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CO$_2$-brine-mineral interfacial reactions coupled with fluid phase flow

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Abstract

Due to their widespread occurrence and large capacities, deep geological saline formations are regarded as an important storage option for anthropogenic CO$_2$. Injection of supercritical CO$_2$ into such a formation will result in a multi-phase flow porous media system. Both the CO$_2$ and brine phase compositions are influenced by multiphase flow and mass transport processes as well as by interfacial reactions (gas dissolution, water vaporization, mineral dissolution and precipitation). For a model based assessment of CO$_2$ storage, most simulation codes apply an operator-splitting approach to solve the coupled problem, where multi-phase flow and geochemical reactions are handled by separate routines sequentially. This approach relies on two approximations: (I) the dissolution of CO$_2$ in the brine, which is usually quantified by the multiphase flow routine by using an equation of state approach, is treated as instantaneous, and (II) the amount of CO$_2$ consumed during geochemical reactions quantified by the reaction routine is small compared to the amount dissolved, as during geochemical reactions CO$_2$ is not resupplied from the CO$_2$ phase by dissolution.

To investigate these two approximations, the multiphase flow and multi-component reactive transport simulator OpenGeoSys was extended and now allows to simulate mineral-brine as well as the brine-CO$_2$ interface reactions either kinetically controlled or by using an equilibrium approach, and to account for the presence of a CO$_2$ phase during brine-mineral reactions. The code is used here to investigate a simple gas-liquid-solid phase (CO$_2$-H$_2$O-CaCO$_3$) system controlled by fast reaction rates. Batch reaction calculations are performed for the multiphase system at various temperature and pressure conditions for different initial CO$_2$ saturations. Two methods of approximating the equilibrium state of the system by an operator splitting approach are compared. The first method determines the gas-liquid and solid-liquid equilibria in separate subsequent steps. At reservoir conditions relevant for storage of CO$_2$ (323 K, 100 bar) and for high CO$_2$ saturations the error in predicted CO$_2$ concentrations in the liquid phase reaches up to -2 %. This error can be reduced to less than -0.5 % by the second method, where a conjoint gas-liquid-solid equilibrium is accounted for in the reaction calculations. Accordingly, the latter approach should preferably be employed in multiphase flow reactive transport modeling based on operator splitting techniques.

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1. Introduction

CO$_2$ capture and storage is discussed as a means of reducing emissions of anthropogenic CO$_2$ to the atmosphere and thereby to reduce its impact on global climate change. Especially deep saline formations are regarded as an important storage option due to their widespread occurrence and large capacities. Injection of CO$_2$ into such a formation will influence the hydraulic, mechanic and geochemical conditions in the injection formation and adjacent geological layers [1-3]. A prognosis of the induced changes is required when forecasting storage mechanisms and estimating storage capacities and efficiencies.

When CO$_2$ is injected into a storage formation, the phase composition will change locally. A large fraction of the CO$_2$ will accumulate as a supercritical fluid phase. Such CO$_2$ together with the original formation brine and the porous rock matrix will generate two new phase interfaces, the gas-liquid interface and the gas-solid interface. Generally, geochemical interactions will occur at all three phase interfaces. Across the CO$_2$-brine interface, gas-liquid two-phase reactions result in dissolution of CO$_2$ into water and dissolution of H$_2$O into the CO$_2$ phase. Mineral-brine interfacial reactions lead to mineral dissolution or precipitation. As the gas-solid interaction is only weak [4], it is usually ignored in reactive transport modeling. Consequently, in this study we consider only gas-liquid and solid-liquid interactions.

Both the CO$_2$ and brine phase compositions are influenced by multiphase flow and mass transport processes as well as by the interfacial reactions. Typically, an operator-splitting approach is used in simulation codes, where multi-phase flow, transport and geochemical reactions are handled by separate routines sequentially. Thus the dissolution of CO$_2$ in brine is simulated within the multi-phase flow routines using an equation of state for the CO$_2$-brine system, while the brine-mineral reactions are simulated within geochemical reaction modules. This approach is implicitly based on two approximations: Firstly, the dissolution of CO$_2$ in the formation brine is treated as instantaneous and can be described by an equation of state approach. Secondly, the amount of CO$_2$ consumed during geochemical reactions is small compared to the amount dissolved, as during geochemical reactions CO$_2$ is not re-supplied from the CO$_2$ phase by dissolution.

To investigate consequences of these two approximations for predictions of CO$_2$ storage in geochemical reservoirs, the multiphase flow and multi-component reactive transport simulator OpenGeoSys (OGS) was extended for the respective process models and now allows to simulate both the mineral-brine as well as the brine-CO$_2$ interface reactions either kinetically controlled or by using an equilibrium approach. Also, the presence of a CO$_2$ phase is accounted for during brine-mineral reactions. The two above mentioned approximations are investigated for their effects using a simple system containing only calcite as a typical mineral controlled by fast reaction rates, as well as brine and CO$_2$. This assessment is carried out under different temperature pressure and CO$_2$ saturation conditions, to account for the variability in geological situations relevant for storage of CO$_2$.

2. Quantification of chemical equilibrium between gas, liquid and solid phases

The high fluid pressures in deep geological storage formations promote the dissolution of CO$_2$ (reaction 1). Dissolved CO$_2$ generates HCO$_3^-$ and H$^+$ (reaction 2), resulting in increased acidity of the aqueous solution. Once the corresponding gas (or rather vapor)-liquid equilibrium (VLE) is reached, the solution maintains a certain level of acidity and pH value. Due to the change of the solution composition, however, the liquid-solid equilibrium (SLE) valid prior to the injection of CO$_2$ will be perturbed, forcing

carbonate minerals to dissolve, and the acidity of the aqueous solution to decrease. This in turn affects the previously established VLE, resulting in the dissolution of more CO_2. The composition of the liquid phase at this time hence is no longer consistent with the composition at the former VLE state. Accordingly, if VLE and SLE are quantified in separate steps, the predicted system states are possibly not representative of the true system composition and an iterative multi-step approximation may be required to achieve a sufficient accuracy in reactive transport simulations.

$$CO_{2,gas} \longleftrightarrow CO_{2,aq} \qquad\qquad 1$$

$$CO_{2,aq} + H_2O \longleftrightarrow HCO_3^- + H^+ \qquad\qquad 2$$

This situation is exemplified by the data presented in Table 1. For the two contrasting cases of CO_2 under saturation or oversaturation in the liquid phase of a CO_2-H_2O-$CaCO_3$ system, a two-steps method (VLE followed by SLE) for calculating the system state was applied, respectively, employing both, the geochemical simulator ChemApp [5] or the Duan and Li [6,7] model. These calculations were compared against conjointly quantified gas-liquid-solid-equilibria (VLSE) for the two cases, also using both models. For the two-steps method a slight underestimation of total inorganic carbon (TIC) in the liquid phase was found, when ChemApp was used, while in case of the Duan and Li model a slight overestimation of TIC was found in comparison to the conjoint VLSE calculations.

Table 1. composition of a hypothetical CO_2-water-calcite system quantified by a two steps chemical reaction (VLE followed by SLE) and full chemical reaction (VLSE) calculations at conditions of 323.15K and 100bar, using ChemApp and the Duan and Li [6,7] model for the cases of CO_2 undersaturation and CO_2 oversaturation

	phases	compo-sition	initial amount	two steps method[(CA)]		two steps method[(DL)]		after VLSE [(CA)]	after VLSE [(DL)]
				after VLE	after SLE	after VLE	after SLE		
CO_2 under saturation	gas	CO_2	4	3.243	3.243	3.868	3.868	3.219	3.879
	liquid	CO_2	1	1.757	1.783 [TIC]	1.132	1.159 [TIC]	1.807 [TIC]	1.148 [TIC]
	solid	$CaCO_3$	1	1.0	0.9742	1.0	0.9728	0.9741	0.9728
CO_2 over-saturation	gas	CO_2	5	5.243	5.243	5.868	5.868	5.219	5.879
	liquid	CO2	2	1.757	1.783 [TIC]	1.132	1.159 [TIC]	1.807 [TIC]	1.148 [TIC]
	solid	CaCO3	1	1.0	0.9742	1.0	0.9728	0.9741	0.9728

note: TIC = total inorganic carbon, CA = ChemApp, DL = Duan and Li model; all concentrations in mol/kg liquid water,.

3. Chemical reactions in coupled simulations

OpenGeoSys (OGS) is a code for numerical simulation of thermo-hydro-mechanical-chemical (THMC) processes in porous media [8] and has been applied for multiphase flow and reactive transport problems in different CO_2 storage applications [9-12]. OGS uses a sequential non-iterative approach for operator-splitting to couple the different processes acting in a reservoir (see Fig 1). In each time step of the simulation period, a process loop is executed, where different process modules are used to quantify the changes in system state variables sequentially.

Multiphase flow can be treated as the movement of two non-mutually-dissolved fluid phases, i.e. the simulation of the fluid state does not incorporate a fluid phase equilibration (VLE) and either the two-steps method (VLE followed by SLE) or a conjoint VLSE calculation is included in the reaction

calculation exclusively (Fig 2, methods 1 and 2). As fluid flow may be influenced by the phase exchange via saturation, density and viscosity changes, this approach here is not further considered. Instead, the multiphase flow process includes the mutual dissolution of the two fluid phases, i.e. a calculation of the VLE is included during the flow simulation, followed either by SLE or a conjoint VLSE in the reaction calculation (Fig 2, methods 3 and 4).
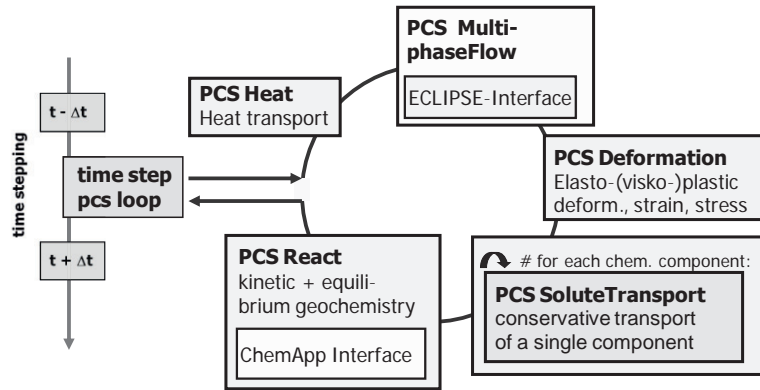

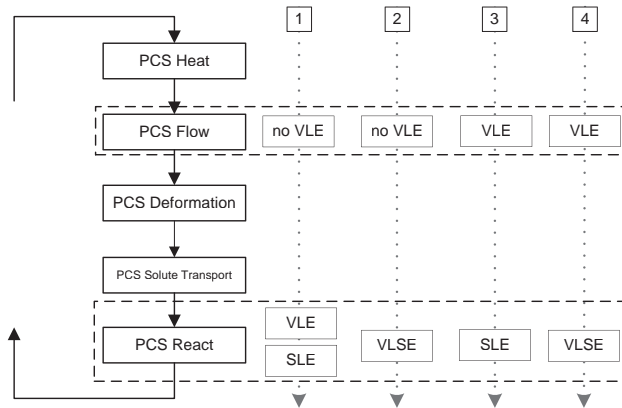Fig. 1. Process coupling in OpenGeoSys by operator splitting (modified from Beyer et al., 2012)

Fig. 2. Different approaches for incorporating gas-liquid equilibriation (VLE) and solid-liquid-equilibration (SLE) in coupled multiphase flow and reactive transport simulations. Methods 1 and 2 do not account for VLE in the flow step, and include VLE and SLE as a two-steps procedure, where where the gas-liquid and solid-liquid reactions are calculated separately (method 1), or by a conjoint VLSE calculation (method 2) in the reaction step,. Methods 3 and 4 include the VLE during the flow step and quantify only the SLE (method 3) or the conjoint VLSE in the reaction step (method 4), respectively.

The latter two approaches (i.e. methods 3 and 4 of Fig 2, denoted as VLE/SLE and VLSE from hereafter) are compared in this study for their impact on the simulation results. A simple batch reaction model which includes stagnant gas (CO_2) and water (H_2O) phases and a solid phase containing $CaCO_3$ is set up for this purpose. Although the fluid phases are stagnant in the batch model, the Eclipse simulator, which is coupled to OGS [10], is used here to quantify the VLE in the multiphase "flow" step. Chemical

reactions are quantified by ChemApp, which also is coupled to OGS [9]. Deformation of the porous medium, heat and solute (component) transport processes are not included in the simulation. Temperature, pressure and CO_2 saturation conditions considered in a set of different scenario calculations are summarized in Table 2.

Table 2. selected conditions for batch reaction simulations

Temperature [K]	298.15	323.15	348.15	363.15					
Pressure [bar]	20	50	100	150	200				
CO_2 Saturation [-]	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

For a batch system, since there is no change in external conditions, after the first reaction step, the system should arrive at the geochemical equilibrium, if all reactions are assumed as fast (i.e. equilibrium) reactions. Hence, after the second reaction step, the state of the system should not change again, if the representation of VLE and SLE in the model is accurate. However, due to the nature of the operator-splitting, there will be a certain deviation between the system states of the two reaction steps, and the second step of the simulation can also be understood as a correction step of the first equilibration calculation in the batch system. After a third reaction step, the system changes are almost negligible, therefore here the comparisons were made between the results of the first two reaction steps of the simulation. As one of basic properties of the system, the CO_2 concentration in the aqueous solution between both reaction steps was selected here to evaluate deviations in the system under the various conditions. This deviation can be regarded as a measure of error to expect from operator-splitting. As mentioned above, the two methods, VLE/SLE and conjoint VLSE (methods 3 and 4 in Fig 2) were employed for this analysis, and the results for the different combinations of CO_2 saturation, pressure and temperature are shown in Fig 3a (VLE/SVE) and 3b (VLSE), where the left panels show absolute deviations (horizontal bars) between first and second reaction step (hollow points attached to the respective bars) in units of mol/m³ and the right panels show the corresponding relative deviations in %. Approximate values can be derived from the figure based on the scaled legend in each diagram.

It can be seen, that under all of the various conditions, the deviation is always negative, i.e. using both methods, the CO_2 solubility predicted by the simulation in a single VLE/SLE or VLSE step is smaller than that of the actual true system state. Accordingly, the CO_2 dissolution process tends to be underestimated in operator splitting. As can be seen by comparison of individual scenario results between Fig 3a and Fig 3b, using the VLSE method of full geochemical equilibration in the reaction quantification, the deviation between first and second reaction steps is significantly reduced.

The deviation of CO_2 concentrations between first and second reaction steps reflects the accuracy of the coupled simulation program. When this deviation is small enough, it can be neglected during a long-term simulation. This is the basic assumption in any operator-splitting approach. Under certain conditions, however, the deviation may increase and accumulate, which may have a significant impact on the final simulation results. At a temperature of 323.15K and a pressure between 100 to 200 bars, which are the most probable conditions for geological storage of CO_2, the VLE/SVE method has a deviation of more than -20 mol/m^3 in the dissolved CO_2 concentration and the relative deviation is about -2%. However, using the VLSE approach, the deviation can be reduced to less than -5 mol/m^3 (or -0.5% relative deviation). Table 3 summarizes the quantitative results of this comparison at reservoir conditions of 323.15K, 100 bar and an initial gas saturation of 0.7 as an example.
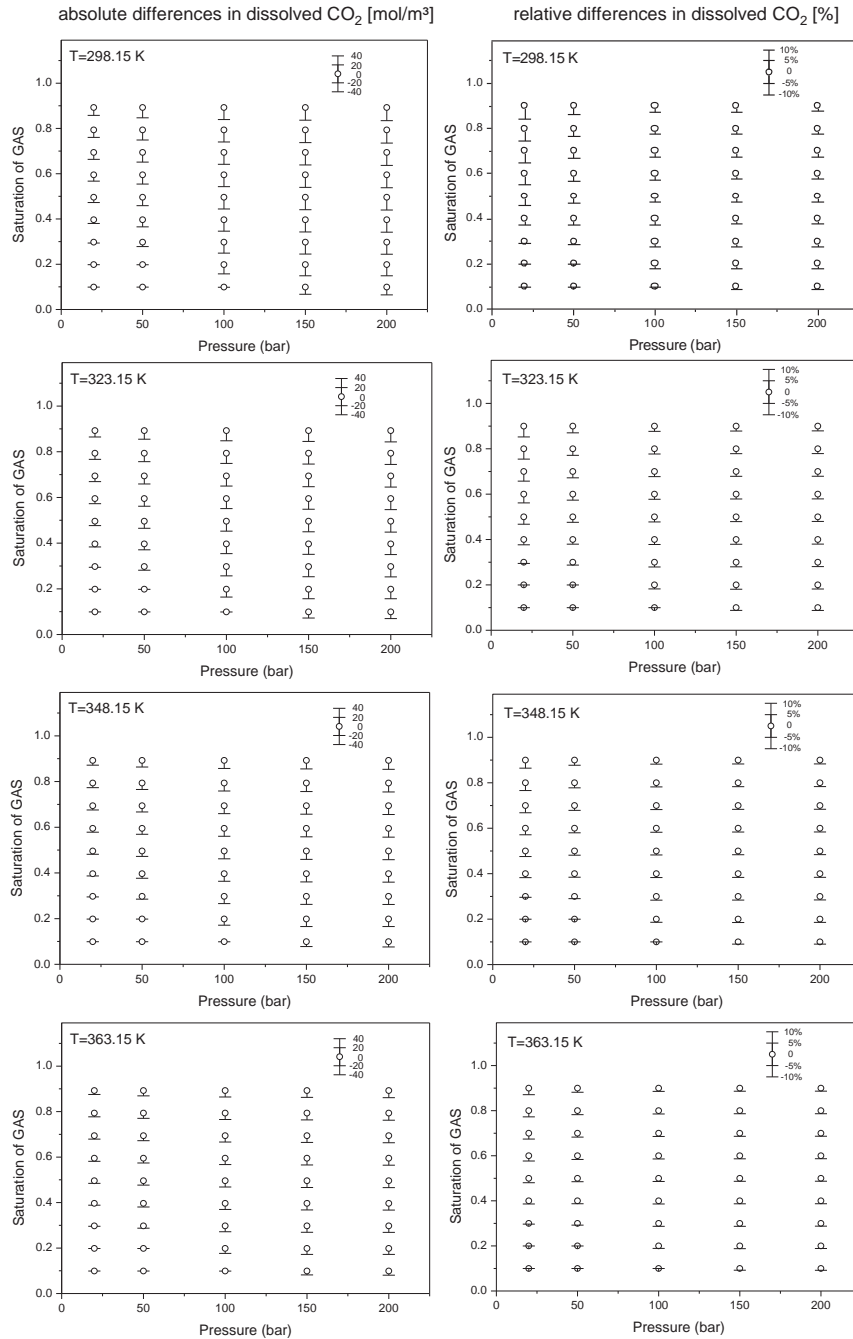
Fig. 3a. Evaluation of batch modeling results using the VLE/SLE method for different initial pressure, temperature and CO_2 (gas) saturation conditions (see Table 2): Shown are the differences in CO_2 concentrations dissolved in water between a single VLE/SLE reaction step (small horizontal bars) and actual equilibrium CO_2 concentration (hollow points connected to the bars) determined by a correction step of batch equilibrium reaction calculations. The left panel shows the absolute values of the deviation units of mol/m^3, while the right panel shows relative differences in %. Respective values can be derived directly based on the scaled legend in the diagrams. (Fig 3b. with results for the VLSE method is continued on next page.)
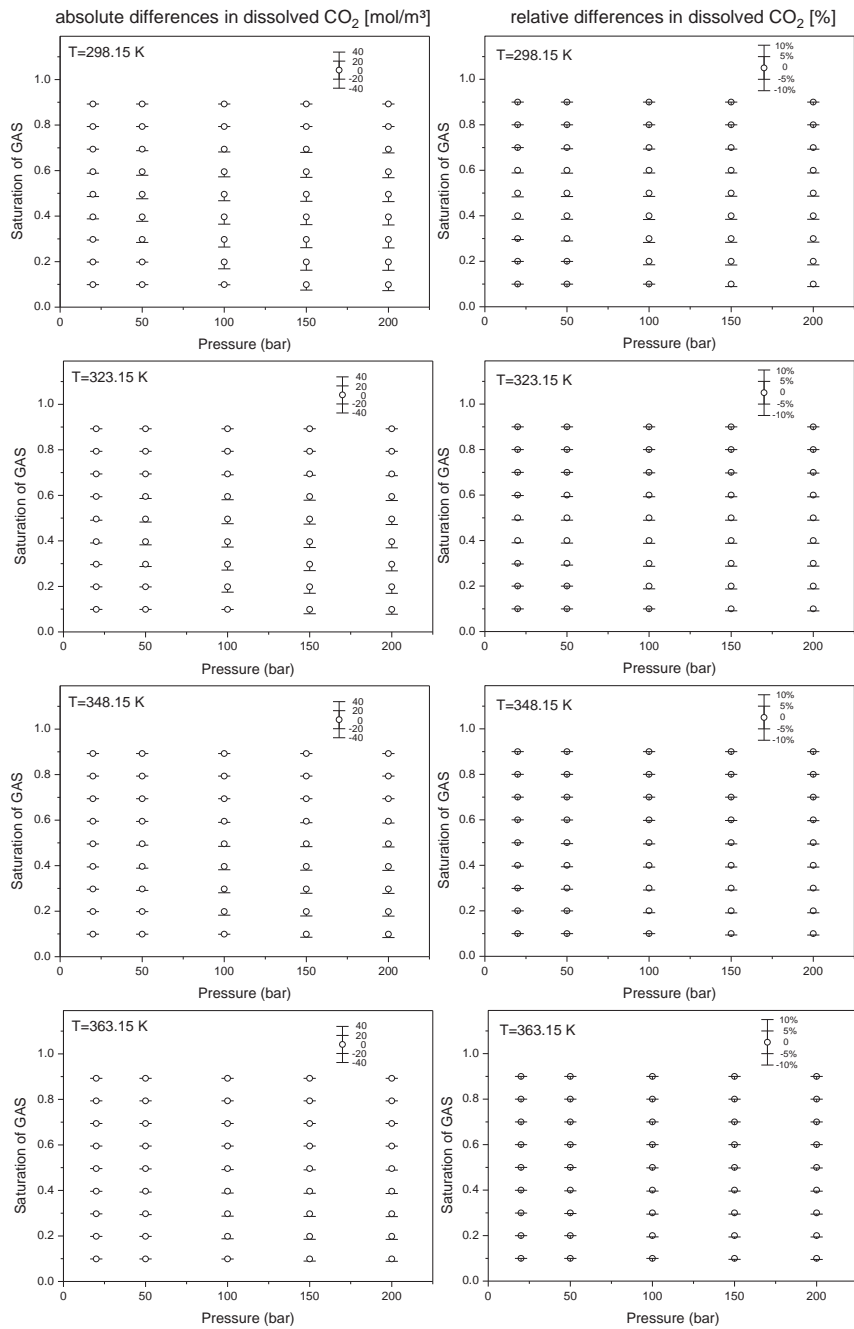
Fig. 3b. (continued). Evaluation of batch modeling results using the VLSE method (for detailed explanations see previous page).

Table 3. composition of liquid phase at reservoir condition of 323.15K, 100 bar and an initial CO2 saturation of 0.7.

	VLE/SLE method		VLSE method	
	after 1st step	after 2nd step	after 1st step	after 2nd step
CO_2 in aq. phase	958.224	980.652	978.732	980.807
H^+ in aq. phase	1.77960×10^{-2}	1.81067×10^{-2}	1.80779×10^{-2}	1.81083×10^{-2}
total Ca in aq. phase	22.5647	22.7190	22.7005	22.7206
TIC in aq. phase	1003.37	1026.11	1024.15	1026.27
calcite	3.71996	3.71116	3.71222	3.71107

note: unit of concentrations for aqueous phase is mol/m^3 of liquid, concentration of calcite is in mol/m^3 of solid phase.

4. Conclusions and Outlook

In order to numerically simulate the behaviour of geological systems like a reservoir for CO_2 storage, complex physical and chemical changes in the system properties need to be accounted for during the simulation process. In fact, all relevant processes like fluid flow, heat and solute transport as well as geochemical reactions act simultaneously, and they also may affect each other at different degrees of non-linearity. Nonetheless, most simulation codes currently in use are built on the basis of the operator-splitting approach, where all processes are quantified sequentially. Therefore, it is necessary to evaluate whether the operator-splitting allows a reasonable approximation of the real system behaviour, and to quantify the magnitude of errors in predictions of the system states due to the splitting process. In this study a structural analysis of the simulation process for a simple chemical batch system containing coexisting gas (CO_2), liquid (H_2O) and solid (calcite) phases was performed. By comparing a two-steps reactions method, where gas-liquid-equilibria and solid-liquid equilibria are quantified in separate steps, with the full (or conjoint) gas-liquid-solid equilibration reaction, it was found that a certain amount of deviation exists between predicted and true system state for both approaches. For the CO_2-H_2O-$CaCO_3$ system at a temperature of 323 K and a pressure of 100 bar, which represent typical conditions for storage of CO_2 in deep geological formations, the error from the two-steps method reaches a maximum for an initial gas saturation around 0.7. The relative deviations of aqueous CO_2 concentrations from the true system state reach up to -2%. The deviation, however, is only less than -0.5% using the full chemical equilibration method under the same conditions. The latter approach hence should be preferred in multiphase flow and reactive transport modelling with operator-splitting. The results for the simple CO_2-H_2O-$CaCO_3$ batch system allow a first assessment of the influence of the operator-splitting approach on the development of the multiphase system. In this analysis, however, other relevant mineral phases in the rock matrix, the flow of CO_2 and brine phases as well as the transport of dissolved components in the brine were not considered. These processes will have an important impact on the geochemical interactions in a CO_2 storage reservoir. Subsequent work will therefore extend the evaluation of this method for scenarios of CO_2 injection at a typical reservoir structure in northern Germany, coupling the multiphase reactions to fluid phase flow and multi-component transport processes under realistic field conditions.

Acknowledgements

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