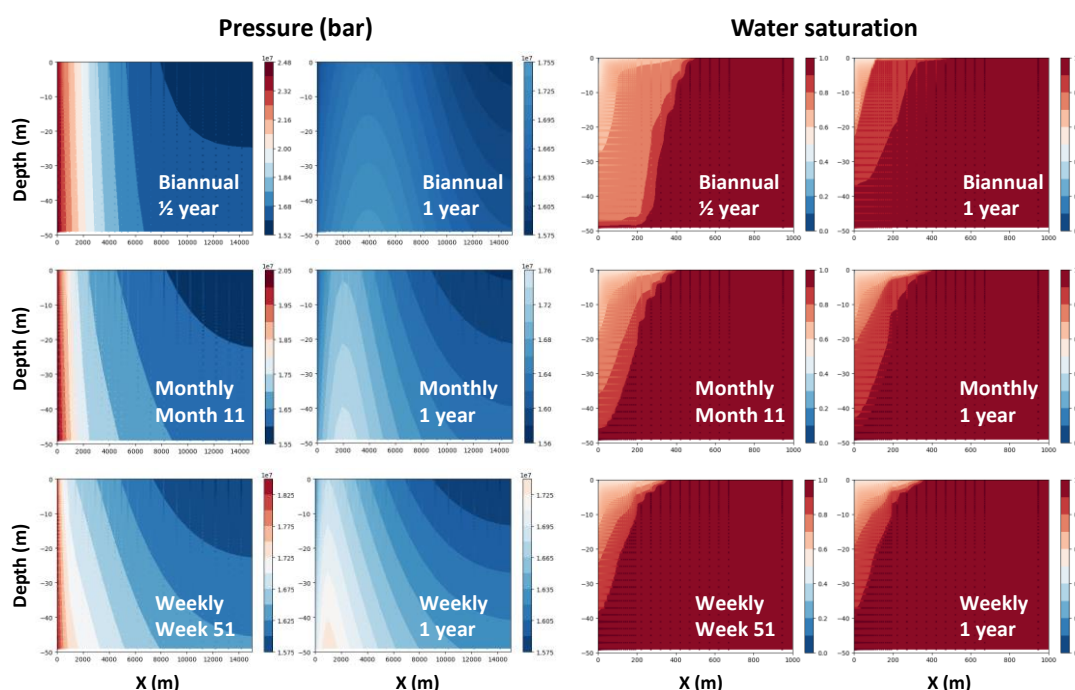


Figure 26. Pressure and water saturation at the final injection/production cycle during one cycle of 1 year (biannual), 6 cycles of 2 months (monthly), and 26 cycles of 2 weeks (weekly).

During CO₂ injection, evaporation of water into the injected gas can result in drying of a small region around the well. Re-wetting of the near-well area would, however, occur during the production periods. To depict these phenomena, Figure 27 shows the water saturation and fraction of halite near the injector/producer at the final injection/production cycle of the three scenarios with different cycle periodicities. For all cycle periodicities, the simulated dry-out region extends approximately 3 m vertically and 8 m horizontally from the well after 1 year. For the scenarios with multiple injection/production cycles, the dry-out region increases after each injection. Thus, in all simulated scenarios water only exists at the well at the very early stages of the simulation. This result has significant impact for the feasibility of the operation, because it indicates that NO₂ and SO₂ impurity reactions will mostly occur some distance from the well.

The brine evaporation at the well results in salt precipitation. For the scenario with biannual cycling, the salt is rather uniformly distributed in the dry-out region, whereas ring-like structures are evident for the simulations with several injection/production cycles. These reflect halite redissolution and inward movement of NaCl saturated solutions during the production phase. This in turn causes the maximum amount of salt precipitated in the pore spaces to be slightly higher, increasing from ~5% for biannual cycles to about 8% for the two other scenarios. While we cannot currently ascertain that these amounts of salts will not affect permeability, they constitute a relatively small amount of the pore volume. Moreover, we expect that the salt would be most

concentrated in the smaller pore spaces, which stronger withhold water during flow, and for which clogging would have lesser impact on permeability than for the large pores. Thus, it is likely that the simulated amount of salt precipitation will not substantially affect the temporary storage operation.

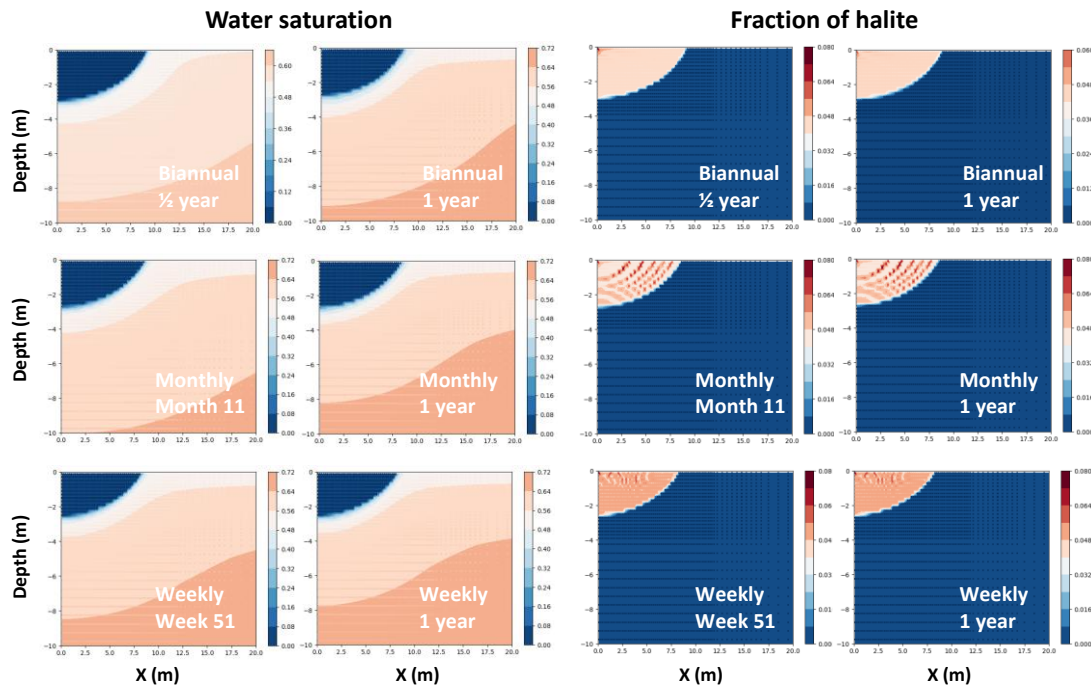


Figure 27. Water saturation and fraction of halite near the injector/producer at the final injection/production cycle during one cycle of 1 year (biannual), 6 cycles of 2 months (monthly), and 26 cycles of 2 weeks (weekly).

Clearly, the simulated results could be affected by the choice of values for parameters describing fluid flow and capillary pressure. To probe to what extent such variation affects results, we conducted simulations with other values (Figure 28). For the two types of simulations, the propagation of the CO₂ front and salt precipitation zone after 1 year are similar for all cycle periodicities and various parameter sets for capillary pressure function. Changes in the pore space taken up by the precipitated salt are below 1%. This indicates reasonably low uncertainty of the simulations of water distribution in the near-well environment.

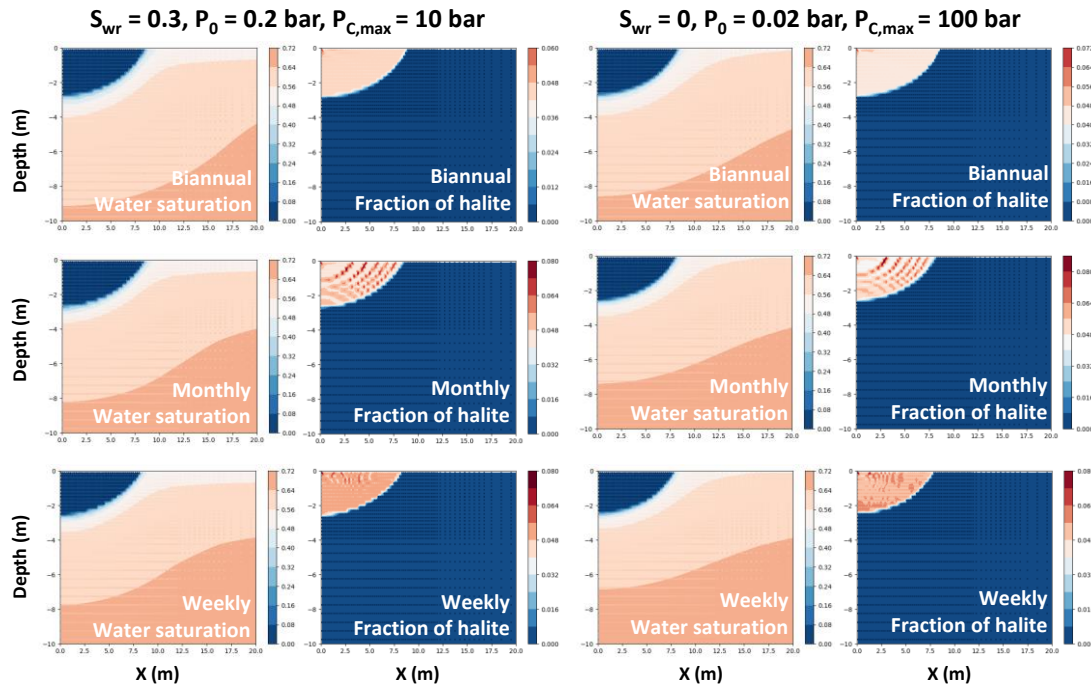


Figure 28. Water saturation and fraction of halite near the injector/producer after 1 year of one cycle of 1 year (biannual), 6 cycles of 2 months (monthly), and 26 cycles of 2 weeks (weekly) modelled under various flow parameters.

The modelling results are promising for temporary storage at Stenlille reservoir: 1) the pressure at the end of the injection periods does not exceed the fracturing pressure despite the high CO₂ injection rate. This ensures reservoir stability under injector/producer operation. 2) After a short initial stage of drying, the near-well environment remains dry for all cycle periodicities; this prevents excessive salt accumulation and the acidification that may occur under drying-out of the re-wetted zone. Thus, the well infrastructure can potentially be protected from corrosion or clogging. 3) The simulation results indicate that a major part of the injected CO₂ can be reclaimed as the injection/production cycles progress, in particular if the cycle durations are shorter.

5.2.2 1D simulations of cyclic injection of impure CO₂

The 2D simulations indicate that regular cycles of CO₂ injection and production at sufficient rates could lead to dry-out at the well within a week. To estimate the impact of impurity reactions on solution composition and reservoir rock within this timeframe, we have performed simulations assuming impurity levels of 50 ppm NO₂, 50 ppm SO₂, and 10 ppm O₂. Given that these simulations are computationally very challenging, we have performed the simulations in 1D with

a total of 72 cells. Figure 29 outlines the geometry of the model. From this figure, it is apparent that the domain of interest is only 1/4 of the full circle if we wish to have results comparable to the 2D simulations. Consequently, the injection rate was set to four times that of the 2D simulations. Shifting from 2D to 1D simulation means that gravity no longer affects the CO₂ distribution. This means, for example, that dry-out zones would be expected to be circular, rather than elliptic. Calculations of fluid flow, evaporation and salt precipitation after 1 year with weekly injection/production cycling show a dry zone extending ~5 m from the well and salt precipitation taking up ~5 % of the pore space. Moreover, the region near the well does not rehydrate after the first injection. These results are like those of the 2D simulations, meaning that 1D simulations of reactions can yield results that are meaningful.

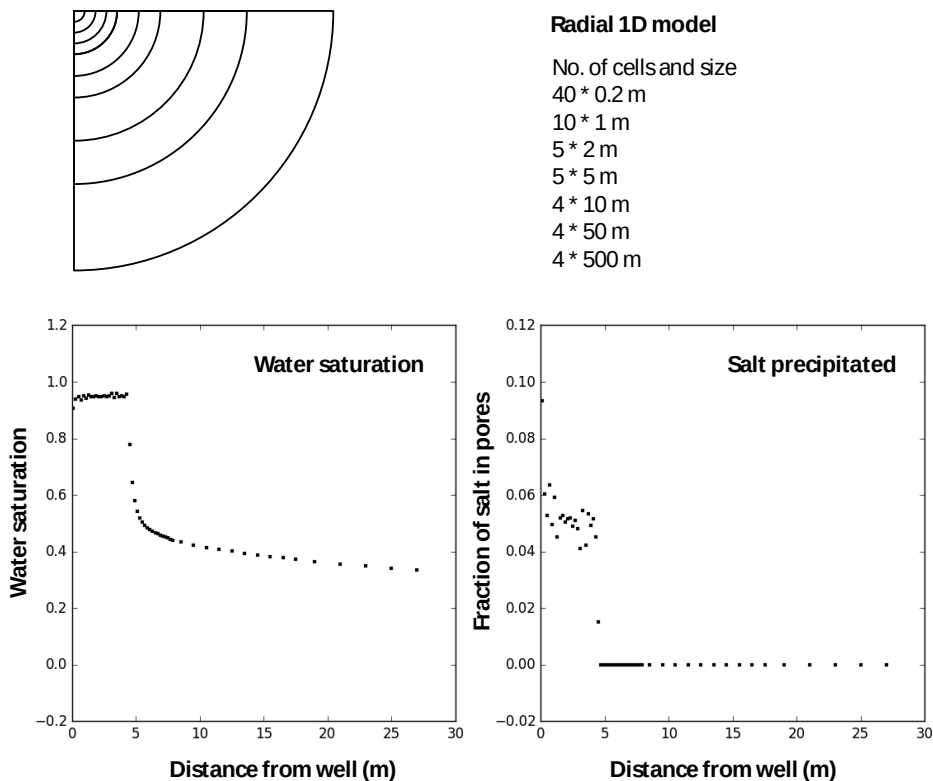


Figure 29. Schematic rendering of the 1D model geometry as well as the water saturation and amount of salt precipitated after 1 year of weekly cycling injection and production.

The simulations with impurities were performed for a formation water and rock composition representing Stenlille or, potentially, the Gassum formation at the nearby Havnsø structure. The rock in the model is composed mainly of quartz but contains small amounts of K-felspar (3%),

oligoclase (1%), calcite (1%) and siderite (1%). All of these were assumed to dissolve under kinetic constraints with the parameters given in *Table 10*. For the silicates we assumed a reactive surface area of 2800000 m²/m³ and for the carbonates, 1200000 m²/m³. Potential reaction products, SiO₂(am), anhydrite, gibbsite and halite were assumed to be governed by equilibrium, i.e., precipitation was set to occur instantaneously upon super saturation. For solution composition, the formation water was assumed to be dominated by Na (~2.5 moles/kgw), Ca (~0.2 moles/kgw), and Cl (~3 moles/kgw).

Table 10. Parameters for the rates of dissolution of minerals

Mineral	k (mol/m ² /s)	Ea (kJ/mol)	Aqueous species	n	Source
Calcite	1.55 * 10 ⁻⁶	23.5	-	-	Pallandri and Kharaka. 2004
	5.01E * 10 ⁻¹	14.4	H ⁺	1	
Siderite	4.57 * 10 ⁻¹⁰	23.5	-	-	Pallandri and Kharaka. 2004; For magnesite
	9.58 * 10 ⁻⁷	66.4	H ⁺	0.96	Gobulev et al.. 2009
K-feldspar	3.89 * 10 ⁻¹³	38	-	-	Pallandri and Kharaka. 2004
	8.71 * 10 ⁻¹¹	51.7	H ⁺	0.5	
Oligoclase	1.4791E-12	69.80	-	-	Pallandri and Kharaka. 2004
	2.1380E-10	65.0	H ⁺	0.457	

Given that the 1D and 2D simulations of fluid flow indicated that the region around the well would quickly dry, 1D simulations of impurity reaction was performed for a simulated time of 1 week. The simulation predicts that a region of about 0.5 m radius will become dry during the first week of injection (Figure 30). In the near well region, some calcite dissolution occurs but siderite and a little calcite remain in all cells. During the injection, SO₂ oxidises to H₂SO₄. This means that nearest to the well, anhydrite forms from the dissolution of calcite. Additionally, the main products of the NO₂ reaction are N₂O (constituting 50% of the injected N) and NO (30% of the injected N). This agrees with the results of the parametric study. The silicate minerals remain virtually intact for the 1 week simulated, which is reasonable given their slow reaction kinetics. Finally, pH decreases slightly in the region where the impurities react (for a given cell, the value in Figure 30 represent that at the time of drying). However, the decrease is slight, from about 4.3 to 3.7. Neither of these results are worrisome. Thus, we conclude that the presence of impurities need not complicate the temporary storage operation, assuming that fluid movement and evaporation occur as simulated.

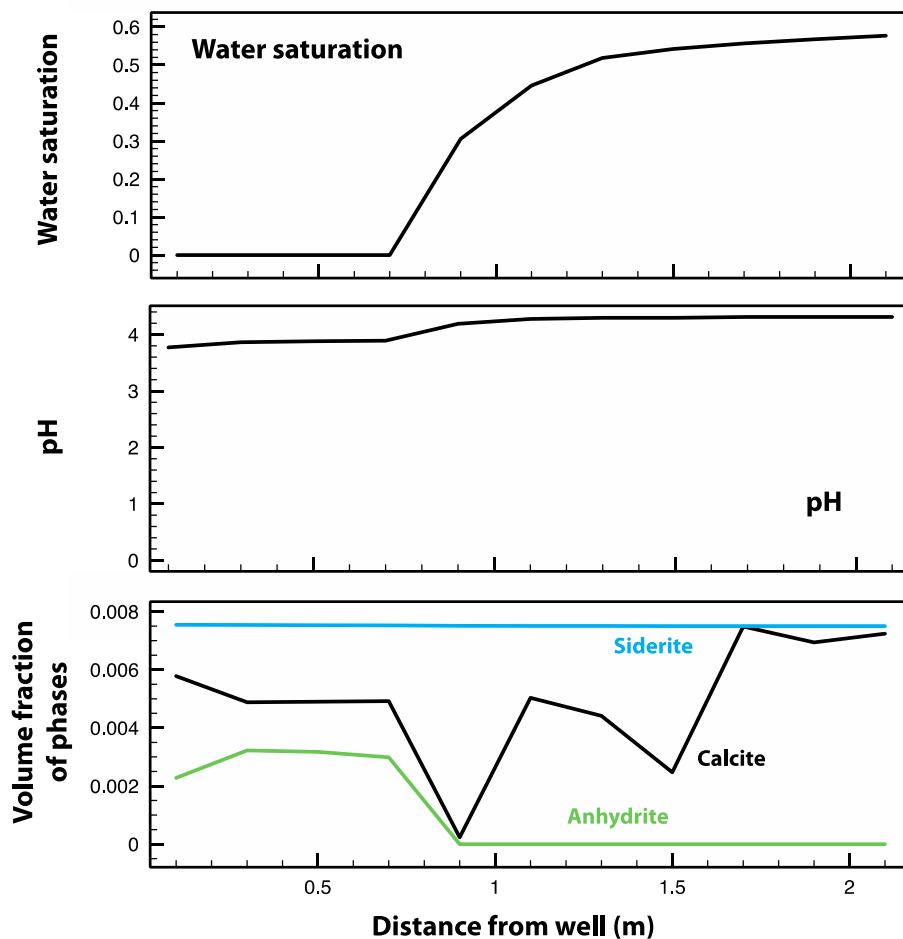


Figure 30. Water saturation, pH and phase assemblage (ignoring silicates) after 1 week of injection

5.2.3 Discussion and Conclusions

Overall, the simulations of cyclic injection/production indicate that temporary storage is feasible. Our results predict that a dry region will form near the well at the simulated injection rates, that the amount of salt precipitated is likely to be so low that permeability will not change substantially, and that the dry region means that the impurities will mostly react deeper into the formation.

However, a successful operation would hinge on several factors:

1) relative permeabilities and capillary pressures are not strikingly different from those in the simulations, resulting in more rapid movement of water to the well. The dependence of relative permeability and capillary pressure on water saturation would depend on the nature of the storage formation and would have to be individually determined through experiments prior to modelling. In addition, we have not included hysteresis between draining and imbibition in our simulations.

We expect, however, that hysteresis would entail that imbibition occurs slower than draining. Given that our parameters describe the draining process, we interpret that hysteresis will not be the cause of additional complication.

2) the CO₂ flow and water evaporation are not very different from that assumed in our model for other reasons. During injection of CO₂, differences in viscosity can cause preferential flow of CO₂ in some directions. This has not been included in our simulations. Also, complete water saturation of the CO₂ might not occur within a single cell as we have simulated, i.e., it might be subjected to kinetic constraints. The impact of such deviations from that simulated is unknown.

3) injection pauses are not very much longer than simulated. Pauses between injections would provide time for water and CO₂ to flow towards its equilibrium distribution. This distribution is unfavourable for recovery, because it entails wetting of the near well region and movement of CO₂ away from the well. Thus, it might be important for temporary storage that injection and production of the reservoir can occur regularly. For natural gas storage at Stenlille, this is the case. However, as a technological field natural gas production and consumption is mature; a similar regularity might not exist for CO₂ capture or consumption in the immediate future.

4) the well can be positioned very near to the top of the storage formation. The movement of CO₂ in porous media is governed by both gravity and capillary pressure. In our model, we have purposely positioned the well at the very top of the reservoir so that gravity works to our advantage. However, a real well might not be positioned so ideally. Our 2D simulations indicate that the dry-out region extends 2-3 m from the reservoir top. Thus, a well position within this range might work adequately. However, achieving a well position with this accuracy could prove challenging.

5) the storage complex geometry and inhomogeneity is such that our 1D and 2D simulations provide an adequate description of the processes that will unfold. This is by no means certain. For example, some storage complexes might have to rely on one or several vertical wells and the reservoir might not be compartmentalised as we have envisioned. Thus, individual models would have to be developed and simulations conducted. We only present conceptual simulation here.

6) the products from impurity reaction (for example SO₄²⁻ and NO₃⁻) do not stimulate bacterial growth and the generation of biofilm, which could clog the well. To our knowledge, this aspect of the impurities has not been studied, but it might be particularly important if a site have already stored natural gas or if it was a hydrocarbon reservoir.

Conclusions

The present ConsenCUS deliverable D4.4 contains the following main results, which allow for improved estimates of the storage efficiency and safety at Stenlille:

1. For the scenario considered and presented in Section 2, the variability of the CO₂ recovery factor during temporary storage at Stenlille is considerably smaller compared to the estimate in deliverable D4.3. This is due to the use of realistic relative permeability functions, constrained by experimental results in deliverable D4.2.
2. Salt precipitation resulting from CO₂ injection into brine-saturated rock leads to a rock permeability decrease of approximately 11% in a vicinity of an injection well at Stenlille, resulting in a corresponding decrease in well injectivity. The associated localized porosity decrease amounts to approximately 3%, which does not significantly impact the reservoir storage capacity.
3. The fluids representation in the Eclipse simulation model at the reservoir scale is consistent with the comprehensive thermodynamic description in the GEM sector-scale model. The most pronounced discrepancy between the two models occurs for CO₂ dissolution in brine.
4. A detailed theoretical and numerical model is developed for the geochemical reactions occurring between NO_x, SO₂, and O₂ at reservoir conditions.

The obtained results will be used to facilitate the development of a site-specific monitoring program for Stenlille, which will be detailed in the upcoming deliverable D4.5.

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