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# A coupling alternative to reactive transport simulations for long-term prediction of chemical reactions in heterogeneous CO<sub>2</sub> storage systems

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## Abstract

Fully-coupled, multi-phase reactive transport simulations of CO<sub>2</sub> storage systems can be approximated by a simplified one-way coupling of hydrodynamics and reactive chemistry. The main characteristics of such systems, and hypotheses underlying the proposed alternative coupling, are (i) that the presence of CO<sub>2</sub> is the only driving force for chemical reactions and (ii) that its migration in the reservoir is only marginally affected by immobilization due to chemical reactions. In the simplified coupling, the exposure time to CO<sub>2</sub> of each element of the hydrodynamic grid is estimated by non-reactive simulations and the reaction path of one single batch geochemical model is applied to each grid element during its exposure time. In heterogeneous settings, analytical scaling relationships provide the dependency of velocity and amount of reactions to porosity and gas saturation. The analysis of TOUGHREACT fully coupled reactive transport simulations of CO<sub>2</sub> injection in saline aquifer, inspired to the Ketzin pilot site (Germany), both in homogeneous and heterogeneous settings, confirms that the reaction paths predicted by fully coupled simulations in every element of the grid show a high degree of self-similarity. A threshold value for the minimum concentration of dissolved CO<sub>2</sub> considered chemically active is showed to mitigate the effects of the discrepancy between dissolved CO<sub>2</sub> migration in non-reactive and fully coupled simulations. In real life, the optimal threshold value is unknown and has to be estimated, e.g., by means of 1-D or 2-D simulations, resulting in an uncertainty ultimately due to the process decoupling. However, such uncertainty is more than acceptable given that the alternative coupling enables using grids in the order of million elements, profiting from much better description of heterogeneous reservoirs at a fraction of the calculation time of fully coupled models.

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## 1 Introduction

Long-term, reservoir-scale, multiphase reactive transport simulations in heterogeneous settings are computationally extremely challenging, often forcing to set up oversimplified models if compared to purely hydrodynamic simulations. Typically, 1-D or 2-D models are preferred wherever symmetry allows for it (e.g., Gaus et al., 2005; White et al., 2005; Audigane et al., 2007; Xu et al., 2010; Beyer et al., 2012); only coarse spatial discretizations are adopted for 3-D models (Nghiem et al., 2004; Kühn et al., 2006; Kühn and Günther, 2007; Zheng et al., 2009). As a result, most studies of reactive transport only consider very simple geometries and homogeneous media, thus disregarding spatial heterogeneities at reservoir scale, which in turn are routinely considered by the usually much more detailed geologic models and pure hydrodynamic reservoir simulations. These oversimplifications concern the chemistry as well, leading to consider only a subset of the potentially reactive minerals. Moreover, the need for sensitivity and uncertainty analysis due to the large amount of uncertain parameters in geochemical simulations (De Lucia et al., 2012; Dethlefsen et al., 2012) cannot be met if the computational effort for one single simulation is too high. The resulting models can be used to highlight qualitative results or to provide rough estimations of the ongoing processes at reservoir scale (Gaus et al., 2008, and references therein). To our knowledge, there is no example of fully coupled reactive transport simulations considering complex chemistry on spatial discretizations with a resolution comparable with the one usually adopted for pure hydrodynamic simulations.

However, a number of relevant questions require a rather careful description of reservoir heterogeneity, or depend on a fine resolution of reservoir features, well beyond the possibility of fully coupled simulators and computationally affordable coarse grids. The migration path in a highly heterogeneous system, for example, heavily affects the volume of reservoir which get exposed to the injected reactant and thus, in the long term, which is affected by chemical reactions (Lengler et al., 2010; De Lucia et al., 2011). Hence, heavily upscaled or geometrically simplified models may not be able

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to satisfactorily capture such migration, adding a decisive imprecision to the coarse coupled simulations.

Especially to solve one of these problems, namely the estimation of the long term mineralization at the Ketzin pilot site (Martens et al., 2013), a simplified scheme for coupling chemistry and hydrodynamics was introduced (Klein et al., 2013; Kempka et al., 2013b). The purpose of the novel method is to avoid upscaling the simulation grid or applying multi-grid methods, but instead to take advantage of some of the characteristics of the modelled processes, by simplifying the *coupling* itself.

In CO<sub>2</sub> storage systems, in fact, relevant mineralization is generally expected to occur hundreds or thousands years after injection stop (IPCC, 2005), since the slow kinetics of the involved reactive chemistry is the typical limiting factor (Marini, 2006; Gaus, 2010). The coupling with hydrodynamic transport of solutes plays only a secondary role under these circumstances. In summary, a typical underground CO<sub>2</sub> storage system is expected to display the following characteristics:

1. the time scale of mineral alterations is much larger than that of the hydrodynamic processes, meaning that most relevant chemical alterations are occurring when the system has reached substantial hydrodynamic equilibrium;
2. the major driving force for these alterations is the presence of the injected CO<sub>2</sub>, either in a separate, dense phase or dissolved in the formation brine;
3. as consequence of the previous facts, the transport of other reactants is far less relevant with regard to reactions outcome; also, given the high salinity of the targeted formation fluids, the presence of other reactants is not a limiting factor for the reactions;
4. the expected mineral reactions do not significantly affect the petrophysical properties of the medium (porosity, permeability) at least until reaching substantial hydrodynamic equilibrium;

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The resulting coupling approach is described in detail in the next Sect. 2.1, highlighting the major underlying hypotheses for its applicability. Section 3 introduces the case study, with the reference geochemical model, the simulation grid and the general setup of the non-reactive and fully coupled reactive transport simulations performed for the validation. Their respective results are analysed in Sect. 4 aiming at verifying the major hypotheses; and finally a comparison of the outcomes of simplified and full coupling concludes the study.

## 2 The simplified one-way coupling

### 2.1 Implementation

The concept of the one-way coupling firstly introduced by Klein et al. (2013) is to combine, in a post-processing approach, independent batch geochemical simulations with non-reactive flow simulations, while applying some criterion to at least ensure partial mass balance and thus compensate for the lack of feedback between the modelled processes. One crucial hypothesis underlying the applicability of the method, as pointed out in the previous section, is that the effects of chemical reactions are small and become significant only when the hydraulics of the reservoir have come to a substantial equilibrium, hence not affecting the hydrodynamic behavior of medium and modelled fluids.

In detail, the procedure is constituted by the following steps:

1. from hydrodynamical simulations derive the *exposure time* to injected CO<sub>2</sub> of each grid element, distinguishing between exposure to gaseous or dissolved CO<sub>2</sub>;
2. compute the *characteristic water saturation* and concentration of dissolved CO<sub>2</sub> during exposure time;
3. one 0-D batch geochemical simulation is *analytically scaled* for each element of the hydrodynamic grid, considering heterogeneous porosity and the water/rock

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ratio, which itself depends on gas saturation (insights about the analytical relationship are given in Sect. 2.2);

4. if the element is exposed only to a dissolved  $\text{CO}_2$  concentration, a *threshold* must be defined for dissolved  $\text{CO}_2$  to be geochemically active. In this case, the mineralization is limited to the maximum dissolved concentration;
5. if the element is exposed only to gaseous  $\text{CO}_2$ , it is assumed that enough  $\text{CO}_2$  is present in the element to achieve the maximum mineralization without further need for a mass balance;
6. the mineralization in each element is finally summed in time to achieve global mineralization in reservoir.

The lack of feedback between hydrodynamics and chemistry is of course the major drawback of this simplified coupling. The absence of direct coupling also does not allow to ensure mass balance between the two processes. These issues therefore permit the application of the method only in case of limited feedbacks not significantly affecting the respective process simulations. However, a control regarding the mass balance has been included into the simplified coupling: in the elements exposed only to dissolved  $\text{CO}_2$ , the amount of mineralization is limited to the actual amount of  $\text{CO}_2$  reaching those elements. This bounding is considered not necessary if a significant saturation of gaseous  $\text{CO}_2$  is reached in the element, since, given the hypothesis of small amount of reactions, it is assumed that in such case enough  $\text{CO}_2$  is available to reach full mineralization for the given time frame.

The simplified coupling is applied to non-reactive hydrodynamic simulations, where indeed no  $\text{CO}_2$  is immobilized in precipitating minerals. As a consequence, the spatial extent of the  $\text{CO}_2$  cloud calculated by non-reactive simulations is always equal or larger than the one predicted if reactive chemistry is considered. This is of course reflected in the spatial extent of the mineralization calculated applying the one-way coupling, which is based on non-reactive simulations.

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Therefore, the *first main hypothesis* needed for the success of the simplified coupling is that the discrepancy of the CO<sub>2</sub> migration predicted by the non-reactive simulations is not too large with respect to the case with active chemistry. It will be shown in the following how the proposed method of defining a *threshold* on the dissolved CO<sub>2</sub> concentration “allowed” to activate the chemistry mitigates this issue to a large extent.

One major feature integrated in the proposed simplified coupling approach is the treatment of spatial heterogeneity of porosity and of gas saturation in the porous medium, the latter also dynamically varying along the simulation run. These parameters namely control speed and total amount of the chemical reactions through the ratio between reactive solution and available mineral surfaces. This scaling can be directly solved by an analytic solution which allows to transform the results of geochemical simulations scaled for a given porosity and water saturation to any other given porosity and saturation. More insights on this matter are given in Sect. 2.2. The gas content, and hence water saturation, and dissolved concentration vary during the simulation and also in particular during the exposure time of grid elements to the injected CO<sub>2</sub>. By comparison with fully coupled simulations, it can be shown that the *maximum gas saturation during exposure time controls the speed of reactions; the maximum concentration of dissolved CO<sub>2</sub> controls the total amount of mineralization in the elements where no gaseous CO<sub>2</sub> arrives.*

For an initially geochemically homogeneous scenario, the simplified coupling foresees the use of one single batch geochemical model which is practically replicated onto all elements of the simulation grid, scaled following the actual local porosity and gas/water saturation ratio. In other words, the simplified coupling assumes that in each element of the simulation grid the reaction path is qualitatively and quantitatively similar to one single underlying model: we will refer to this property in the following as *self-similarity* of reactions in the reservoir. This assumption is quite strong, and constitutes the *second major hypothesis* that needs to be verified by analysis of fully coupled reactive transport simulations.

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The medium considered throughout this study is *homogeneous in terms of volume fractions of reactive minerals*: heterogeneity is in the present study only referred to porosity and permeability. In presence of different facies or a spatially heterogeneous distribution of volume fractions, the method can still be applied using as many batch geochemical simulations as there are different facies in the reservoir, then assigning the corresponding chemistry to each element of the hydrodynamic grid. However this possibility has not been explored in the present study.

## 2.2 The analytical scaling relationship

Klein et al. (2013) introduced the analytical relationships relating the outcome of a single geochemical simulation, scaled for a given porosity and water saturation, to any other given porosity and saturation. In the following it will be demonstrated that the equations are a direct consequence of the particular form of the kinetic law implemented in the models, and of the choice for representing the minerals' reactive surface and possibly its variation along the simulation.

Consider a reference rock volume  $V_r$ . A common rate expression per mass unit of solvent (with dimensions of  $[\text{mol}^{1+\gamma} \text{s}^{-1} \text{kg H}_2\text{O}^{-1-\gamma}]$ ) takes the form (Lasaga, 1998):

$$r = k \cdot A_s \cdot (1 - \Omega^\alpha)^\beta \cdot a^\gamma \quad (1)$$

where  $k$  is the kinetic coefficient  $[\text{mol m}^2 \text{s}^{-1}]$ ,  $A_s$   $[\text{m}^2 \text{kg H}_2\text{O}^{-1}]$  is the specific (per mass unit of solvent) reactive surface of the mineral in contact with the solution,  $\Omega$  the saturation ratio of the mineral and  $\alpha$ ,  $\beta$  two fitting parameters;  $a$  is the activity of a solute species acting as catalyzer and its exponent  $\gamma$  defines the *order* of the kinetic law. The specific reactive surface can be written as:

$$A_s = V_m \cdot A_m \quad (2)$$

where  $V_m$   $[\text{m}^3 \text{mineral kg H}_2\text{O}^{-1}]$  is the volume of the mineral in contact with the unit mass of solvent in the considered system and  $A_m$   $[\text{m}^2 \text{m}^{-3} \text{mineral}]$  the specific reactive



surface per unit of mineral volume.  $A_m$  is a parameter intrinsic to the mineral – e.g. related to grain size. The expression of  $V_m$  in terms of porosity and water saturation for the reference rock volume  $V_r$  reads:

$$V_m = \frac{\text{volume of mineral in } V_r}{\text{mass of solvent in } V_r} = \frac{V_r \cdot (1 - \varphi) \cdot f_m}{V_r \cdot \rho_{\text{H}_2\text{O}} \cdot S_w \cdot \varphi} \quad (3)$$

5 where  $\varphi$  the porosity,  $f_m$  the volume fraction of mineral m referred to all minerals and  $\rho_{\text{H}_2\text{O}}$  the density (mass of water per unit volume of solution).

The rate  $r$ , including its dependency on porosity and water saturation, reads then:

$$r = k \cdot \frac{f_m \cdot (1 - \varphi)}{\rho_{\text{H}_2\text{O}} \cdot S_w \cdot \varphi} \cdot (1 - \Omega^\alpha)^\beta \cdot a^\gamma \quad (4)$$

10 Consider now two distinct rock volumes  $V_1$  and  $V_2$  with initially equal mineral volume fractions and chemical composition (concentrations) of the reactive solution and differing only per porosity and saturation, respectively  $\varphi_1$ ,  $S_1$  and  $\varphi_2$ ,  $S_2$ . The rates as seen by the volume unit of solution are:

$$r_1 = k \cdot \frac{f_m \cdot (1 - \varphi_1)}{\rho_{\text{H}_2\text{O}} \cdot S_1 \cdot \varphi_1} \cdot (1 - \Omega_1^\alpha)^\beta \cdot a^\gamma$$

$$r_2 = k \cdot \frac{f_m \cdot (1 - \varphi_2)}{\rho_{\text{H}_2\text{O}} \cdot S_2 \cdot \varphi_2} \cdot (1 - \Omega_2^\alpha)^\beta \cdot a^\gamma \quad (5)$$

15 It is not needed to explicitly integrate these equations to compute their respective time scales. It is namely straightforward to recognize that the chemical reaction will proceed in the two volumes with different velocities, and thus different characteristic time scales, but going through a *succession of equal states*. To this purpose it is illustrative to proceed discretizing Eq. (6) considering the *amount of reaction per mass unit of solvent*  $\xi$

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[mol kg H<sub>2</sub>O<sup>-1</sup>], which is often called *progress of reaction*. We have:

$$r(t) = \frac{d\xi}{dt} \Rightarrow \begin{cases} V_1 : r_1(t_1) = \frac{d\xi_1}{dt}(t_1) \\ V_2 : r_2(t_2) = \frac{d\xi_2}{dt}(t_2) \end{cases} \quad (6)$$

Sought are the times  $t_1$  and  $t_2$  at which the reactions in  $V_1$  and  $V_2$  reach the same progress, or  $\xi_1(t_1) = \xi_2(t_2)$ . Consider time steps  $\Delta t_1 = t_1 - t_0$  and  $\Delta t_2 = t_2 - t_0$  small enough that the rates  $r_1$  and  $r_2$  can be considered constant and the changes in water saturation and porosity become negligible. One can write:

$$r_1(t_0) \approx \frac{\Delta \xi'}{\Delta t_1}; \quad r_2(t_0) \approx \frac{\Delta \xi'}{\Delta t_2} \Rightarrow \Delta t_2 = \frac{r_1(t_0)}{r_2(t_0)} \cdot \Delta t_1 \quad (7)$$

Substituting Eq. (5) into Eq. (7) and simplifying for the  $f_m$ ,  $\rho_{\text{H}_2\text{O}}$  and the  $\Omega$  terms, which by definition are equal for both  $V_1$  and  $V_2$  at the time  $t_0$ , we finally obtain:

$$\Delta t_2 = \frac{(1 - \varphi_1)}{S_1 \cdot \varphi_1} \frac{S_2 \cdot \varphi_2}{(1 - \varphi_2)} \cdot \Delta t_1 \quad (8)$$

Upon reaching respectively  $t_1$  and  $t_2$ , the solutions in  $V_1$  and  $V_2$  are again completely equivalent, and so are the  $(1 - \Omega)$  terms, which only depend on activity coefficients and aqueous concentrations. Hence, the procedure can be repeated, meaning that for any given time  $t_1$  in  $V_1$ , the same reaction progress is reached in  $V_2$  at the time  $t_2$  if:

$$t_2 = \frac{(1 - \varphi_1)}{S_1 \cdot \varphi_1} \frac{S_2 \cdot \varphi_2}{(1 - \varphi_2)} \cdot t_1 \quad (9)$$

Furthermore, if  $\Delta \xi'$  is the amount of reaction per unit mass of solvent, the total amount of reaction  $N$  in the given rock volume is:

$$N_1(t_1) = V_1 \cdot \rho_{\text{H}_2\text{O}} \cdot \varphi_1 \cdot S_1 \cdot \Delta \xi' \quad (10)$$

$$N_2(t_2) = V_2 \cdot \rho_{\text{H}_2\text{O}} \cdot \varphi_2 \cdot S_2 \cdot \Delta \xi' \quad (11)$$

Dividing the two equations and rearranging, it finally reads:

$$N_2(t_2) = \frac{V_2 \cdot \varphi_2 \cdot S_2}{V_1 \cdot \varphi_1 \cdot S_1} N_1(t_1) \quad (12)$$

Equations (9) and (12) are the scaling equations introduced by Klein et al. (2013), given here in a slightly more general form.

Notably, this result holds also for kinetic laws where the total rate is a linear combination of terms of the same form of Eq. (1), and for mixed kinetics/equilibrium simulation as well, since equilibrium is a special case of kinetics where the kinetic constant  $k$  is very large. One major assumption still has to be respected, which is that the reactions do not significantly affect the porosity  $\varphi$  and the water saturation  $S$ .

### Scaling relationship for the TOUGHREACT simulator

The TOUGHREACT simulator (Xu et al., 2011) implements the calculation of reactive surfaces canceling out its dependence on water saturation to prevent diverging rates when water saturation is small (Xu et al., 2008, Appendix G, p. 175). Hence, the scaling equations for this simulator read:

$$\begin{cases} t_2 = \frac{(1 - \varphi_1)}{\varphi_1} \frac{\varphi_2}{(1 - \varphi_2)} \cdot t_1 \\ N_2(t_2) = \frac{V_2 \cdot \varphi_2 \cdot S_2}{V_1 \cdot \varphi_1 \cdot S_1} N_1(t_1) \end{cases} \quad (13)$$

### 3 Validation of the simplified scheme

The procedure for validating the one-way coupling involves the comparison and analysis of a case study for which both the simplified coupling approach and the fully coupled reactive transport simulation are applied.

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The case study has been chosen in order to ensure typical conditions for the application range of the simplified coupling, and is inspired by published models for the Ketzin pilot site (Kempka and Kühn, 2013; Klein et al., 2013). For all simulations the TOUGHREACT/ECO2N (Pruess and Spycher, 2007; Xu et al., 2011) simulator was adopted. However, the simplified coupling is a general method and is independent from the simulator used for the validation.

The influence of spatial heterogeneity, here limited to porosity and permeability, and of the characteristic time scale of reactions relative to the characteristic time scale of CO<sub>2</sub> migration were also investigated.

### 3.1 Geochemical model

The chemical system chosen for the validation reflects the analyses published by Förster et al. (2010); Norden et al. (2010); Würdemann et al. (2010) and is based on the model for the Ketzin test site published by Klein et al. (2013). The chosen model displays a typical complexity for CO<sub>2</sub> storage problems; there is no need and no claim of being an accurate quantitative reference for the site, nor to investigate its plausibility or the quality of the thermodynamic database adopted for the simulations.

The Stuttgart Formation is the target reservoir of the Ketzin pilot site. It is mainly constituted by sand channels and floodplain facies. Reservoir simulations (Kempka and Kühn, 2013) show that the sandy facies receives the major amount of the injected CO<sub>2</sub> due to their higher conductivity, and can therefore be retained as the reference facies for investigating the chemical processes.

The rock-forming phases considered reactive are anhydrite, albite, hematite, illite and chlorite, together amounting to 24 % in volume of the rock. The rest of the rock – principally quartz, up to 40 % in volume – is considered inert. Secondary phases included in the model are kaolinite and the carbonates siderite, magnesite, dolomite and calcite. The cement phase anhydrite and the secondary minerals calcite and dolomite are considered at local equilibrium in the model, whereas all other minerals follow the parametrization for kinetic laws and given by Palandri and Kharaka (2004) and the

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estimation of specific surface areas by Klein et al. (2013). Notably, one order of magnitude is preserved between the specific reactive surface areas of clay minerals (kaolinite, chlorite and illite) and the non-clays. For the initial brine composition the available analyses of Würdemann et al. (2010) have been considered without further refinement besides the concentrations of  $\text{SiO}_2$  and  $\text{AlO}_2^-$  which were taken from the re-evaluation performed by Klein et al. (2013).

The batch model, also simulated with TOUGHREACT, is defined as a porous medium of  $1 \text{ m}^3$  volume, represented as one single cubic element in the program. The minerals' volume fractions listed in Table 2 are assigned to the medium. The rest of pore space not occupied by the brine is assumed filled with  $\text{CO}_2$  at an initial pressure of 70 bar, which is an average value derived by the analysis of the hydrodynamic simulations of Kempka and Kühn (2013). The impact of pore pressure was investigated by Klein et al. (2013) by means of batch models with constant pressure, and found negligible with respect to the speed of reactions at least in the range of pressure expected in Ketzin. In the present case the system is closed, and thus the simulation is performed at *constant volume* for the gas phase. The change in porosity and the consumption of water due to reactions, as well as the solubility of  $\text{H}_2\text{O}$  in the gas phase, are negligible in terms of volume change. Hence, the initial pressure governs how much  $\text{CO}_2$  is contained in the reference volume and therefore available for reactions. The reference simulation is for this reason chosen with an initial porosity  $\varphi = 0.5$  and a water saturation of  $S_w = 0.5$ .

Figure 1 displays the outcome of the reference batch simulation. Anhydrite (not shown in the picture), is undersaturated at the beginning of the simulation and, being included as equilibrium phase in the model, is from the very first step of the simulation dissolved, staying substantially constant afterwards. Chlorite is dissolved and initially also albite. However, the latter inverts its trend and starts reprecipitating after around 3000 simulation years. Illite starts precipitating from the beginning, reaching a plateau after around 3000 years and staying constant afterwards. At this point also kaolinite starts precipitating.

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The most relevant feature of the model is the sequence of precipitating carbonate minerals. The first, starting from ca. 1500 simulation years, is the iron-bearing siderite, which is followed by a temporary appearance of calcite. Calcite starts redissolving as dolomite starts precipitating. Precipitation of siderite and dolomite continues until the end of simulation time. There is no appearance of magnesite in the model and a negligible dissolution of hematite.

Prolonging the simulation to around 200 000 years sees the model approaching but not reaching an equilibrium state. At this point the precipitated volume of siderite reaches around  $3000 \text{ cm}^3 \text{ m}^{-3}$  of rock, or 0.3 % of the total rock volume. The precipitation of carbonates and illite, however, is partially compensated by dissolution of chlorite and anhydrite, and thus the calculated change in porosity after 200 000 years is  $-0.00056$  porosity units, which represents a relative change of around  $-0.11$  % from the initial value of 0.5. It can be safely considered negligible in terms of impact on the hydrodynamic properties of the medium.

### 3.2 Coupled simulations: spatial discretization and CO<sub>2</sub> injection

The simulation grid chosen for the coupled simulations in this study displays the typical complexity – and limitations – of reactive transport simulations in the domain of CO<sub>2</sub> storage, being coarse enough to allow for fully coupled reactive transport simulations in an affordable CPU time.

The spatial discretization of about  $2.5 \text{ km} \times 3.5 \text{ km}$  near-field subset of the Stuttgart formation of the Ketzin anticline comprises 2950 hexahedral elements arranged in one single layer with a 3-D structure following the topography of the target formation (Fig. 2). The thickness of the layer is around 75 m and thus comprises both main stratigraphic units of the Stuttgart Formation. Faults and discontinuities defined in the geological model have been geometrically smoothed in the one-layer model.

Pore volume multipliers at the border elements provide constant boundary conditions throughout the simulations. The construction model ensures a realistic pressure

build-up and is large enough that the injected CO<sub>2</sub> does not arrive at the borders in the investigated time span.

Two distinct cases were investigated: an homogeneous medium with constant porosity  $\varphi = 0.2$  and permeability of  $1 \times 10^{-13} \text{ m}^2$  and a spatially heterogeneous medium with porosity ranging from 0.08 to 0.22 and permeability from  $2.8 \times 10^{-14}$  to  $3.0 \times 10^{-12} \text{ m}^2$ . The heterogeneous distributions of porosity and permeability have been obtained by upscaling to the simulation grid respectively with arithmetic and geometric average the reservoir model described by Norden and Frykman (2013); Kempka et al. (2013a) and history-matched by Kempka and Kühn (2013). No further refinement of the upscaling was done, i.e., to obtain the same total pore volume in the simulation grids between the homogeneous and heterogeneous cases, or more sophisticated permeability upscaling.

The initial pressure for the models is set after equilibration runs assuming a hydrostatic gradient. All simulations are isothermal at a temperature of 35 °C. 67 000 t of CO<sub>2</sub> are injected at a constant rate in 5 years in the element highlighted in Fig. 2. This represents the amount of CO<sub>2</sub> injected at the Ketzin site. After injection, the system is let free to evolve until a total simulation time of 2200 years is reached.

It has to be stressed that the many adopted simplifications do not allow to consider the resulting model as an attempt to investigate the Ketzin site in a way coherent with the available monitoring data and previous modelling work. Again, the purpose of these numerical experiments is to validate the simplified coupling approach while mimicing the complexity (in this case: heterogeneity of porosity and permeability) of a real-life problem.

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## 4 Results

### 4.1 CO<sub>2</sub> migration in reactive and non-reactive simulations

For the purpose of this study it is important to evaluate the discrepancy between the reactive and fully coupled non-reactive simulations concerning the migration pattern of – and hence the reservoir volume exposed to – the injected CO<sub>2</sub>. The simplified coupling is applied on the outcome of non-reactive simulations, and it must therefore be ensured that the bias with respect to the fully coupled simulations is quantitatively manageable. The *reservoir volume exposed to the injected CO<sub>2</sub>*, either gaseous or dissolved, is therefore one of the crucial parameters in view of the application of the simplified coupling.

After injection, the CO<sub>2</sub> would starts rapidly its migration mainly in upward direction towards the anticline top, spreading and progressively dissolving in the formation brine along the way. Due to the coarseness of the simulation grid, the gaseous phase tends to progressively disappear, so that at the end of simulation time the majority of elements in which gas is still present display only a small residual gas saturation and almost the whole injected CO<sub>2</sub> is dissolved in the formation brine. The spatial distribution of dissolved CO<sub>2</sub> is displayed in Fig. 3, which collates snapshots after 2100 simulation years for both the homogenous and heterogeneous cases. The significant differences in migration in the homogeneous and heterogeneous cases stem on one hand from the difference in total pore volume around the injection between the two simulations, and on the other from the preferential flow paths which enhance the total spreading of the CO<sub>2</sub> (Lengler et al., 2010).

The non-reactive simulations show a quite enhanced spreading of the dissolved CO<sub>2</sub> compared to the reactive case. However, this mainly consists of elements with small concentration located at the border of the CO<sub>2</sub> plume. Its central part, where the highest concentrations are, show a similar spatial pattern. This is particularly evident in the homogeneous case, where the cloud has a much lower expansion than in the heterogeneous case.

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Figures 4 and 5 show the quantification of the exposed volumes respectively for the homogeneous and the heterogeneous cases. In the diagrams the reservoir volume exposed to gaseous  $\text{CO}_2$  (the black curves) is compared with the reservoir volume exposed only to dissolved  $\text{CO}_2$  in both fully coupled and non-reactive simulations (blue and red curves). It appears evident how soon after injection the reservoir elements showing a gaseous phase reach a maximum and start decreasing immediately afterwards. However, the discrepancy between reactive and non-reactive simulations is quite small in both cases: the presence of gas phase in an element is not significantly overestimated by the non reactive simulations.

Much more significant is the difference between the volumes exposed to dissolved  $\text{CO}_2$ . Hereby two threshold values used to include the elements in the statistic are highlighted in blue and red, pointing out the large sensitivity of the outcomes on this choice. This is due to the fact that many elements are actually exposed only to low  $\text{CO}_2$  concentrations. Furthermore, a major discrepancy is found, both in the homogeneous and heterogeneous case, between the fully coupled and the non-reactive simulations: the latter curves display a constant increase of exposed volume, whereas the reactive reach a maximum after around 500 years for the homogeneous case and around 1000 for the heterogeneous, afterwards substantially decreasing or hitting a plateau. This behavior actually means that in the non-reactive simulations the  $\text{CO}_2$  plume continues increasing its extent during the whole simulation time. Such discrepancy is actually a measure of the *overestimation* of the migration pattern caused by not accounting for chemical reactions.

However, the importance of the threshold, is not only *spatial*, but has also an impact on the definition of the considered *exposure time*. The larger the threshold, the later the arrival time of dissolved  $\text{CO}_2$  is considered. In the simplified coupling the total mineralization of the elements exposed only to dissolved  $\text{CO}_2$  is limited on one hand to the actual maximum amount of  $\text{CO}_2$  reaching the element; but on the other it gets also limited by the arrival time of  $\text{CO}_2$ , which is retained as the starting point of the chemical reactions. Therefore, the significance of the threshold is twofold, and it is the

combination of its spatial and temporal effects which helps mitigating the overestimation of CO<sub>2</sub> migration returned by the non-reactive simulations.

In summary, the reservoir volume exposed to gaseous CO<sub>2</sub> is accurately predicted by the non-reactive simulations and does not need a particular treatment. At the contrary, for the elements exposed only to dissolved CO<sub>2</sub>, the discrepancy between the non-reactive and fully coupled reactive simulations is significant and imposes the choice of a threshold value for the CO<sub>2</sub> concentration considered geochemically active to mitigate it.

## 4.2 Spatial self-similarity of reactions

The second major hypothesis is the *self-similarity* of chemical reactions in the fully coupled simulations. In fact, the hypothesis underlying the simplified coupling is that the same reaction path is replicated in every element of the simulation grid, translated in time by the corresponding arrival time of CO<sub>2</sub> and scaled according to the actual porosity and characteristic gas saturation of the element. Such replicated reaction path happens to be exactly the reference 0-D batch geochemical model depicted in Fig. 1. The discrepancies among the elements of the coupled simulations can be imputed to the hydrodynamic transport of solute species, which is the only physical process responsible for “perturbing” the reactions, since by definition they all start from the same initial state in the whole domain.

The comparison is visually represented in Figs. 6 and 7, which show two exemplary elements taken respectively from the homogeneous and heterogeneous simulation. The first is an element exposed to gaseous CO<sub>2</sub>, while the second is exposed only to dissolved CO<sub>2</sub>. The dotted lines represent the outcome of the fully coupled simulation and the solid lines the output of the (scaled) 0-D model for one element of the simulation grid. The time axis of the scaled 0-D simulation have been translated to match the actual arrival time of CO<sub>2</sub> in that element.

We can anticipate that from a quantitative point of view the agreement between the fully coupled and the 0-D scaled simulations is generally more than acceptable

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in the majority of grid elements, which supports the hypothesis the simplified coupling is based on. Common discrepancies are represented by a slight delay in precipitation of some minerals (i.e. calcite in Fig. 6, the black line).

A numerical measure of the self-similarity is needed in order to control the initial hypothesis. This is achieved comparing the mineral changes in each element to the 0-D reference simulation. Noted with  $\Delta M_i$  the changes of a mineral  $M$  (in mass unit per  $\text{m}^3$  rock) at the time steps  $i = 1, \dots, N$  from the fully coupled simulations and with  $\Delta M_i^*$  the changes from the reference model (after translation of its time axis to match the arrival time of  $\text{CO}_2$  in the element), the similarity is defined as the average quadratic relative error over the time samples:

$$\text{Similarity} = \sqrt{\frac{1}{N} \sum_{i=1}^N \left( \frac{\Delta M_i - \Delta M_i^*}{\Delta M_i^*} \right)^2} \quad (14)$$

From such definition follows that the similarity is a positive function, equal to zero if the compared reactions are exactly the same, and taking higher values for increasing discrepancy. Similarities can be computed for each mineral separately or for one of their possible linear combinations. In the following we will concentrate on the most relevant linear combination for the purpose of this study, which is the *total amount of precipitating carbonates*.

The results confirm that indeed the hypothesis of self-similarity holds: in Fig. 8 are shown the histograms of the calculated similarities for each element of the fully coupled simulations reached by  $\text{CO}_2$  in the homogeneous and heterogeneous case respectively. For readability the histograms have been truncated to a value of 20 for the similarity function, which represents the 95th percentile in the homogeneous and the 99th percentile in the heterogeneous case. In both cases the vast majority of values are concentrated around 5 or less, with particularly small values – and thus high degree of similarity – for the heterogeneous simulations. Figures 6 and 7 display similarities of 4.5 and 52.26, respectively. Even for such a high value as in the latter case, the

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discrepancy of total amount of mineralized CO<sub>2</sub> in the element is around 10% at the end of the simulation time: in that particular case the delay in the mineralization of siderite and the temporary appearance of calcite explain such difference.

Figures 9 and 10 display the spatial distribution of the similarity function in the reservoir, for the homogeneous and heterogeneous cases. It appears that the best (lowest values of the similarity function, in blue) similarities are located, in both cases, in the external part of the CO<sub>2</sub> cloud, whereas the core part of the cloud shows lower degree of similarity. On one side this is due to the longer exposure time and hence duration of reactive chemistry in such portion of reservoir, which amplifies and propagates the discrepancies; on the other side, this is an indirect measure of the influence of hydrodynamic transport: it is in the central portion of the cloud that the brine flow is the highest and thus most perturbs the chemistry.

In summary, for at least 95% of the elements in which CO<sub>2</sub> mineralization occurs, the fully coupled simulations predict reactive chemistry which is qualitatively and quantitatively nearly identical to the reference 0-D simulation. The second major hypothesis for the application of the simplified coupling can be thus considered as verified.

### 4.3 Total mineralization

The next step is to evaluate the actual performance of the simplified coupling with respect to the outcome this method has been built for: the prediction of the total CO<sub>2</sub> mineralization in the reservoir.

This result is shown in Fig. 11, highlighting the influence of the choice of the threshold on the result.

The diagram confirms that indeed the results of the simplified coupling (the dotted and the dashed lines) are quite on par with the outcome of the full coupling (the solid lines) for both the homogeneous and heterogeneous cases. It is also apparent that the chosen threshold value has a significant impact on the predictions. For the simulations of this study the optimal concentration threshold, found by trial and error, is comprised between 0.0002 and 0.0005 in mass fraction. The evolution of the mineralization is

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nicely reproduced throughout the simulation time, with the exception of a slightly more significant deviation (in form of delay) in the first 500 simulation years for the homogeneous simulation and around 1000 years in the heterogeneous. After that, the simplified coupling approximates with excellent agreement the prediction of fully coupled simulations: under 3 % in terms of the total injected CO<sub>2</sub>.

Based on Fig. 11, a further consideration is possible, in particular from the observation of the heterogeneous case (the blue curves). As result from the enhanced spreading of the injected CO<sub>2</sub> and the heterogeneity in porosity, contributing to the speed of reactions, the mineralization is quite quick if compared with the homogeneous case, reaching a value of around 60 % of the injected CO<sub>2</sub> after 1700 years. Under these conditions, a further prolongation of the simulation cannot be justified: the discrepancy in spreading and migration of CO<sub>2</sub> as estimated by the non-reactive simulations, which are of course not accounting for the feedback of chemistry, will be obviously overestimated to an excessive degree, violating one of the hypotheses the simplified coupling is based on. Therefore, Fig. 11 is bounded on the *y* axis: the outcome of the comparison is not credible if the mineralization is too high.

The influence of the kinetics relative to the transport scenario was furthermore tested by replacing the chemical system considered until now with one with kinetic constants one order of magnitude smaller. The comparison procedure was repeated in an homogeneous case, running the new 0-D batch geochemical model and the fully coupled reactive transport, while the non-reactive simulations are the same as in the previous case. The considered simulation time for this case is 10 000 years. The outcome in terms of total mineralization is shown in Fig. 12.

Here one would expect that the slower kinetics would produce lower mineralization, and thus that the difference between reactive and non-reactive simulations would be reduced; overall, a better agreement between full coupling and simplified coupling would be anticipated. However, surprisingly, the discrepancy between the two approaches proved to be larger. Only a very small concentration threshold allow to match the predictions of the full coupling with the same precision of the case of faster kinetics. The

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explanation of this result is the decrease in self-similarity of reactions: in other words, for slower kinetics the relative importance of hydrodynamic transport of solutes becomes more relevant, and thus one single geochemical model is less capable of representing the reactions in all elements of the spatial discretization. A faster kinetics would reinforce the hypothesis that only the presence of  $\text{CO}_2$  in the element drives the chemistry, reducing the relative importance of hydrodynamic transport. In this case it is more likely to experience more severe errors in the mass balance for the injected  $\text{CO}_2$ , which would also limit the applicability of simplified coupling approach.

In summary, the simplified coupling achieves an estimation of the total amount of mineralization which is in excellent agreement with the fully coupled simulations if an optimal value for the threshold is employed.

## 5 Discussion and conclusion

### 5.1 The optimal choice for the threshold

A threshold value for the minimum dissolved  $\text{CO}_2$  concentration considered “active” has been defined to filter out the overestimation of reservoir volume exposed to  $\text{CO}_2$  (in both a spatial and a temporal sense) which comes from the non-reactive simulations. If too large, its choice can lead to severe underestimation, if too small, to severe overestimation of the total mineralization.

In a real application for the simplified coupling such optimal value is of course a priori unknown, since no fully coupled simulations are available. The strategy to determine realistic values – or at least to define a realistic *bandwidth* – is always dependent on the investigated problem, and only guidelines can be outlined here.

A first consideration regards the proportion of elements exposed to dissolved  $\text{CO}_2$  in the simulations. In a typical storage system in saline aquifers, the reservoir volume exposed exclusively to dissolved  $\text{CO}_2$  can be much larger, in the time frame for which chemical reactions are relevant, than that exposed to gaseous  $\text{CO}_2$  (Kempka and Kühn,

2013). However, the simulated concentration of dissolved  $\text{CO}_2$  is often quite small, particularly at the front of the  $\text{CO}_2$  plume.

Coarse spatial discretizations resulting in elements with very large volumes may induce an overestimation of the spatial extent of dissolved  $\text{CO}_2$ . In fact, most simulators allow the existence of gaseous  $\text{CO}_2$  in a separate, dense phase only if the dissolved  $\text{CO}_2$  exceeds the saturation limit in the formation water in that element. Therefore, in particular in presence of large volume elements, and particularly at the border of the  $\text{CO}_2$  plume, the presence (and hence propagation) of dissolved  $\text{CO}_2$  is favored with respect to the gaseous phase, ending up in overestimating the total dissolved  $\text{CO}_2$ . Very small calculated concentrations of dissolved  $\text{CO}_2$  propagate to adjacent elements to an extent which is not completely physical. Numerical dispersion may contribute to this effect. Notably, all these issues become more relevant for increasing coarseness of the simulation grid. Therefore, it can be expected that the fine hydrodynamic grids the simplified coupling is designed to be applied on should be far less sensitive to the threshold than the coarse model used in the present study for validation.

One-dimensional tests not showed in the present work support this hypothesis: through grid refinement not only the choice of threshold became less significant, but also the optimal threshold value was increased in the finer grids. Future work is however needed to thoroughly assess this aspect. Another interesting option to explore in future work is the definition of a time-dependent threshold, and in particular increasing along the progress of simulations.

A computational way to determine the optimal threshold is represented by the setup of 1-D or 2-D models mimicing the typical element dimension found in the full 3-D grid, the typical exposure time to  $\text{CO}_2$ , and of course the same chemistry as in the original model.

## 5.2 Applications and future work

The simplified coupling has been developed to apply reactive chemistry on structurally complex, fine resolved, million-element grids routinely used in pure hydrodynamic

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reservoir simulations, with no need to meet compromises such as the number of elements and the spatial heterogeneity described in the models.

This approach frees the reactive transport modelling from the limitations which hamper many of its real life applications. It applies to hydrodynamic reservoir models, which are usually well matched, without grid upscaling and therefore profiting of the best possible description of heterogeneity. This also includes boundary conditions and transitory regimes (think about injection rate of CO<sub>2</sub> and its consequences on reservoir pressure), which are problematic to depict using oversimplified grids. The price for this ability – if all the hypotheses are met, which is usually the case in CO<sub>2</sub> storage systems – is not a computational or numerical burden, but an approximation of the total outcome of reactive chemistry, determined as bandwidth following the uncertainty of only one parameter: the concentration threshold.

Kempka et al. (2014) presents the application of the simplified coupling in the form described in the present work to a real-life scenario concerning the Ketzin pilot site. The simulation grid used for the hydrodynamic model amounts to 648 420 elements and the simulation time reaches 16 000 years; it would have been impossible to achieve these results with the currently available fully coupled reactive transport simulators.

The storage in saline aquifer is actually an unfavorable case given its hydrodynamical complexity; much easier would be the case of CO<sub>2</sub> storage in depleted gas reservoirs, where the water phase is present only in limited amount or residual saturations (Audi-gane et al., 2009; De Lucia et al., 2012). In such cases the hypothesis of self-similarity of reactions will be met to an even better extent, since the solute transport in the formation brine will be quite reduced, if present at all.

The simplified approach is not limited to CO<sub>2</sub> or gas storage, but can be employed wherever its underlying assumptions are respected, and notably where the reactions are initiated or controlled by the arrival time or presence of a limited number of solute species. In this sense the presented method can be truly considered as an alternative to fully coupled reactive transport simulations and not the simplification of one particular CO<sub>2</sub> storage model.

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A crucial application of the method is furthermore the ability to perform *sensitivity and uncertainty analysis* of the underlying components: both the hydrodynamic and the geochemical model. The advantage is of course represented by the separation of the processes, which can be therefore efficiently simulated on their own, and quickly “reassembled” in the post-processing approach, without the computational burden of fully coupled simulations.

Finally, a combination of full coupling and simplified one-way coupling can be used for speeding up reactive transport simulations. Namely, in the framework of sequential coupling, in which at each time step first hydrodynamics is calculated on the simulation grid, and afterwards chemistry on each grid element, one could imagine to substitute such expensive calculation of chemistry by scaling one single batch model as proposed in the simplified one-way approach. This would ensure consistency between CO<sub>2</sub> available for transport and mineralized, eliminating the major uncertainty connected to the application of the simplified approach in “post processing mode”. Also some other ideas presented in the present work could lead to improvements or further computational speedups. In particular the check for self-similarity of reactions could be applied in heterogeneous settings in order to identify a reduced number of reaction paths that need to be actually included in the reactive transport simulations, much in a sense of the reduction of complexity of the chemical system discussed by De Lucia and Kühn (2013) or Hellevang et al. (2013).

## 6 Conclusions

The simplified one-way coupling introduced by Klein et al. (2013) has been validated by means of comparison with fully coupled reactive transport simulations in a typical CO<sub>2</sub> underground storage setting in a saline aquifer, exploring one homogeneous and one heterogeneous case in terms of porosity and permeability. It was demonstrated that for such case studies the chemical reactions in each element of the simulation grid are with good approximation self-similar, which means on one side that one single

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0-D geochemical model can be used as proxy for the reactions occurring in all elements of the simulation grid, and on the other side that the hydrodynamic transport of solutes plays a secondary role in comparison to the presence or not of the injected CO<sub>2</sub>, which is the true driving force of the chemical reactions. The choice of a *threshold value* for dissolved CO<sub>2</sub> considered geochemically active governs the convergence of the one-way coupling with the fully coupled simulations. This is particularly true for the given case study in which the migration of and exposure to dissolved CO<sub>2</sub> represents the single most significant discrepancy between the non-reactive and the fully coupled simulations. For the considered case studies an optimal mass fraction concentration of around 0.0005 was found to ensure the best matching of the outcome of the fully coupled simulations. Since in a real application this parameter is a priori unknown, the outcome of the simplified coupling has to be determined rather as *bandwidth*, for example by means of 1-D or 2-D simulations. However, given the advantage of performing coupled simulations on finely discretized grids with no simplifications and upscaling of heterogeneous features of the reservoirs, the uncertainty due to the simplified coupling appears justified. Furthermore, removing the computational burden for reactive transport simulations makes the simplified approach particularly adapted to sensitivity analyses, which are much needed given the uncertainty inherent to geochemical modelling.

**Code availability**

The analyses and methods outlined in this study are significant, in the opinion of the authors, rather from a methodological point of view than for their implementation, which is actually quite trivial and can be achieved using many different tools and programming environments. However, the R scripts (R Core Team, 2014) and the simulations needed to reproduce at least part of the presented results can be obtained directly contacting the corresponding author.

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**Table 1.** Initial brine composition.

Ion	Concentration [mola]
$\text{AlO}_2^-$	$1.20 \times 10^{-8}$
$\text{Ca}^{+2}$	$5.67 \times 10^{-2}$
$\text{Cl}^-$	4.34
$\text{Fe}^{+2}$	$1.05 \times 10^{-4}$
$\text{HCO}_3^-$	$9.65 \times 10^{-4}$
$\text{K}^+$	$1.03 \times 10^{-2}$
$\text{Mg}^{+2}$	$4.06 \times 10^{-2}$
$\text{Na}^+$	4.19
$\text{SiO}_2$	$1.28 \times 10^{-4}$
$\text{SO}_4^{-2}$	$4.49 \times 10^{-2}$
pH	6.6
temperature	$35^\circ\text{C}$



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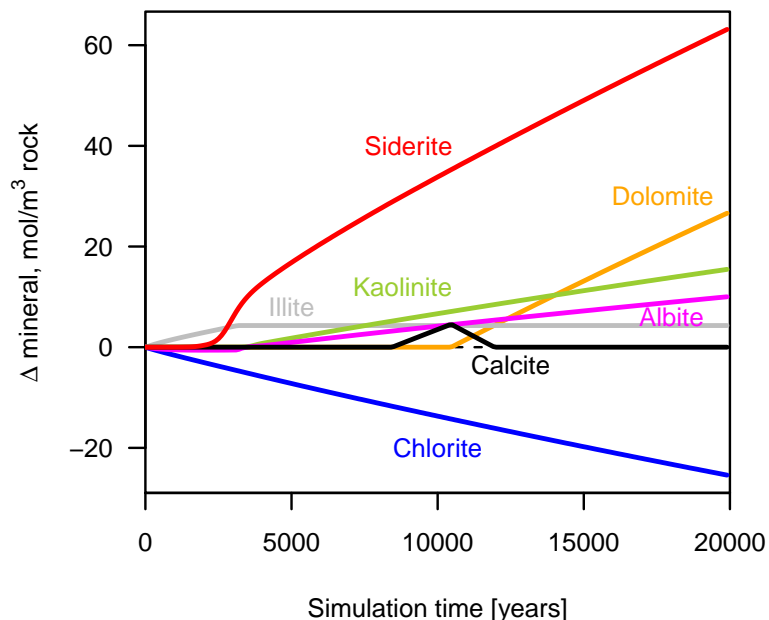
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**Table 2.** Minerals included in the model.

Mineral	Volume fraction	Specific area [cm <sup>2</sup> g <sup>-1</sup> ]
Primary		
anhydrite	0.05	at equilibrium
albite	0.1	1.13
hematite	0.01	1.13
illite	0.03	11.3
chlorite	0.05	11.3
Secondary		
calcite	not applicable	at equilibrium
dolomite	not applicable	at equilibrium
kaolinite	0.0	11.3
magnesite	0.0	1.13
siderite	0.0	1.13

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**Figure 1.** The reference geochemical model, scaled for initial porosity  $\phi = 0.5$  and initial water saturation  $S_w = 0.5$ . Siderite (red) and dolomite (orange) are the main precipitating carbonate phases contributing to mineral trapping; calcite (black) is predicted to appear only transiently. Kaolinite (green), illite (grey) and albite (magenta) also precipitates. The newly formed phases are compensated by dissolution of anhydrite cement (not shown) and of chlorite (blue). In terms of porosity changes these reactions can be safely considered negligible in the considered time frame.

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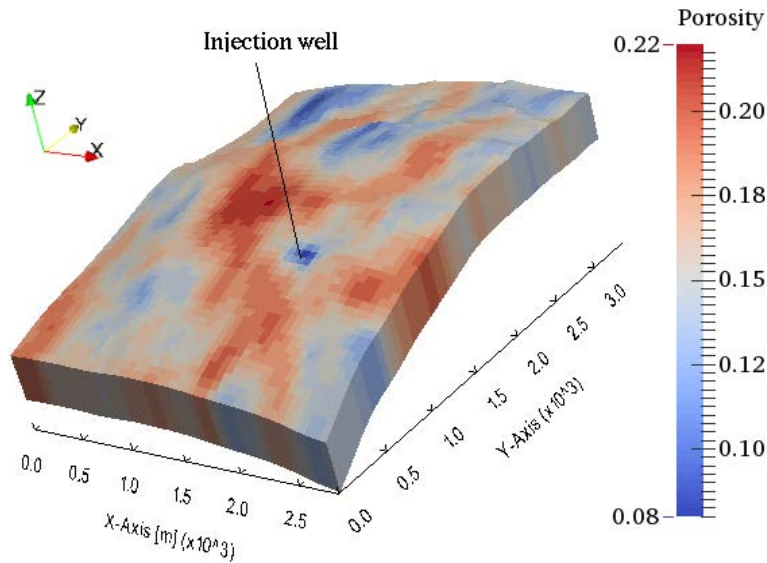
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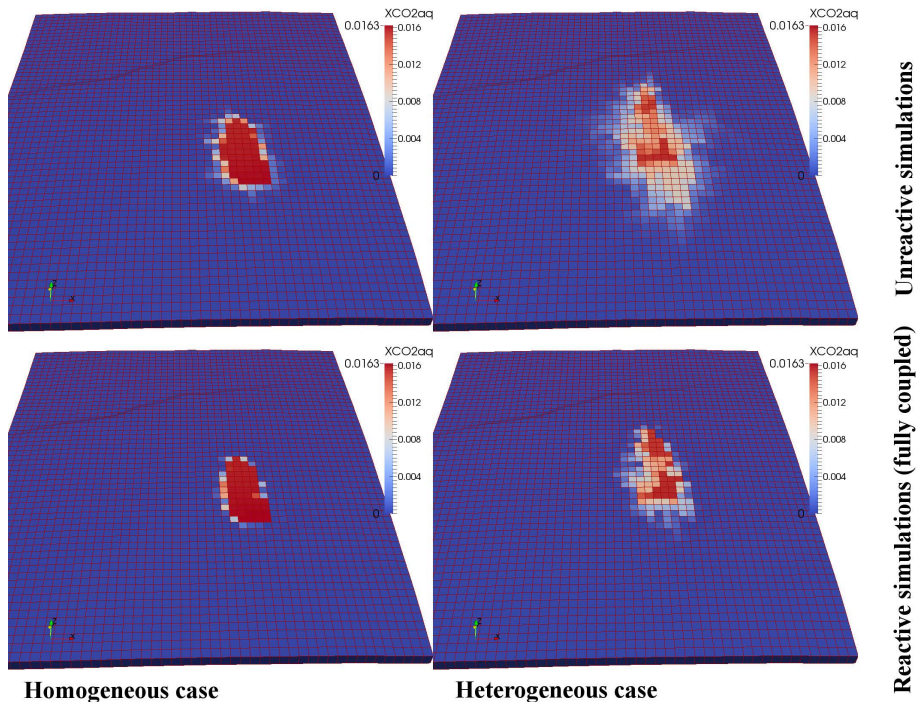
**Figure 2.** The spatial discretization of the near-field Ketzin anticline used for the reactive transport model (Northing direction is along the y axis). It comprises 2950 elements in one single layer, but with a 3-D structure following the topography of the target formation (magnified 5 times in the z direction). Here is depicted the heterogeneous distribution of porosity, derived from the upscaled Ketzin geological model.

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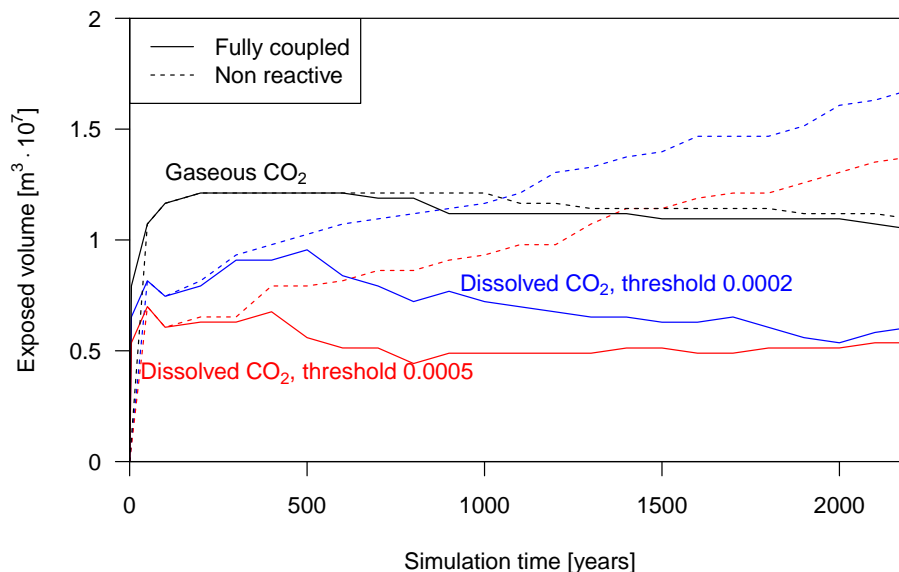




**Figure 3.** Spreading of dissolved  $\text{CO}_2$  in terms of aqueous mass fraction (“XCO2aq”) after 2100 years. Compared are the homogeneous (left column) and heterogeneous (right column) cases; first row shows the non-reactive and second row the reactive simulations (full coupling). At this simulation time there is a significant difference between the reservoir volume affected by dissolved  $\text{CO}_2$  depending on whether or not chemistry is included in the simulation. Since the simplified coupling makes use of non-reactive simulations to estimate the exposure time of each element, this discrepancy will impact its outcome. However, this effect is mitigated by the introduction of a *threshold* filtering out small concentrations of aqueous  $\text{CO}_2$  as *geochemically inactive* (see text for further details).

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**Figure 4.** Homogeneous simulations: reservoir volume exposed to CO<sub>2</sub> distinguishing between elements exposed to gaseous phase (black lines) and to dissolved CO<sub>2</sub> only (red, blue following the threshold for the minimum considered concentration in terms of mass fraction).

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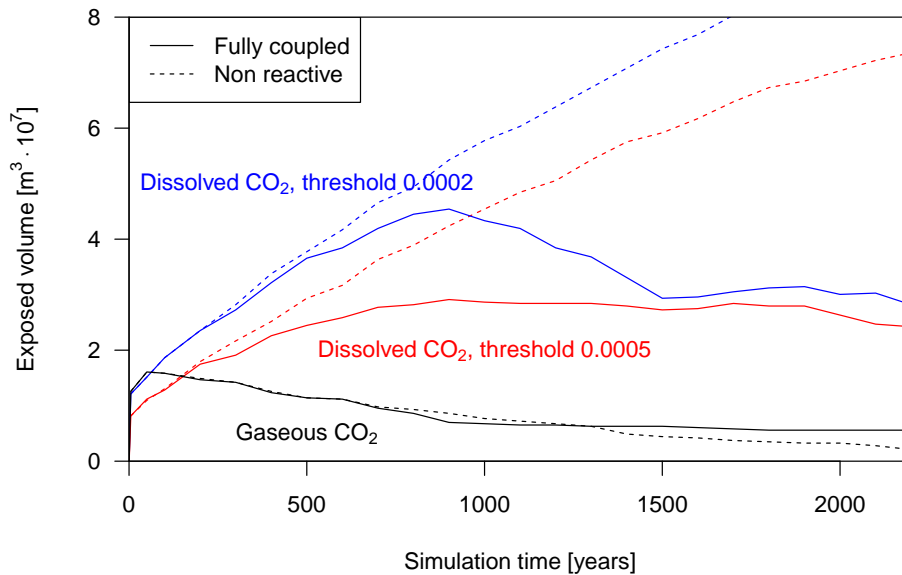
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**Figure 5.** *Heterogeneous* simulations: reservoir volume exposed to gaseous and dissolved CO<sub>2</sub>.

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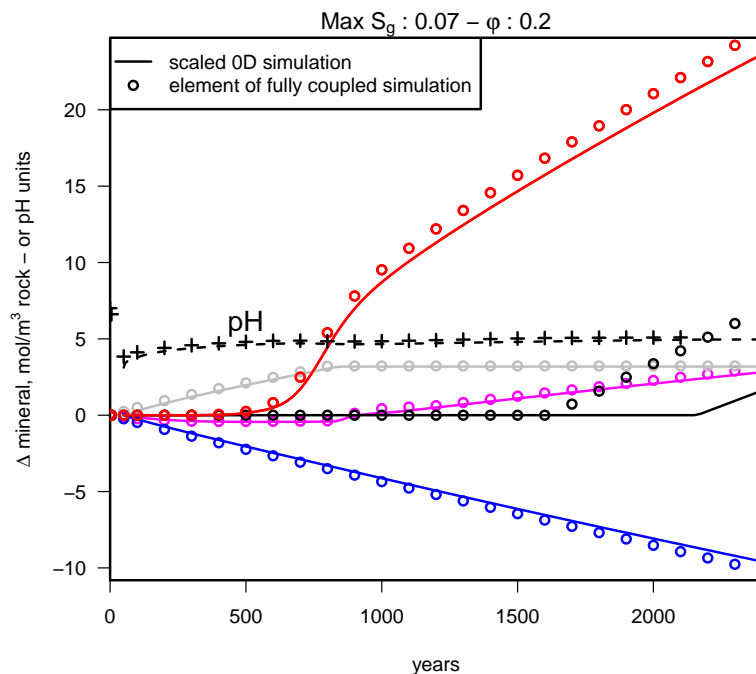
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**Figure 6.** Comparison between the mineral changes predicted by the fully coupled simulations in one single element as opposed to the outcome of the scaled 0-D reference geochemical model. Depicted, with the same colours of Fig. 1, are siderite (red), albite (blue), chlorite (magenta) and calcite (black). For completeness also the pH in the two cases is represented (dashed line for the scaled batch and the cross symbols for the fully coupled simulation). The calculated similarity function for this element is 4.5.

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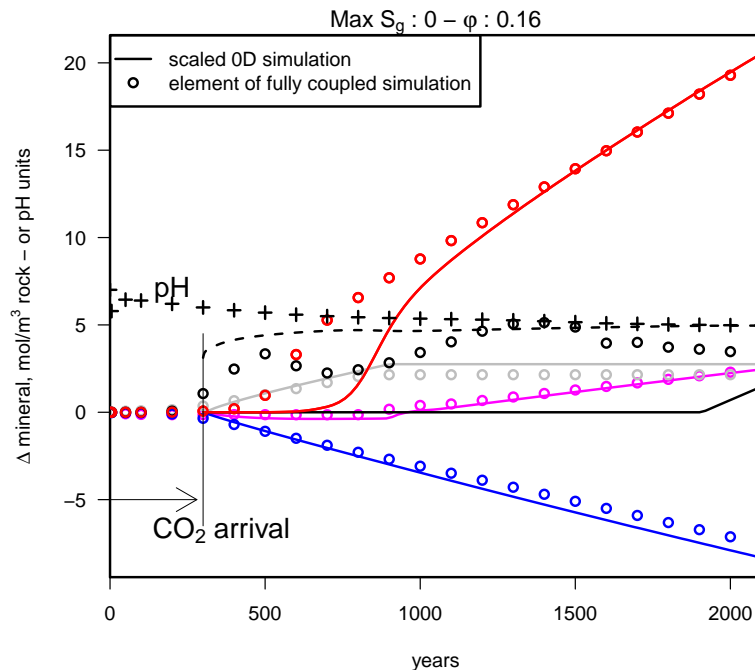
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**Figure 7.** Comparison between the mineral changes in one element of the heterogeneous case with weak similarity (52.26). This element has been only exposed to dissolved CO<sub>2</sub>. Even with such high value of the similarity function, the difference between the precipitated carbonates at the end of simulation time is below 10%.

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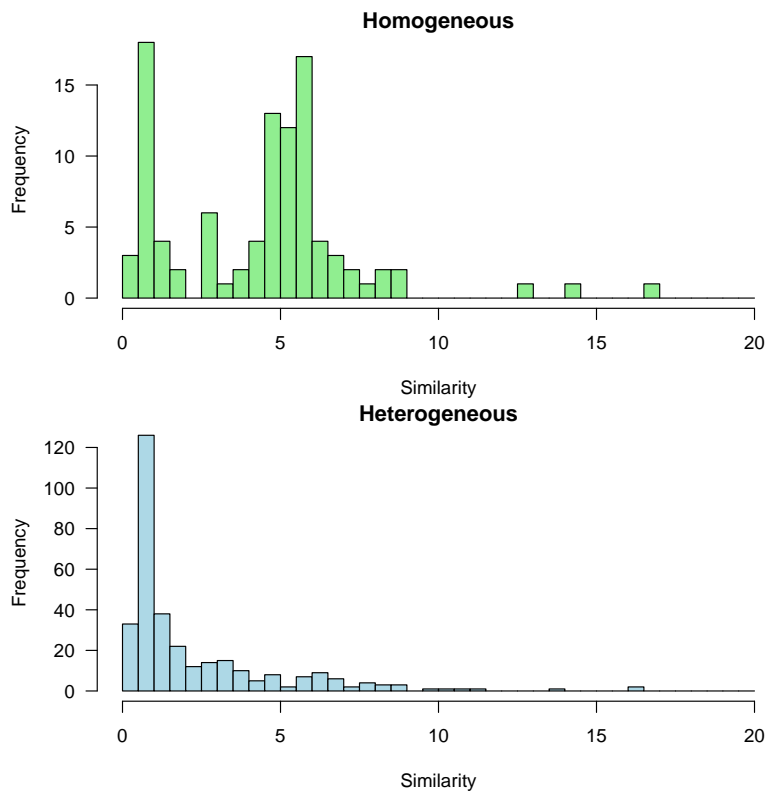
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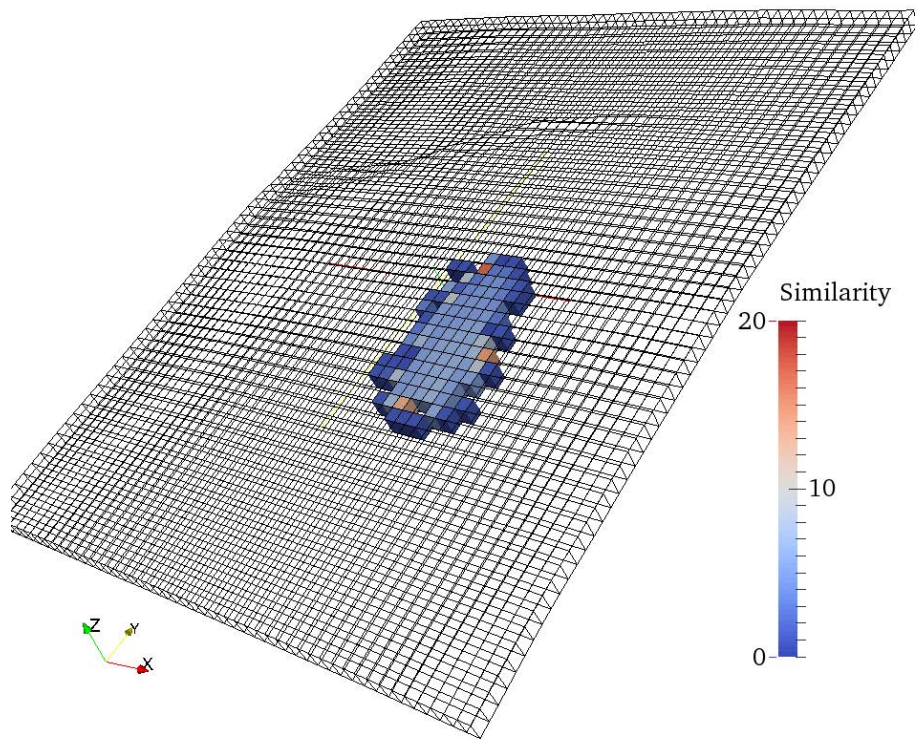






**Figure 8.** Histogram of similarities of total carbonate mineralization in the homogeneous and heterogeneous cases.

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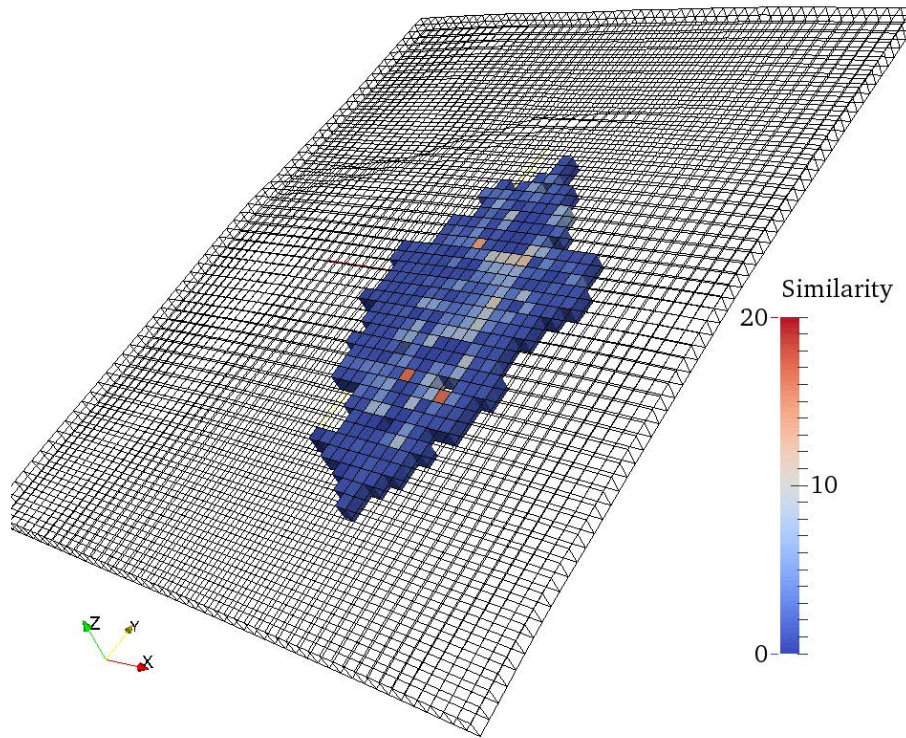
**Figure 9.** Spatial distribution of the *self similarity* (cfr. text for definition) of chemical reactions relative to total carbonate mineralization for the fully coupled reactive transport simulations in the *homogeneous* case.

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**Figure 10.** Spatial distribution of the *self similarity* for the *heterogeneous* case.

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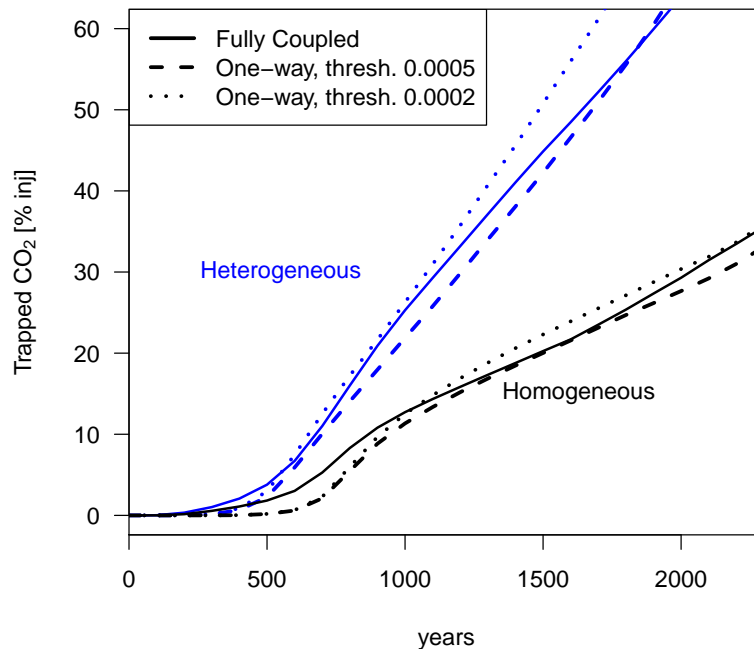
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**Figure 11.** Total carbonate mineralization in reservoir: comparison between full and simplified coupling. Influence of the choice of threshold value for dissolved  $\text{CO}_2$  considered “active” for the coupling in the homogeneous and heterogeneous cases.

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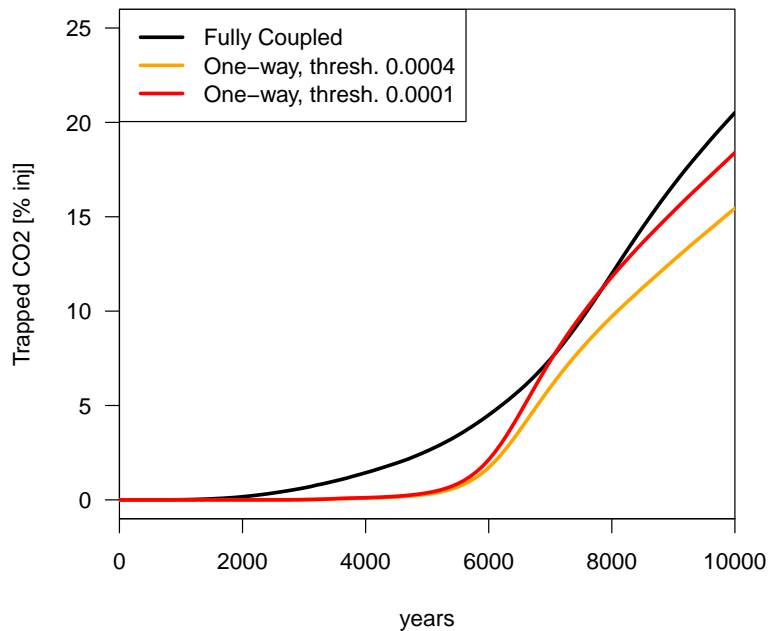
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**Figure 12.** Influence of the threshold in case of slower kinetics, homogeneous case.

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