Reactive transport modeling of leaking CO_2-saturated brine along a fractured pathway

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ABSTRACT

One concern regarding the underground storage of carbon dioxide (CO_2) is its potential leakage from reservoirs. Over short period of time, the leakage risk is related mainly to CO_2 as a separate supercritical fluid phase. However, over longer periods upon complete dissolution of injected CO_2 in the fluid, the leakage risk is associated with dissolved phase CO_2. Over the geological time scales, large-scale groundwater motion may cause displacement of brine containing dissolved CO_2 along the conducting pathways. In this paper, we present a comprehensive modeling framework that describes the reactive transport of CO_2-saturated brine along a fracture in the clay caprock based on the future, hypothetical leakage of the dissolved phase CO_2. This study shows that the transport of leaked dissolved CO_2 is significantly retarded by a combination of various physical and geochemical processes, such as mass exchange between conducting fracture and the neighboring rock matrix through molecular diffusion, sorption and calcite dissolution in the rock matrix. Mass stored in aqueous and adsorbed states in the rock matrix caused retention of dissolved CO_2 along the leakage pathway. Calcite dissolution reaction in the rock matrix resulted in consumption of leaking dissolved CO_2 and reduced its mass along the leakage pathway. Consumption and retention of dissolved CO_2 along the leakage pathway have important implications for analyzing the potential reduction of CO_2 fluxes from storage reservoirs over large periods and long travel pathways.

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1. Introduction

The CO_2 geological sequestration has been proposed for mitigating the imbalance of gas emissions (Holloway, 1997, 2005; IPCC, 2002; Middleton et al., 2012). CO_2 is injected in deep subsurface geological reservoirs in a dense supercritical state (IPCC, 2005). Due to its lower density compared to the resident brine, the injected CO_2 tends to accumulate towards the top of the reservoir (Arts et al., 2005; Audigane et al., 2005; Pruess, 2006a; Orr, 2009). Over short periods (up to 100 years), CO_2 is stored as a separate fluid phase (CO_{2g}) in the reservoir (physical trapping) (Audigane et al., 2005). However, CO_{2g} dissolves in the formation brine at the brine–CO_{2g} interface (solubility and ionic trapping) (Orr, 2009; IPCC, 2005). The resulting CO_2-saturated brine becomes slightly denser with respect

to its original value, which causes gravity-driven downward flow, produces fingering, enhances fluids mixing, and increases CO_{2g} dissolution (Audigane et al., 2007). It might take almost 10,000 years for complete dissolution of injected CO_{2g} into the formation fluid (Audigane et al., 2005, 2007). Dissolution of CO_{2g} in the formation fluid lowers the pH of the resulting brine, driving heterogeneous geochemical reactions that result in fixation of CO_2 through precipitation of carbonate minerals (Audigane et al., 2005; Gunter et al., 1993). This process, termed mineral trapping, dominates over thousands to millions of years (Gunter et al., 1993; IPCC, 2005).

One concern related to the underground storage of CO_{2g} is its potential to leak from the storage reservoir (Haugan and Joos, 2004; Pruess, 2005; Stone et al., 2009). As long as injected CO_{2g} stays as a separate fluid phase in the reservoir (tens of years), higher leakage risk exists due to its lower density as compared to the resident fluid (Pruess, 2006a, 2006b). At large times, upon complete dissolution of CO_{2g} in the formation fluid, leakage risk is associated to the presence of CO_2 in dissolved phase (Bachu et al., 1994). Audigane et al. (2007) found that all the injected CO_{2g} was completely

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dissolved in the formation fluid after 10,000 years whereas only 5% was consumed through mineral reactions. Thus, after thousands of years, only CO_2-saturated brine in the reservoir is expected, and the risk for leakages of CO_2 is associated only with its dissolved phase (CO_{2aq}).

Large-scale groundwater motion may cause bulk displacement of brine out of the reservoir with associated CO_{2aq} leakage risk (Bachu et al., 1994; IPCC, 2005; Gaus, 2010). In the sedimentary basins, groundwater flow velocities can be expected on the order of millimeters to centimeters per year (Bachu et al., 1994). Thus due to low groundwater velocities the leakage risk of CO_{2aq} is substantially lower than that of CO_{2g}. Transport of CO_{2aq} may take place by advection, dispersion and diffusion processes (Bachu et al., 1994). Although fractures act as the principal conductors for flow, the neighboring rock matrix also plays a significant role in the solute transport processes (Grisak and Pickens, 1980). The species that diffuse from the fractures into the matrix may undergo sorption on the surface of the solid and may react with the minerals in the rock matrix, which would significantly inhibit the transport of reactive or non-reactive species in fractured rocks (Bodin et al., 2003; Cvetkovic et al., 1999; Neretnieks, 1980; Xu et al., 2001). Thus, the interplay between the conducting fracture and the matrix through diffusion is important for understanding the transport of leaking CO_2-saturated brine.

Particularly, along the transport pathway, CO_{2aq} may undergo physical and geochemical interactions with the existing rock formation minerals. These CO_2–rock interactions can enhance transport by increasing hydraulic conductivity, linked to the porosity increases caused by mineral dissolution, or decrease transport by decreasing the permeability due to mineral precipitation. For example, a carbonate mineral filling the fracture could dissolve and widen the existing flow path (Gaus, 2010). Calcite dissolution and precipitation along the leakage pathway may result in a net conversion and uptake of CO_{2aq}. Kaufmann and Dreybrodt (2007) have reported the conversion of CO_{2aq} due to calcite dissolution in a ternary $CaCO_3$–H_2O–CO_2 system. This indicates the relevance of studying the physical and geochemical interactions of leaking CO_2-saturated brine in rock formations along the flow pathway.

To date, no studies have been published in which retention and consumption of CO_{2aq} is analyzed based on a physico-geochemical formulation of coupling transport in fractures, molecular diffusion in the porous rock matrix (matrix diffusion) and reactions on available rock surfaces in the matrix. So far, only few experimental and relatively simple numerical modeling studies have been published related to the leakage of dissolved CO_2 (Gaus, 2010). Gherardi et al. (2007) performed numerical simulations of the geochemical interactions of caprock with leakage of the CO_2 gas phase and the associated brine simultaneously. These authors found that calcite dissolution or precipitation was the most significant process that controlled the chemical evolution of the caprock and responsible for changes in the porosity near the reservoir–caprock interface. Ellis et al. (2011) conducted a seven-day experiment to investigate the evolution of a fractured carbonate caprock due to geochemical interactions with leaking CO_2-acidified brine. Andreani et al. (2008) reported experimental studies regarding the fracture evolution due to cyclic flows of CO_2 dissolved in brine and the free-phase CO_2. These authors reported an increase in porosity of 50% near the fracture, mainly due to calcite dissolution. Nogues et al. (2013) analyzed the evolution of medium porosity and pore-scale permeability caused by inflowing CO_2-saturated water. These authors concluded that the geochemical modeling could be simplified by not including the reactions of minerals kaolinite, anorthite, and albite whenever carbonate minerals are abundant. Peters et al. (2014) reported that a complex set of factors and processes are involved in permeability variations resulting from dissolution of calcite in the caprock flow pathways caused by acidified brine containing CO_{2aq}. These

authors recommend including the complex geochemical interactions of CO_2-saturated brine with calcite into reactive transport models to properly predict the flow paths' permeability evolution.

The aim of the present study is to provide a quantitative understanding of the transport of CO_2-saturated brine along fractured pathways, leaking from deep storage reservoir caused by large-scale groundwater flow over geological time scales. This study analyzes the retention and consumption of CO_{2aq} due to various physical and geochemical processes in the rock matrix adjacent to the main flow conducting pathway. In this study we present a comprehensive reactive transport model capable of analyzing the evolution of porosity along the leakage pathway due to dissolution and precipitation of calcite over the period of time. The novel approach adopted here explicitly couples the relatively fast transport of CO_{2aq} in the fracture with slow transport in the neighboring rock matrix through molecular diffusion, while accounting for various physical and geochemical processes, such as sorption, various aqueous phase equilibria, and calcite mineral kinetic reactions in the rock matrix.

The full system of equations describing the reactive transport in terms of the chemical components is presented here in a comprehensive form that can be efficiently solved using numerical methods. The model framework is applied to a scenario that is believed to represent the leakage of CO_{2aq} in a brine solution that is slowly flowing through a fracture in a clayey caprock caused by regional-scale groundwater motion. Various transport scenarios are performed over a period of 500 years to evaluate the significance of various physical and geochemical processes on the mobility and consumption of CO_{2aq} in geochemical reactions along the leakage pathway. Sensitivity analysis is then performed to analyze the effects of various parameters (i.e. advective velocity in the fracture, sorption partition coefficient, pressure and temperature conditions, and diffusion coefficient) on the retention and consumption of CO_{2aq} along the leakage pathway. Comparative analysis between various reactive transport scenarios is presented in terms of variations in medium porosity, retention of CO_{2aq} caused by mass stored in aqueous and adsorbed states, mass uptake of CO_{2aq} in geochemical reactions, and transport retardation along the leakage pathway.

2. Mathematical and numerical model

2.1. Numerical solution technique

The batch and the reactive transport modeling are performed in COMSOL that is based on the finite element method. Fast aqueous phase reactions are modeled as equilibrium reactions governed by the law of mass action. In contrast, the kinetics of calcite mineral are considered slow and modeled as kinetically controlled. Aqueous phase reactions are considered in both the fracture and the surrounding rock matrix whereas mineral kinetic reactions are considered only in the rock matrix. In this study the concentration of chloride (Cl^-) is taken equal to a constant value of 0.5 mol/(kg water) by considering it as a conservative solute that does not participate in any of the geochemical reactions.

In this study the transport problem and the geochemistry are solved in a partially coupled mode. Transport of aqueous species in the conducting fracture is modeled through the advection-dispersion-reaction transport equation, whereas diffusion and reaction are considered as the transport processes in the rock matrix. While considering a constant velocity in the fracture, the transport processes in the fracture are modeled independently of variations in porosity and permeability taking place in the rock matrix. Diffusion in the rock matrix is characterized by an effective diffusivity, being a function of porosity of the rock matrix, and thus