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Chemical interactions of a geothermal battery in the Malm reservoir of Munich

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Abstract

The Malm reservoir in the South German Molasse Basin, characterized by its highly heterogeneous karstified carbonate structure, offers significant potential for geothermal energy production and seasonal heat storage. This study investigates the chemical interactions and risks associated with the operation of a geothermal battery, a subsurface heat storage system, in this reservoir. Using reactive transport simulations, we model the effects of injecting CO₂-inhibited thermal water at elevated temperatures (135 °C) during thermal charging and cooled thermal water (60 °C) during thermal discharging and compared the results to conventional geothermal operation. The study highlights the influence of heterogeneity, reactive surface area-to-volume ratios, and dolomitization on chemical interactions in the reservoir. Our results reveal that CO₂ inhibition effectively mitigates scaling risks and prevents formation damage near the storage well, while driving modest porosity increases through calcite dissolution near both storage and injection wells. Conversely, in fully dolomitic zones, minor porosity reductions are observed during thermal charging. Significant chemical changes are confined to the near-wellbore region. The chemical de-risking conducted in this study contribute to the feasibility of integrating geothermal batteries into renewable energy systems, potentially providing an economically viable solution to seasonal energy storage while supporting the decarbonization of district heating networks.

Introduction

The Malm reservoir, located in the South German Molasse Basin, is a deep sedimentary formation which stands out for its geothermal potential, primarily due to its exceptional productivity of Upper Jurassic carbonates. This formation, consisting of limestone, dolostone, and marl, creates a sequence up to 600 m thick. The reservoir exhibits significant heterogeneity, influenced by factors such as primary facies, diagenesis, fractures, and intense karstification (Böhm et al. 2013; Meyer and Schmidt-Kaler 1990; Stier and Prestel 1991). Karstification plays a crucial role, enhancing permeability and creating discrete zones of elevated permeability (DZEP, Cross and Burchette 2025), which are responsible for a large share of inflow contribution of wells (Hörbrand et al. 2024; Schölderle et al. 2021). The reservoir is currently developed with 42 operating

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geothermal wells, generating a total output of 400 MW (thermal). The implementation of seasonal heat storage in this unique geological setting represents a strategic solution to address the seasonal fluctuations in Munich's thermal energy demand. The city's seasonal heat demand profile requires significantly less energy in summer compared to winter. As a result, once the summer base load is met with geothermal energy, additional geothermal wells either operate at reduced capacity or remain idle. However, these wells are also insufficient to meet the peak energy demands of winter, necessitating the integration of additional carbon-neutral heating technologies, such as hydrogen combustion. Seasonal heat storage offers a viable solution by utilizing the idle geothermal production capacity during summer and making the stored energy available during the heating season, thereby bridging the gap between supply and demand.

A geothermal battery enables the storage of excess heat generated during summer, which can later be utilized during the heating season. We use "geothermal battery" as an umbrella term for energy storage in geological media, irrespective of depth, temperature differentials, or heat transfer mechanisms. It is thus synonymous with geological thermal energy storage (GeoTES, Witter et al. 2025). Energy storage in natural groundwater systems, termed Aquifer Thermal Energy Storage (ATES) have the lowest specific investment costs for large scale heat storage solutions (Herrmann et al. 2026) and are thus an economically interesting technology to provide large amounts of energy for the decarbonization of the energy system. In contrast to ATES projects, which are typically realized in shallow aquifers, the herein presented concept of a geothermal battery targets the geothermal Malm reservoir in the northern Munich area at a depth of approximately 2000 m with a reservoir temperature of ~ 80 °C. This temperature allows a combined extraction of geothermal heat and stored heat (e.g. Major et al. 2018). A geothermal battery in the Malm reservoir has been previously examined at the Dingolfing test site, where short term heat injection tests were successfully conducted in a shallower part of the Malm reservoir (< 500 m depth, Ueckert and Baumann 2019). Dissolution in the reservoir due to the CO₂ inhibitor leads to higher required amounts of CO₂ in subsequent storage cycles, which is the reason why a triplet well configuration was developed (Ueckert 2016; Ueckert and Baumann 2019). In this concept, the third well is needed to dispose of the reproduced water to manage the amount of CO₂ inhibitor. We extended this concept by a fourth well in order to use the geothermal production capacity during the heating period (Fig. 1). The production well (PW) produces water at reservoir temperature (~ 80 °C) which is then heated to 135 °C and injected into the Storage Well (SW) during the thermal charging of the system (Table 1). During thermal discharging, the storage well switches to production mode and the produced water is cooled to 60 °C using heat exchangers before being reinjected into the injection well (IW). Simultaneously, the production well is operated during the thermal discharging period and injecting into a second injection well, delivering geothermal heat during the heating season.

Tzoufka et al. (2024) evaluated the thermal performance of the storage well under similar conditions, resulting in a thermal recovery of 68% in the first cycle and 87% after 10 years, while the recovery temperature remains above 110 °C even in the first cycle. The mixed production temperature of the production well (81 °C) and the storage well (110–135 °C) thus is between 95 and 108 °C, which requires post-heating with steam during the heating season.

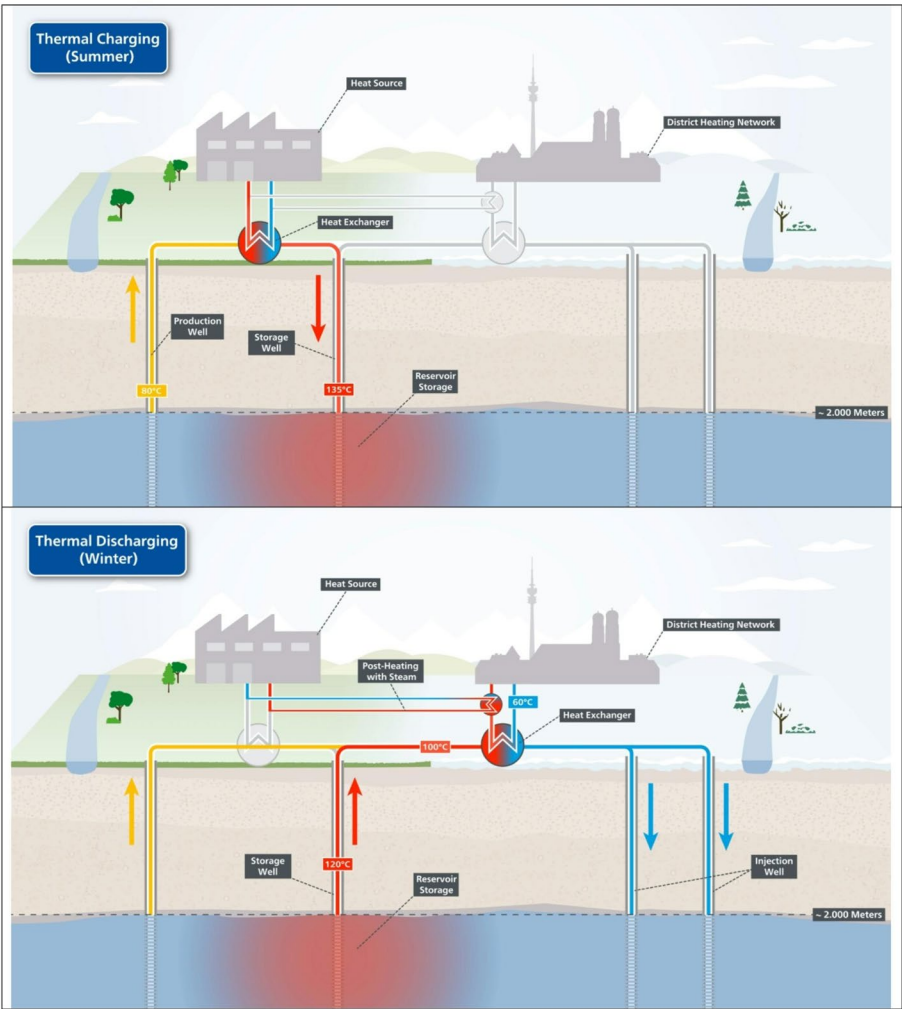


Fig. 1 Schematic of the operational principle of the geothermal battery in the Munich area. Top: Thermal charging, the injection wells are idle and no energy is produced from the site. Bottom: Thermal discharging, all wells are in operation and supply heat to the district heating network

Table 1 Operational scheme table illustrating the operating mode of the geothermal battery

	Storage well	Production well	1st Injection well	2nd Injection well
Summer				
Status	Injection	Production	Idle	Idle
Temperature	135 °C	81 °C	-	-
Flow rate	-150 l/s	150 l/s	-	-
Winter				
Status	Production	Production	Injection	Injection
Temperature	135–110 °C	81 °C	60 °C	60 °C
Flow rate	150 l/s	150 l/s	-150 l/s	-150 l/s

The operational aspect of the geothermal battery introduces challenges such as formation damage and scaling (Dobson et al. 2023; Fleuchaus et al. 2020). To the best of our knowledge, no geothermal heat storage system is currently in continuous operation with a temperature differential comparable to that examined in this study, primarily due to chemical concerns. Based on the low mineralization of the thermal water and operational experience, we expect predominantly scaling from retrograde soluble carbonates,

which also occur during conventional geothermal operation (Köhl et al. 2020). Due to heating the thermal water prior to storage, a massive amount of carbonate scaling can occur (e.g. Nitschke et al. 2023), if no chemical treatment is applied. Scaling would thus be expected to lead to clogging of the primary cycle and potentially the reservoir within a short timeframe. This requires the application of precise treatment strategies like CO₂ inhibition (Dijkstra 2020; Ueckert and Baumann 2019) or polymeric inhibitors (Broda et al. 2024), tailored to reduce scaling risks and maintain rock permeability in the reservoir.

The introduction of chemical and temperature gradients in the reservoir leads to the question, whether any formation damage can occur in the near- or far-field of the wells. To tackle this question, reactive transport simulations with coupled hydraulic, thermal and chemical processes can be applied (Banks et al. 2021; Holmslykke and Kjølner 2023; Kumar et al. 2024a, b). Chemical simulations of carbonate reservoirs require appropriate thermodynamic data for the relevant minerals such as calcite and dolomite. For fast reacting minerals (such as calcite), a local equilibrium assumption may be applicable, if the time step length is larger than the time required for the chemical reaction to reach equilibrium (Molins and Knabner 2019). For these minerals, equilibrium constants at geothermal temperatures would be sufficient (Bénézech et al. 2018; Plummer and Busenberg, 1982). However, slower reacting minerals such as dolomite require the use of kinetic simulations if their spatio-temporal behavior is to be predicted correctly. Kinetic models of calcite and dolomite are an area of intense research (Busenberg and Plummer 1982; Gautelier et al. 2007; Palandri and Kharaka 2004). Ueckert (2016) benchmarked the available kinetic models for calcite and dolomite using laboratory experiments on outcrop analogue samples of the Malm reservoir. The presence of intense karstification (heterogeneity) within the reservoir further complicates reactive transport simulations as it introduces significant uncertainty on heterogeneity and reactive surface areas. Reactive surface areas are already a domain of extreme uncertainty, as it is difficult to measure the accessible surface area for reactions (Beckingham et al. 2017; Ma et al. 2021). Generally, reactive surface areas are significantly lower on a reservoir scale compared to core-scale measurements (Beckingham et al. 2017) making the application of measured values difficult to apply for field scale simulations. This leads to reactive surface areas spanning multiple orders of magnitude in literature review and simulation studies (Jia et al. 2021; Qin and Beckham 2021; Zhang and DePaolo 2017). We are not aware of a measured dataset, which would provide reactive surface areas for karstified reservoirs on the field scale thus leaving this parameter largely unconstrained. We suspect, that in karstified parts of the reservoirs, the rock-fluid interface area is significantly lower than in porous reservoirs as much of the primary porosity has been destroyed and the fluid flow is circulating in the secondary porosity system (vugs, karst channels etc.) and not in a “porous” reservoir (Mazzullo 2004; Vacher and Mylroie 2002). This can be seen as similar to wormholing, which has been described on the laboratory scale and field scale (Polak et al. 2004; Snippe et al. 2020). Chemical dissolution and alteration processes can change the porosity structure in the subsurface (Schuster et al. 2025), raising questions about their mechanical stability. Nolting et al. (2021) investigated the mechanical stability of caves in carbonate reservoirs and demonstrated that water-filled caves (essential for chemical alteration during geothermal operation) can remain stable at burial depths of up to 10,000 m.

Previous studies on chemical interactions in the Malm reservoir are limited to the injection wells of geothermal doublets (Arab et al. 2017) or did not apply reactive transport simulations (Ueckert and Baumann 2019). The primary objective of this study is to address the chemical risks, such as scaling and formation damage, associated with implementing a geothermal battery in the Malm reservoir using 1D hydrochemical and 3D reactive transport simulations. Mitigating chemical risks is crucial for successfully realizing efficient heat storage solutions that can be operated for decades. Additionally, the study aims to evaluate the impact of heat storage and accompanying chemical processes on the volumetric balance within the reservoir, providing a comparison with injection wells of a conventional geothermal doublet. Through this assessment, the study seeks to thoroughly understand and quantify the chemical impacts of geothermal battery, ensuring its sustainable development and integration into energy systems.

Model description

Simulation environment

For simulation, we used the thermo-hydraulic-chemically Transport Simulation Environment (TRANSPORTSE) v1.0.1. This code employs the finite difference method to solve the density-driven Darcy flow equation, incorporating the equations for heat and chemical species transport on structured grids using simple explicit, weighted semi-implicit, or fully-implicit numerical schemes (Kempka 2020; Kempka et al. 2022). PHREEQC (Parkhurst and Appelo 2013) is used as a thermodynamic backend in TRANSPORTSE via the phreeqpy Python package (Müller et al. 2011). We used the phreeqc.dat parameter file from PHREEQC 3.6.2. The chemical simulation is executed for every cell in the grid, which makes the simulations numerically expensive and poses a strong limit on the number of cells in the model if longer timeframes are investigated. We therefore limited the chemical simulations to the cells representing the net reservoir and excluded the under- / overburden, which are practically impermeable. The simulations were run with parallelized chemistry on Standard_F48s_v2 (48 cores) in the Azure cloud. We employed the code in a one-way coupling configuration, where chemical reactions modify porosity through mineral dissolution and precipitation. These porosity changes do not feed back into the flow model: permeability is kept constant and not updated based on evolving porosity, so hydraulic properties and flow fields remain unchanged during reactive transport.

Spatial and temporal discretization

We used a quarter domain model (i.e. $\frac{1}{4}$ of the full model domain) with one vertical well at the model edge. This approach leverages the symmetry of the problem to reduce computational expenses. The model was discretized with a tartan-grid with 10 m cell size at the well and a maximum cell size of 250 m at the farthest distance from the well, using a factor of 1.3 for the cell size growth. The model comprises 15 layers (z) and 13 cells in the x- and y-direction resulting in 2535 cells.

The boundaries adjacent to the well (left and bottom; Fig. 2) were assigned no-flow (Neumann zero-flux) boundary conditions to ensure consistency with the quarter-domain representation. The right and top boundaries were defined as specified-head (Dirichlet) boundary conditions for hydraulic flow, combined with fixed-concentration boundary conditions for the chemical composition of inflowing fluid. The boundary

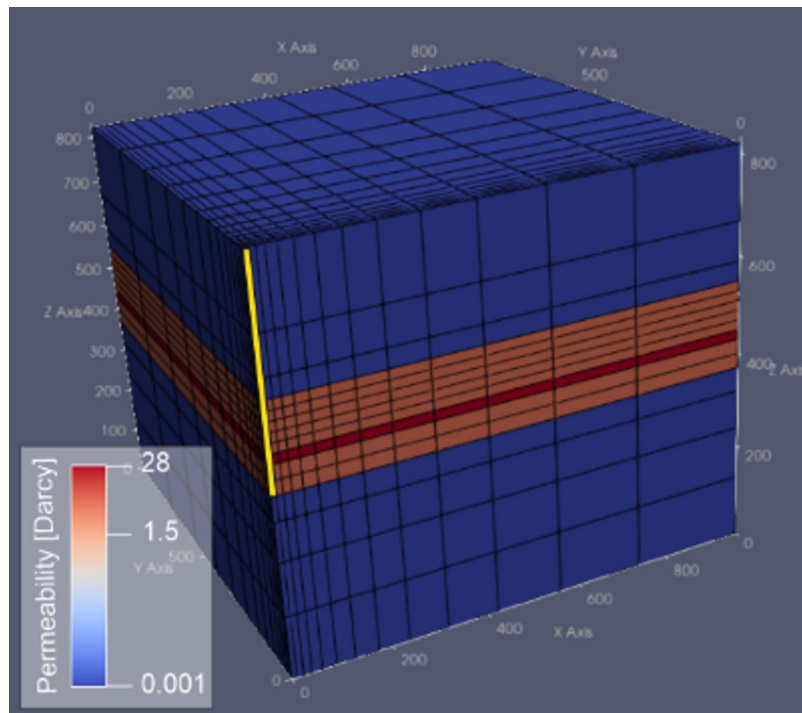


Fig. 2 Quarter domain model with tartan-grid used for reactive transport simulation. The blue layers represent the overburden above the reservoir and the unproductive reservoir below the orange net reservoir. The red layer represents the 20 m DZEP and the orange layers the matrix reservoir. The well boundary conditions are set in the net reservoir at the location of the well (yellow)

composition corresponds to the calibrated fluid composition reported in Table 2. Well flow rates were imposed using flux (Neumann) boundary conditions, with both fixed volumetric rate and fluid composition (see chapter “simulation scenarios” for composition imposed during injection).

The total simulation time was 10 years, with a time step of approximately 3 h, determined by the Courant–Friedrichs–Lewy criterion implemented in TRANSPORTSE. Each scenario had a simulation runtime of ~5 h on 48 cores.

Geology and petrophysical parameters

The architecture of the Malm reservoir is described in detail by Hörbrand et al. (2024) who demonstrate that the system is highly heterogeneous and characterized by discrete zones of enhanced permeability (DZEPs) associated with karstification. The model developed in this study builds directly on this framework. Key reservoir properties (e.g., transmissibility, DZEP intensity, and net thickness) as well as the fluid composition were derived from the closest offset wells in the geothermal battery target region (northern Munich) illustrated in Hörbrand et al. (2023). As these wells are located within a few kilometers of a potential site, the resulting dataset provides a consistent and representative basis for the Munich North region.

We modelled the reservoir using an equivalent porous media approach, integrating a DZEP of 20 m thickness within the 180 m of net reservoir (Fig. 2). We used a transmissibility of 800 Dm inferred from offset data, of which 70% were assigned to the DZEP (28 Darcy) and the rest to the reservoir matrix with a thickness of 160 m (1.5 Darcy).

Table 2 Calibrated thermal water composition used for the initial and boundary conditions of the simulations

	Measured Sample	Calibration Step 1	Calibration Step 2	Simulated heating and CO ₂ conditioning
Input				
Temperature (°C)	85	81	81	135
Pressure (bar)	200	200	200	10
pH	7.20	6.86	6.86	6.15
Ca ²⁺	0.70	0.70	0.84	0.84
Mg ²⁺	0.35	0.35	0.16	0.16
Na ⁺	4.79	4.79	4.79	4.79
K ⁺	0.33	0.33	0.33	0.33
SO ₄ ²⁻	0.06	0.06	0.06	0.06
HCO ₃ ⁻ (Alkalinity)	4.83	4.83	4.83	4.83
S ²⁻	0.01	0.01	0.01	0.01
Fl ⁻	0.12	0.12	0.12	0.12
Cl ⁻	1.87	1.87	1.87	1.87
Equilibrium results				
SI Calcite	0.20	-0.08	0.00	0.00
SI Dolomite	0.86	0.24	0.00	0.70
TIC	5.25	5.86	5.86	17.91

Units of ions are in mmol/kg. Total dissolved solids are 606 mg/L. SI abbreviates saturation index

Porosity was calculated using the correlation described by Schölderle et al. (2025) for a reservoir with an average depth of 2070 m, resulting in a value of 7.7%.

Reservoir mineralogy and thermal water chemistry

Cuttings evaluation from previously drilled wells show that the reservoir is composed of calcite and dolomite. The calcite and dolomite content varies spatially between wells and vertically within the reservoir, where some units are strongly calcitic and others strongly dolomitic (Böhm et al. 2010, 2011, 2013). We thus model the reservoir to consist equally of dolomite and calcite.

The thermal water composition used in this study is based on measured data from a geothermal site in northern Munich, located within the target region of the geothermal battery. Because the thermal water contains dissolved gases that degas under atmospheric conditions, sampling was performed under pressure and subsequently opened in the laboratory by an external contractor to quantify the released gases. As a consequence, the measured composition does not directly represent in-situ reservoir conditions and requires calibration prior to its use in reactive transport simulations (Baumann 2016). Evidence for degassing is reflected in the calculated saturation indices of the measured sample, where both calcite and dolomite appear supersaturated. In a first calibration step, the degassed CO₂ (0.61 mmol/kg) was reintroduced using PHREEQC equilibrium calculations, and the temperature was adjusted to the reservoir conditions considered in this study. This increases the total inorganic carbon (TIC) and results in a state that is slightly undersaturated with respect to calcite and slightly oversaturated with respect to dolomite. However, the objective of this study is to investigate induced geochemical changes rather than small deviations from thermodynamic equilibrium. Therefore, a second calibration step was applied to bring the fluid into exact equilibrium with the carbonate phases. Without this adjustment, fluid entering the model domain

(via Dirichlet boundaries or injection wells) would react immediately due to its initial disequilibrium, thereby masking the effects induced by the simulated processes. While the first calibration step is physically justified by degassing and temperature correction, the second step is a technical requirement to ensure clear and interpretable simulation results. Achieving simultaneous equilibrium between calcite and dolomite is non-trivial due to their shared ionic components. In this study, equilibrium was enforced by adjusting calcium and magnesium concentrations. This approach is supported by the long residence time of the thermal water of more than 10,000 years (Winter et al. 2025; Winter and Einsiedl 2022) which suggests that equilibrium or near-equilibrium conditions with carbonate phases should be attained under natural conditions. Any remaining minor disequilibrium is likely to be attributed to uncertainties in equilibrium constants, uncertainties in thermal water analyses or dolomitization / dedolomitization reactions, which are not included in chemical equilibrium simulations.

The resulting calibrated thermal water composition is shown in Table 1 and has a total salinity of <1 g/L. To counteract scaling due to heating, the thermal water will be conditioned with 12.05 mmol/kg of CO₂ in order to reduce the calcite saturation index to 0, which is about 8 times the amount required for the Middenmeer ATES (Dijkstra 2020). The conditioning with CO₂ leads to a lower pH and a significant increase in TIC.

Chemical model and reactive surface area

The reaction rate under kinetic laws is typically expressed as the product of the intrinsic reaction rate (r_m), the ratio of reactive surface area (A) to fluid volume (V), and a mineral-dependent term that accounts for changes in reactive surface area caused by precipitation or dissolution (Appelo et al. 1998).

$$R = r_m \left(\frac{A}{V} \right) * \left(\frac{M}{M_0} \right)^t$$

For karstified carbonate reservoirs, field-scale measurements of A/V ratios (or reactive surface areas) are unavailable. As discussed in the introduction, carbonate reservoirs that have undergone extensive diagenesis and karstification exhibit significantly altered pore structures dominated by large voids, such as vugs and karst channels. These structures result in a reduced fluid-rock contact area because large pores have a much lower reactive surface area compared to numerous small pores (Fig. 3). This relationship can be derived geometrically from packing density principles, where the surface area of pores and pore channels per unit bulk volume (s_b) decreases as the grain radius (r)—and consequently the pore size—increases (Carman 1937; Salem and Chilingarian 1999)

$$s_b = \frac{\pi}{2r}.$$

To account for this variability, we constrained the parameter range for A/V ratios to two end-member scenarios: matrix reservoir and a strongly karstified zone. Ueckert (2016) determined an A/V ratio of 800 cm²/L for dolomite grains (grain size: 0.063–2 mm) in laboratory experiments, which we assume is representative of the matrix reservoir. Conversely, we modeled an extreme low-reactive surface area scenario, approximating the A/V ratio of an idealized karst channel with a pipe diameter of 0.5 m. For this scenario, the A/V ratio is estimated at 40 cm²/L.

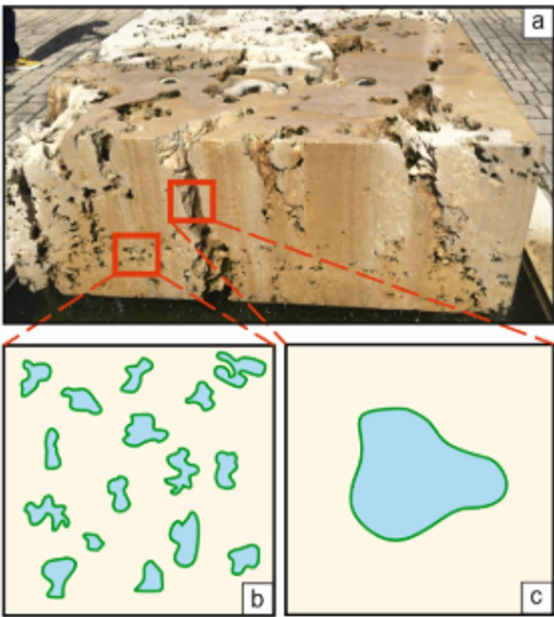


Fig. 3 Illustration of pore space in an analogue sample of the Malm reservoir. **(a)** Pore space observed in the matrix reservoir is characterized by vuggy porosity. **(b)** Schematic representation of the matrix reservoir, with the green outline of the vugs indicating the reactive surface area used in reaction rate calculations. Compared to karstified sections of the analogue sample **(c)**, the reactive surface area of numerous individual vugs is significantly greater than that of a single karst tube

Table 3 Summary of simulation cases considered in this study

Case description	Identifier	Inhibition	Injection temperature [°C]
Thermal charging without inhibitor	S1	no	135
Thermal charging with CO ₂ inhibitor	S2	yes	135
Thermal charging with CO ₂ inhibitor and dolomitic DZEP*	S3	yes	135
Injection of inhibited thermal water	I1	yes	60
Injection during conventional geothermal operation	I2	no	60

* This case also involves mineralogical heterogeneity, such that the DZEP is entirely dolomitized in contrast to the other scenarios where they are equally dolomitic and calcitic

For dolomite, the kinetic model proposed by Ueckert (2016) was applied, which utilizes the Arrhenius equation on kinetic data from Gautelier et al. (2007). Calcite kinetics were based on the rate law from the *phreeqc.dat* database (Plummer et al. 1978), with modifications to ensure consistency with the adopted surface area formulation. In the standard *phreeqc.dat* implementation, the reactive surface area is calculated by multiplying the mineral mass by the specific surface area $[PARM(1) \cdot M_0]$. In our approach, this product was replaced by the A/V ratio, which directly defines the reactive surface area available per unit fluid volume for each hydrogeochemical time step. The resulting volumes were subsequently scaled to the individual model cells according to the local fluid content.

Simulation scenarios

This study aimed to examine two distinct processes. First, it investigated the chemical impact of injecting heated thermal water at 135 °C near the storage well (Scenarios 1–3, cf. Table 3). Second, it assessed the chemical effects at the cold well, where CO₂-inhibited thermal water, having reacted within the reservoir, was injected at 60 °C. Additionally,

the chemical effects at the cold well were compared to those observed during conventional geothermal injection (I2).

In the ATEs injection scenario (I1), the chemical composition of the injected thermal water varies over time, reflecting changes in the thermal water composition caused by the decreasing production temperature of the storage well. To model this, we used the chemical composition from the simulation output of the corresponding storage scenario (S4) as input for the reinjection chemistry at the injection well. The temporally variable fluid composition was interpolated into 10 steps for each half-year injection period.

Results

Reaction path modelling

To enhance understanding of the 3D THC-coupled simulation, we illustrate the key processes using reaction path modelling (batch kinetic simulations). As the thermal water travels through the system, it undergoes various chemical changes in equilibrium simulations (Fig. 4). Initially, the saturation indices in the reservoir are zero. During thermal charging, the thermal water is heated from 81 °C to 135 °C, significantly increasing the saturation indices of dolomite and calcite. CO₂ is injected as an inhibitor to prevent mineral precipitation, lowering the saturation indices and stabilizing calcite at equilibrium. Possible inhibitors to prevent carbonate scaling comprise polymeric inhibitors (e.g. crystal growth or threshold inhibitors), complexing agents and thermal water acidification (e.g. CO₂). For the use in the Bavarian molasse basin, two inhibitor solutions are approvable by the authorities. One threshold inhibitor (NC 47.1B) and CO₂, both of which have been effectively tested on existing geothermal wells (Broda et al. 2022). NC 47.1B degrades quickly at high temperatures as evidenced by reduced inhibitor concentration prior to reinjection and is thus questionable to prevent formation damage in the reservoir. CO₂ in contrast does not lose its effectiveness, as it acidizes the thermal water and

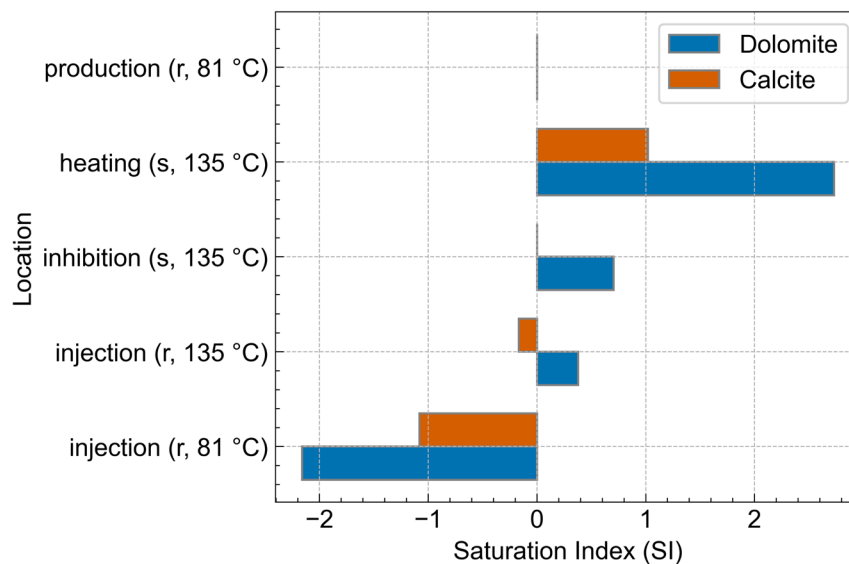


Fig. 4 Saturation state of the thermal water from the production-side reservoir to the injection-side reservoir. (r): reservoir, (s): surface. Strong supersaturation of retrograde carbonate minerals occurs due to heating, which can be mitigated by using CO₂ as an inhibitor. Reinjection causes slight undersaturation of calcite due to pressure changes (~200 bar); however, this effect is much less pronounced compared to cooling the reservoir to ambient temperature, where the dissolution potential of CO₂ leads to significant undersaturation

does not degrade. We therefore selected CO_2 as a reliable solution to prevent scaling in the plant and formation damage in the reservoir. The inhibitor is dosed at a low concentration (~ 12 mmol/kg) at the surface, causing only a minor increase in the bubble point (1.4 bar) with overall bubble points staying well below the operating pressure of the geothermal heating plant. As a result, the CO_2 remains fully dissolved in the thermal water, maintaining a single aqueous phase with no two-phase flow occurring. In the real application, CO_2 would obviously be injected prior to heating, to prevent scaling at the heat exchanger.

Upon re-injection into the reservoir, the increase in pressure slightly reduces the saturation indices. As the thermal water flows away from the storage well, it gradually cools to the ambient reservoir temperature of 81°C . Due to the retrograde solubility of carbonate minerals, this cooling induces significant undersaturation, resulting in a strong dissolution potential near the injection well (IW).

Kinetics govern the temporal evolution of chemical reactions in the system. Comparing two A/V ratios, we found that the higher A/V ratio leads to faster reactions and distinctly different outcomes. For example, at 81°C , equilibrium is achieved within half a year for the high A/V ratio (Fig. 5b), whereas equilibrium is not even approached for the low A/V ratio (Fig. 5a).

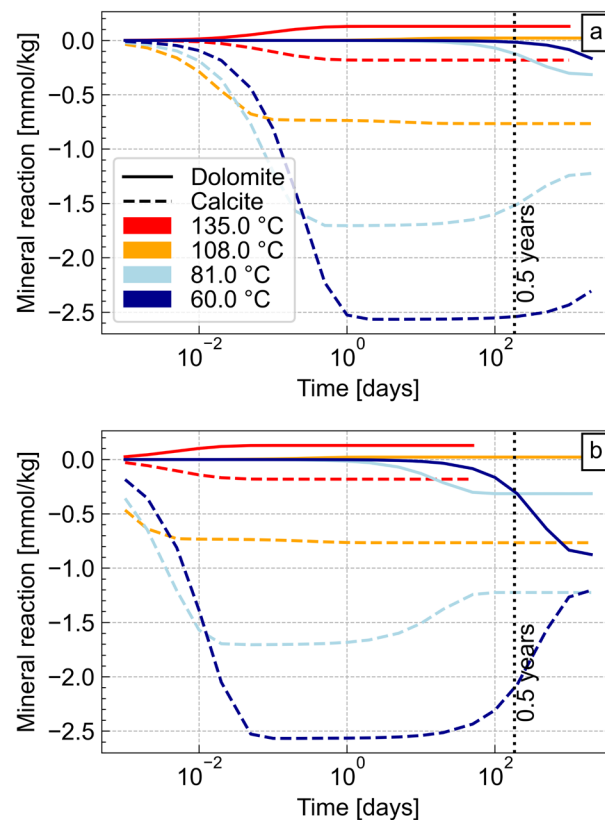


Fig. 5 Mineral Reactions in the Kinetic Model. (a) Simulation using an A/V ratio of $40\text{ cm}^2/\text{L}$ and (b) using an A/V ratio of $800\text{ cm}^2/\text{L}$. The 135°C curve in (b) terminates before 0.5 years due to convergence issues for large time steps after equilibrium was reached. At higher temperatures, reaction rates are significantly faster, achieving equilibrium in less than one day, whereas at geothermal reinjection temperatures (60°C), chemical changes occur more gradually, over more than six months. Reactions are generally more pronounced at lower temperatures due to the greater distance from equilibrium (cf. Figure 4)

The chemical system's response is strongly influenced by temperature, with reactions being amplified at lower temperatures due to the greater distance from equilibrium (Fig. 4). At higher temperatures (135 °C and 108 °C), calcite dissolves while dolomite precipitates. In contrast, lower temperatures (81 °C and 60 °C) exhibit a more complex interplay between calcite and dolomite. On short time scales, dolomite is kinetically inhibited, resulting in the dissolution of calcite as the dominant process. As calcite dissolution affects the dolomite equilibrium, this increases the dolomite disequilibrium, leading to a significant supersaturation. Over longer time scales, the process thus reverses: calcite begins to precipitate while dolomite undergoes dissolution.

Thermo-hydro-chemical simulation

The thermo-hydro-chemical processes described in the previous chapters are governed by two primary mechanisms: (1) the establishment of a chemical gradient through CO₂ conditioning of the thermal water, and (2) changes in mineral saturation states driven by temperature variations within the reservoir. Injection of hot water at 135 °C results in localized heating of the reservoir near the wellbore (Fig. 4). This effect is particularly pronounced in the excess-permeability zone, which receives the majority of the injected water. After ten cycles of hot water injection (corresponding to 9.5 years of simulation), the thermal front extends several hundred meters into the reservoir (Fig. 4b). The high permeability of the reservoir (1.5 Darcy) facilitates thermal convection, leading to slight heat accumulation in the upper part of the reservoir, compared to the lower part. In contrast, cold water injection induces localized cooling of the reservoir, albeit with a more limited propagation of the cooling front in the geothermal battery scenario (Fig. 6c), compared to the geothermal scenario (Fig. 6d) due to the seasonally reduced impact (no injection during the thermal charging period, cf. Figure 1). The lower temperature gradient during cold water injection (a temperature difference of 21 °C compared to 34 °C during thermal charging) results in less significant thermal convection with only a slight accumulation of cold water in the lower part of the reservoir.

Chemical changes at the storage well

Chemical changes at the storage well occur due to the change in saturation indices from heating and inhibition (Fig. 4). S1: In the absence of an inhibitor, both dolomite and calcite precipitate (Fig. 7c), leading to a significant reduction in porosity near the wellbore of up to 2.2%pt (percentage points). This reduction is most pronounced in cells close to the injection well. S2: When CO₂ inhibition is applied, porosity development reverses (Fig. 7f, i). In the near-wellbore region, calcite undergoes dissolution, resulting in increased supersaturation with respect to dolomite, which then precipitates in these areas. However, due to slower reaction kinetics, the rate of dolomite precipitation is approximately one order of magnitude lower than calcite dissolution. This process generates a porosity increase of up to 0.9%pt (Fig. 7f). S3: In a purely dolomitic DZEP, only dolomite precipitation occurs, as calcite is absent. This leads to a slight reduction in porosity (<0.2%pt, Fig. 7i). In contrast, mixed calcitic-dolomitic zones exhibit a porosity increase of comparable magnitude.

Despite the application of a kinetic model, significant chemical alterations are largely restricted to the vicinity of the wellbore (Fig. 7). Beyond a radial distance of 50 m from the storage well, porosity changes are negligible. The DZEP, which receives

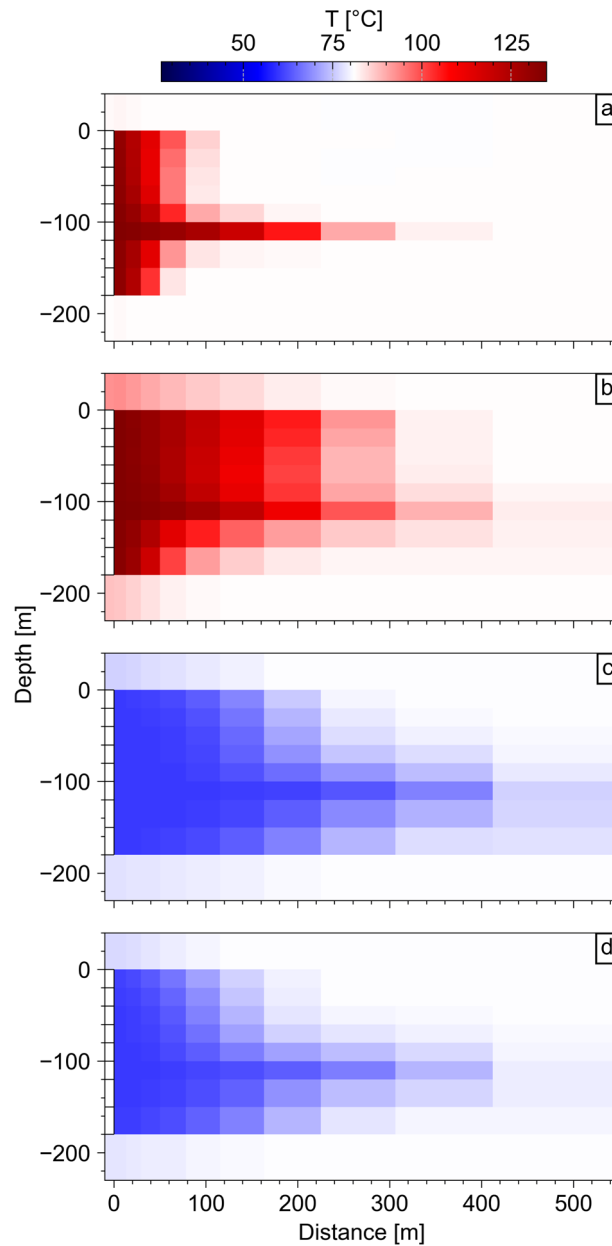


Fig. 6 Temperature Distribution in the Reservoir. **(a)** Temperature distribution after the first storage cycle and **(b)** after the 10th storage cycle. Over 10 years, heat migrates upward within the reservoir due to density-driven flow. **(c)** Reservoir cooling after 10 years for geothermal reinjection (injection period: 12 months per year at 60 °C) and **(d)** after 10 years injection during geothermal battery operation (6 months per year at 60 °C). The geothermal battery demonstrates a reduced thermal impact due to its seasonal operation. The depth is shown as depth below top reservoir and the distance as distance from the well. Black-outlined cells on the left margin indicate the locations where well boundary conditions were applied

approximately 70% of the injected fluid volume, undergoes the most pronounced chemical changes. This occurs because the high fluid volume overcompensates the lower reactivity associated with reduced surface area-to-volume A/V ratios of this zone. Higher flow rates and slower reaction kinetics enable chemical processes to extend tens of meters from the wellbore in this zone. In contrast, the matrix reservoir, characterized by higher A/V ratios and lower flow rates, limits significant porosity changes to just a few meters from the wellbore. While chemical reactions also occur at greater depths within

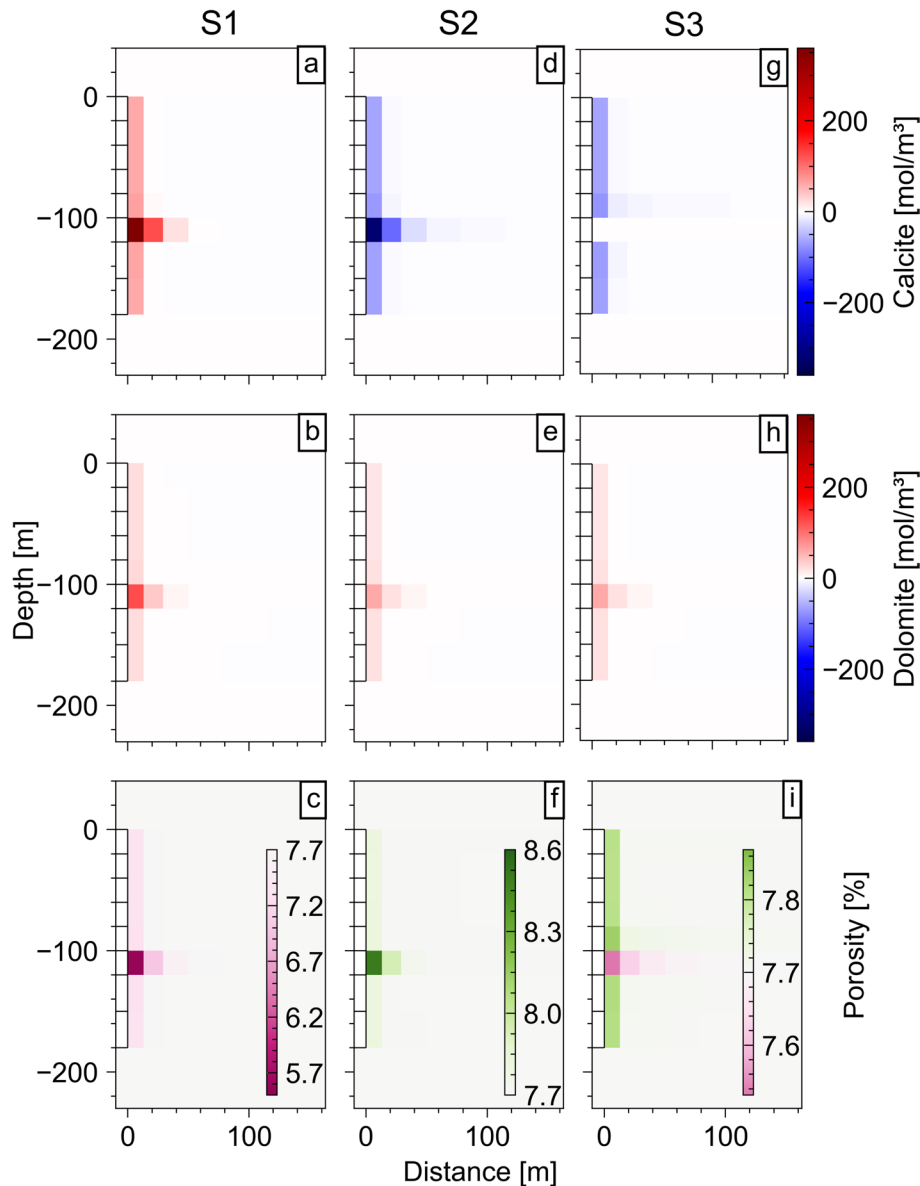


Fig. 7 Calcite, dolomite and porosity changes of the storage scenarios in the vicinity of the wellbore after 10 years of simulation. Chemical changes are most pronounced in the DZEP, as 70% of the fluid volume is injected and produced from this zone. In Scenario 1 (S1), where no inhibitor is applied, significant calcite (**a**) and dolomite (**b**) precipitation occurs, leading to a porosity reduction near the wellbore (**c**). When an appropriate amount of inhibitor is used, calcite dissolves near the wellbore (**d**), while a smaller amount of dolomite precipitates (**e**), resulting in porosity generation close to the wellbore. When the DZEP is composed of dolomite only, no calcite precipitation occurs in this zone (**g**), while dolomite is precipitated (**h**), leading to a porosity reduction in the DZEP while porosity is increased in the rest of the reservoir (**i**). The depth is shown as depth below top reservoir and the distance as distance from the well. Black-outlined cells on the left margin indicate the locations where well boundary conditions were applied

the reservoir, the establishment of equilibrium with dolomite is notably slow. Furthermore, the radial configuration of geothermal production and injection leads to cell volumes increasing quadratically with distance from the well, resulting in the volumetric dilution of disequilibrium states. Combined with the reduced temperature and chemical gradients at greater distances, this leads to negligible porosity changes far from the wells.

The chemical evolution at the storage well is shown in Fig. 8 and reflects the changes in saturation indices induced by heating and CO₂ inhibition (cf. Figure 4). As the injected thermal water is adjusted at surface conditions to a saturation index of 0, the pressure increase upon injection shifts the system into disequilibrium under reservoir conditions, resulting in calcite undersaturation and dolomite supersaturation. Consequently, calcite dissolves, increasing dissolved calcium concentrations, while dolomite precipitates, leading to a reduction in dissolved magnesium during injection. When the well operation is reversed to production, the temperature decreases in time and the produced fluid represents a mixture of injected and native formation water. This results in a pronounced decrease in total inorganic carbon (TIC), as the native thermal water contains significantly lower TIC compared to the injected fluid (Table 2). During this phase, calcium concentrations continue to increase due to enhanced calcite dissolution at lower temperatures. In contrast, magnesium concentrations exhibit a more complex behavior controlled by the interplay of kinetic dolomite reactions, mixing effects, and temperature-dependent changes in equilibrium conditions. While calcite remains close to equilibrium throughout production, dolomite shows persistent supersaturation, with saturation indices ranging between 0.25 and 0.35. This indicates that equilibrium with dolomite is not reached within the considered time frame, consistent with its comparatively slow reaction kinetics.

Chemical changes at the injection well

This study compares two scenarios of cooled thermal water injection at 60 °C: (1) a conventional geothermal doublet and (2) reinjection of chemically inhibited, reproduced

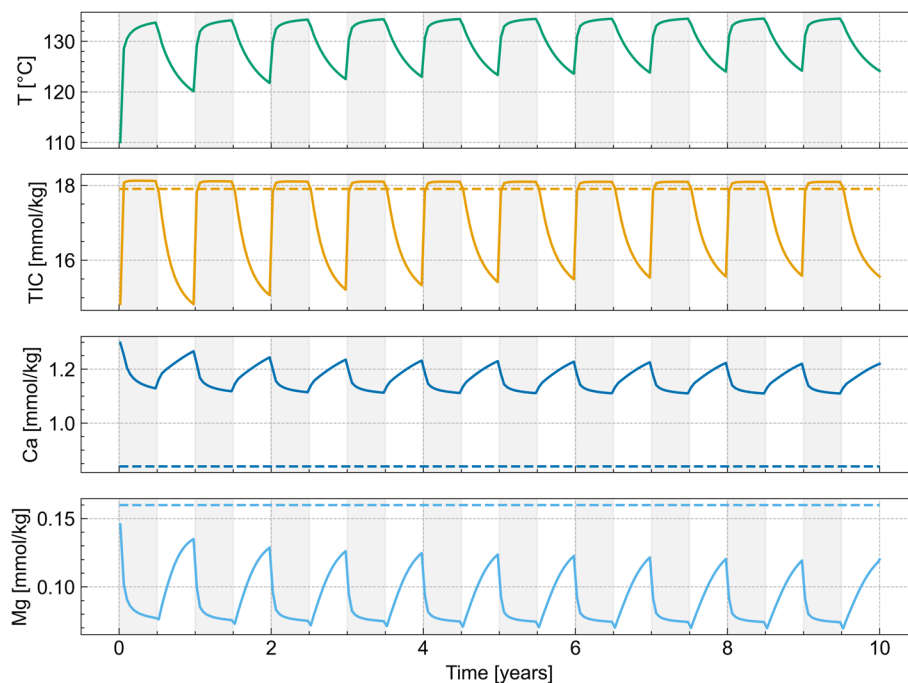


Fig. 8 Evolution of temperature and chemical composition at the storage well. Dashed lines represent the composition of injected water, which was treated with CO₂ (Table 2). Solid lines represent the evolution of the respective parameters. Injection phases are shown with grey background, production phases with white background. During injection, the composition closely follows the temperature, while during production, mixing effects between injected water and native formation water appear

thermal water during thermal discharge. Both scenarios assume a base reservoir temperature of 81 °C.

In the conventional geothermal doublet scenario, no chemical changes are induced; only the lower injection temperature affects saturation indices. In contrast, the reinjection scenario incorporates the temporally variable chemical composition of the storage scenario (S2), as outlined in the section “Chemical model”. Both scenarios result in a notable increase in porosity near the injection well (Fig. 8). However, the porosity increase is significantly higher in the reinjection scenario, reaching up to 2.7%pt (Fig. 8a), compared to 0.7%pt in the conventional geothermal doublet (Fig. 8b).

Despite the injection well operating only half as long as in the conventional geothermal doublet, the chemical changes are more pronounced in the reinjection scenario. This is attributed to the residual disequilibrium from CO₂ injection, which overcompensates for the shorter operational time. At the storage well, the CO₂-inhibited thermal water reacts with the surrounding reservoir to reach equilibrium with calcite at elevated temperatures (initially 135 °C during production, decreasing to 120–125 °C by the end of the thermal discharge period). The remaining dissolution potential, corresponding to the temperature drop from ~120 °C to 60 °C, is realized at the injection well. This results in the highest chemical interactions of all scenarios occurring at the injection well of the geothermal battery.

Volumetric balance of the reservoir

To evaluate the reservoir’s volumetric balance, the total change in rock volume due to chemical reactions was calculated across the entire simulation domain (Fig. 9a, b). In the storage scenario without inhibition (S1), calcite and dolomite precipitate at a combined rate of 35 m³ per year.

For the inhibited storage scenarios (S2, S3), the evolution of rock volume exhibits a cyclic pattern, characterized by dissolution during the charging phase and minor

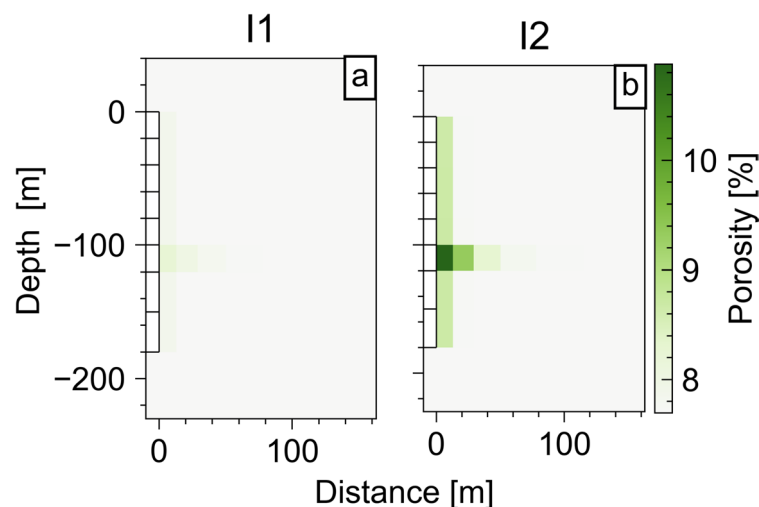


Fig. 9 Porosity Changes Due to Dissolution at the Injection Well After 10 Years of Simulation. **(a)** Porosity changes for a conventional geothermal doublet (Scenario I1), showing only minor changes, and **(b)** porosity changes for the geothermal battery (Scenario I2). Despite operating the injection well of the geothermal battery for only 6 months per year, significantly greater dissolution is observed, driven by the residual undersaturation caused by the CO₂ inhibitor. The depth is shown as depth below top reservoir and the distance as distance from the well. Black-outlined cells on the left margin indicate the locations where well boundary conditions were applied

precipitation during the discharging phase. While the dissolution during the charging cycle was discussed in the previous section, the precipitation observed during the discharging cycle warrants further explanation. This phenomenon is attributed to thermal water, which is initially in equilibrium with calcite and slightly undersaturated with dolomite at the ambient reservoir temperature of 81 °C, being drawn into the heated zone near the wellbore. As the thermal water heats up, it becomes supersaturated with respect to calcite and dolomite, resulting in their precipitation within the heated regions. The slightly lower dissolution observed in S3 is due to the composition of the high-permeability zone, which contains only dolomite. As a result, fluid in this zone does not interact with calcite.

The injection scenarios (I1, I2) lead to net dissolution, however the amount of dissolution is much higher for the injection of the thermal water during thermal discharging (I2) than the conventional geothermal injection well (I1). The reason for this has been explained in the previous chapter, leading to a dissolution volume of 1050 m³ (combined) in scenario I2, as opposed to ~100 m³ in I1.

Discussion

Porosity and permeability changes

Porosity changes typically affect reservoir permeability. However, in this study, we chose not to couple permeability to porosity changes using a poro-perm relationship. This decision is based on the well-established observation that carbonate reservoirs, especially karstified ones, often lack a clear poro-perm relationship. Instead, we propose that the permeability behaviour in the Malm reservoir is governed by distinct processes within its karstified and porous zones. In karstified sections of the reservoir, dissolution is expected to have minimal impact on permeability. Enlarging pre-existing decimetre-scale conduits, such as karst tubes, is unlikely to significantly alter their flow behaviour. Furthermore, these structures are considered robust against minor precipitation and resistant to damage from fines migration (Grifka et al. 2023). In contrast, the matrix sections of the reservoir, characterized by much smaller pore throats, are more sensitive to precipitation and dissolution. We anticipate that any significant permeability changes will occur in these regions. However, the extent of these changes is expected to be less pronounced than in sandstone reservoirs, given the Malm reservoir's advanced diagenetic history.

Our simulations indicate no significant precipitation at the interface between the DZEP and the matrix reservoir (Fig. 7d, f). In scenarios where the DZEP is composed entirely of dolomite, increased dissolution at this transition (Fig. 7g, i) may enhance connectivity between the matrix and karst. These findings suggest that the permeability contrast between zones is unlikely to pose challenges for the long-term operation of the geothermal battery. In fact, the results indicate a slight permeability enhancement near the storage and injection wells during operation, demonstrating that CO₂ inhibition effectively mitigates the risk of formation damage.

Porosity changes in the reservoir are modest. The highest volumetric change, observed at the injection well in scenario I2, involves approximately 1,000 m³ of dissolved rock. This volume is equivalent to a cube with 10 m edges. Notably, anecdotal evidence from other wells in the Malm reservoir confirms the existence of uncollapsed cavities of similar size (Böhm and Steiner 2012; Hörbrand et al. 2024). For the geothermal battery,

dissolution is distributed throughout the reservoir, resulting in an average porosity increase of less than 0.3%pt in the near-wellbore region, raising the porosity from 7.7% to 8% (Fig. 10). This moderate increase is unlikely to create stability concerns. At the storage well, porosity changes are even smaller when a CO₂ inhibitor is used.

In order to advance the process understanding of near-field porosity and permeability improvement, we compared the porosity changes from our simulations with thermo-hydro-mechanical results from Egert et al. (2022), who modelled a similar temperature gradient (60 K) and pore pressure change (1 MPa) in a Malm reservoir injection well. The higher porosity changes resulting from chemical processes suggest, that permeability enhancement in the near-field reservoir may in some scenarios be driven by chemical processes, however it seems likely that both processes contribute relevantly to permeability enhancement, especially if DZEPs are strongly dolomitic resulting in little chemical changes due to slower kinetics (Fig. 10, S3).

Sensitivities on parameter changes

The variation of three key parameters—presence of a DZEP, A/V ratio, and CO₂ dosage rate—was analysed and compared to scenario S2 (Fig. 11). The figure displays the porosity changes as a difference (delta) relative to S2. If absolute porosity were shown, dissolution would appear homogenous around the well in the absence of a DZEP. However, since the porosity is expressed as a difference from S2, the excess dissolution potential

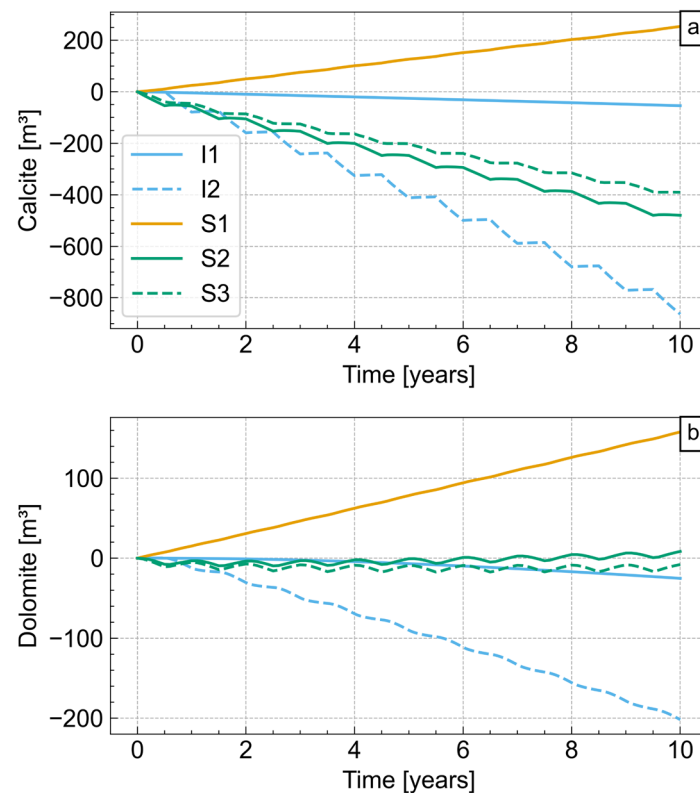


Fig. 10 Volumetric Changes in the Reservoir for the Simulated Scenarios. **(a)** Volumetric changes in calcite across the entire quarter-domain model, showing that the most pronounced chemical changes occur during geothermal battery operation. **(b)** Volumetric changes in dolomite across the quarter-domain model. Significant dolomite changes are observed only for the injection well of the geothermal battery (Scenario I2) and when no inhibitor is applied (Scenario S1). In other scenarios, dolomite changes remain minimal due to oscillating effects (S2, S3) or low reaction rates (I1)

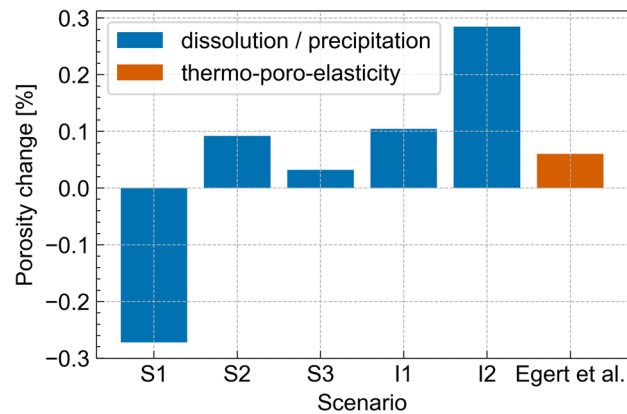


Fig. 11 Average Porosity Change Within 23 m of the Injection Well. For example, a value of 0.1 indicates an increase in porosity from 7.7% to 7.8%. The most pronounced porosity changes are observed in the injection scenarios, where dissolution dominates, and in the scenario without an inhibitor (S1), where precipitation is the primary process. In contrast, the other storage scenarios exhibit lower porosity changes due to the balance between injection-induced dissolution and precipitation. For comparison, thermo-poro-elastic changes simulated by Egert et al. (2022) for an injection well at another site in the Malm reservoir (with a 60 K temperature change and a 1 MPa pore pressure change) are included. Except for the storage scenario with a fully dolomitic DZEP (S3), porosity changes driven by chemical reactions consistently exceed those caused by thermo-poro-elastic effects

in the DZEP is redistributed uniformly across the matrix reservoir, resulting in maximum changes of -0.5%pt (Fig. 11a). Doubling the CO₂ inhibitor dosage in S2 produces a significant additional porosity increase of 3.0%pt, reaching up to 11.6% in the DZEP (Fig. 11b). This increase is substantially larger than the initial S2 increase from 7.7% to 8.6%, as the excess CO₂ remains fully reactive. In contrast, the dissolution potential in S2 with an appropriate inhibitor dosage is reduced by the temperature increase. Increasing the A/V ratio by one order of magnitude shows only a negligible effect, with porosity changes of less than 0.1%pt (Fig. 11c). As calcite equilibrium is already achieved with the lower A/V ratios in S2, only dolomite precipitation is affected. The saturation indices (SI) indicate that the thermal water is closer to equilibrium (SI ~ 0.15 compared to ~ 0.3) with higher A/V ratios, but the resulting precipitation is minimal and does not significantly impact the overall balance. The minimal impact of reactive surface area observed in our simulation cases appears to be a unique characteristic of the scenarios studied, as chemical changes are predominantly governed by the rapid reactivity of calcite. If additional minerals with slower reaction rates were present, we anticipate that variations in reactive surface area would have a much more pronounced effect on the outcomes.

The influence of density-driven flow was also examined. Such flow becomes relevant only when the combination of a sufficient temperature gradient (maximum 54 K in this study) and high reservoir permeability is achieved. In a test using a homogenous model with varying permeability, significant density-driven flow was observed for permeability values exceeding 0.3 Darcy. Given the reservoir's permeability of at least 1.2 Darcy, density-driven flow is present in the model (Fig. 4). However, it does not lead to meaningful differences in chemical interactions between the upper and lower reservoir, as the effects are on the order of 0.01% and therefore negligible Fig. 12.

Limitations of the model

Limitations of the model arise from discretization, uncertainty of initial equilibrium states in the reservoir and the definition of the chemical system. The model uses a coarse

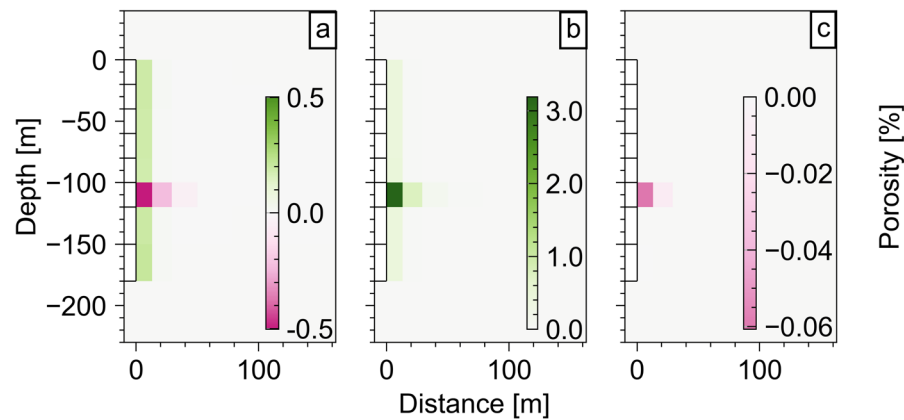


Fig. 12 Sensitivity of porosity on parameter changes, shown as the change in porosity compared to S2. **(a)** Removing the DZEP from the model (homogenous model) leads to a redistribution of porosity changes from the DZEP to the matrix reservoir. Therefore, a relative decrease can be seen in the DZEP, while the other zones show an increase. **(b)** Doubling the amount of CO₂ leads to an additional porosity increase of 3.1% in the DZEP. **(c)** Increasing the A/V ratio of the DZEP and the matrix by one order of magnitude leads to very small changes, as calcite is already in equilibrium and only dolomite reactions are affected

grid discretization (10 m size at the well) due to numerical constraints, as finer resolution would significantly increase simulation time and require high-performance computing resources. This coarseness results in some averaging in the near-wellbore region due to the grid size and is thus not able to predict e.g. wormholing (Snippe et al. 2020). The heterogeneity represented in this study, modeled as a single DZEP within a matrix reservoir, is a simplification intended to improve process understanding. In reality, DZEPs are likely thinner than 20 m and more dispersed, deviating from the layer-cake model used here. Furthermore, the matrix reservoir is expected to exhibit greater heterogeneity. Accurately capturing such complexities would require finer grid discretization, which in turn demands either more powerful computational resources or the implementation of faster chemical solvers (e.g., Reaktoro, Leal et al. 2014). This is particularly important as computational costs are predominantly driven by the processing speed of the PHREEQC backend.

To calibrate the thermal water composition, adjustments to the balance of earth alkali cations were made to prevent instantaneous precipitation or dissolution caused by slight over- or undersaturation, stemming from uncertainties in equilibrium constants (see “thermal water chemistry” in the model description). These adjustments slightly influence predictions at specific saturation indices but do not fundamentally alter the results. It furthermore remains uncertain whether dolomite would realistically precipitate under injection conditions (60 °C). However, in our modeling study, we observe predominantly dissolution at these temperatures, with no significant dolomite precipitation. Field and laboratory studies have indicated that dolomite precipitation occurs at elevated temperatures above 80 °C (Machel 2001; Montes-Hernandez et al. 2016), suggesting that allowing for precipitation in the simulations should be reasonable. The dissolution of calcite and dolomite follows a competitive, incongruent dissolution process: when thermal water in equilibrium with calcite interacts with dolomite, dolomite dissolves until equilibrium is reached, leading to calcite precipitation due to supersaturation (Appelo and Postma 2004). At high temperatures, uncertainties in equilibrium constants exacerbate incongruent dissolution in simulations, even for very small saturation indices

(<0.01). However, natural systems are likely to exhibit pseudo-stability due to nucleation and crystallization energy barriers. For this reason, additional carbonate minerals such as siderite and ankerite were excluded from the study. Including them would intensify incongruent dissolution issues, and their precipitation is unlikely given that crystal growth on available calcite and dolomite surfaces in the reservoir will likely be energetically preferred (Zimmermann et al. 2015). However, we cannot exclude that a minor amount of carbonate precipitation from these mineral phases would occur.

Overall, this study should be viewed as an effort to enhance understanding of the underlying processes and to provide an estimate of the magnitude of chemical changes that may occur during the operation of a geothermal battery.

Conclusion

Our study explored the chemical interactions driven by temperature and chemical changes in a highly heterogeneous carbonate reservoir, with a focus on distinguishing reaction rates between the low-reactive surface DZEP and the higher-reactive surface matrix reservoir. This distinction is particularly relevant for reactive transport studies, as strong heterogeneity can be either induced by geological diagenesis or fracturing but can also result from dissolution due to reactive transport. Our findings highlight the significant influence of DZEPs, surface area-to-volume A/V ratios, and mineralogical changes due to dolomitization on simulation outcomes. The fundamental questions arising from these topics have only been touched but were not systematically answered, meriting further research in the context of heat or CO₂ storage.

For the operation of a geothermal battery in the Malm reservoir, our results indicate that CO₂ is an effective inhibitor, preventing formation damage at the storage well and potentially enhancing permeability at both storage and injection wells. A minor exception was observed in the case where the DZEP was fully dolomitic, resulting in a slight local porosity decrease, however it seems unlikely that this scenario occurs or results in a relevant decrease in productivity. The corrosive nature of CO₂ raises important concerns about long-term well integrity, even if small amounts like in our case are introduced. While this study focused on the reservoir-scale processes, the results of our investigation into corrosion processes will be addressed in a subsequent publication. Over the long term, geothermal battery operation results in modest porosity increases, primarily driven by calcite dissolution, with the most pronounced changes occurring at the injection well in which the previously inhibited thermal water is injected. These changes are largely confined to the wellbore near-field but are distributed across a broader reservoir volume, making stability issues from dissolution highly unlikely. Estimating the severity of these processes using 1D simulations at endmember temperatures (e.g., 60–135 °C) tends to overestimate the impact, as such models fail to account for the spatial distribution of chemical alterations. The quadratic increase in fluid volume with distance from the wellbore results in rapid volumetric dilution of chemical effects, further mitigating the potential for widespread porosity changes. The chemical de-risking conducted in this study supports the integration of geothermal batteries into renewable energy systems, presenting a potentially cost-effective solution for CO₂-neutral coverage of mid- and peak-load demands in district heating networks.

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Author contributions

TH and TK conceptualized the study. TH performed the numerical investigation and prepared the main manuscript text. All authors contributed to the discussion and interpretation of the results. TK secured the funding for the research. All authors reviewed and approved the final manuscript.

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Data availability

No datasets were generated or analysed during the current study.

Declarations

Competing interests

The authors declare no competing interests.

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