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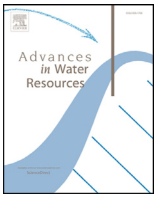

The role of advection and dispersion in the rock matrix on the transport of leaking CO_2-saturated brine along a fractured zone☆

Nawaz Ahmad[a,b,*], Anders Wörman[a], Xavier Sanchez-Vila[c], Andrea Bottacin-Busolin[d]

[a] *Department of Civil and Architectural Engineering, KTH Royal Institute of Technology, Brinellvägen 23, 10044, Stockholm, Sweden*
[b] *Policy Wing, Ministry of Petroleum and Natural Resources, Government of Pakistan, Pakistan*
[c] *Hydrogeology Group, Department of Geotechnical Engineering and Geosciences, Universitat Politècnica de Catalunya, UPC-BarcelonaTech, 08034 Barcelona, Spain*
[d] *School of Mechanical, Aerospace and Civil Engineering, University of Manchester, United Kingdom*

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ABSTRACT

CO_2 that is injected into a geological storage reservoir can leak in dissolved form because of brine displacement from the reservoir, which is caused by large-scale groundwater motion. Simulations of the reactive transport of leaking CO_{2aq} along a conducting fracture in a clay-rich caprock are conducted to analyze the effect of various physical and geochemical processes. Whilst several modeling transport studies along rock fractures have considered diffusion as the only transport process in the surrounding rock matrix (diffusive transport), this study analyzes the combined role of advection and dispersion in the rock matrix in addition to diffusion (advection-dominated transport) on the migration of CO_{2aq} along a leakage pathway and its conversion in geochemical reactions. A sensitivity analysis is performed to quantify the effect of fluid velocity and dispersivity. Variations in the porosity and permeability of the medium are found in response to calcite dissolution and precipitation along the leakage pathway. We observe that advection and dispersion in the rock matrix play a significant role in the overall transport process. For the parameters that were used in this study, advection-dominated transport increased the leakage of CO_{2aq} from the reservoir by nearly 305%, caused faster transport and increased the mass conversion of CO_{2aq} in geochemical reactions along the transport pathway by approximately 12.20% compared to diffusive transport.

1. Introduction

CO_2 storage in geological formations is a method to slow the atmospheric accumulation of greenhouse gases (Holloway, 2005; Middleton et al., 2012). Environmental hazards that are related to geological CO_2 storage are associated with its potential leakage from storage reservoirs (Stone et al., 2009; Haugan and Joos, 2004). The leakage risk is the greatest when the injected CO_2 remains as a supercritical free-phase (CO_2) in the reservoir because of its lower density than the resident fluid (Pruess, 2006a,2006b). However, the leakage risk diminishes with time because of the progressive dissolution of supercritical CO_2 in the formation fluid (IPCC, 2005). Upon the complete dissolution of CO_2 in the formation fluid (over 10,000 years), the leakage risk is mostly associated with the dissolved phase (CO_{2aq}) (Bachu et al., 1994).

Recently, a relatively safer method of CO_2 geological sequestration has been investigated, in which brine that carries CO_{2aq} is injected into the reservoir rather than supercritical CO_2 (Aradóttir et al., 2012; Gislason and Oelkers, 2014; Ahmad et al., 2016). The downward movement of this brine that carries CO_{2aq} is expected because the injected fluid is denser than the resident one. This mode of sequestration exhibits relatively faster and higher consumption of CO_{2aq} through mineral trapping (Aradóttir et al., 2012). However, large-scale groundwater motion may displace the brine from the reservoir, creating an associated risk of CO_{2aq} leakage (Bachu et al., 1994; IPCC, 2005; Gaus, 2010).

The transport of CO_{2aq} may occur through a combination of processes, including advection, dispersion, and diffusion (Bachu et al., 1994). In some cases, fractures or faults may serve as the main leakage pathways (Grisak and Pickens, 1980). Leaking CO_{2aq} may undergo various physical and geochemical interactions with the rock formation. Mass exchange between the conducting fracture and the rock matrix, sorption, and geochemical reactions may immobilize solute species in the fractured rocks (Neretnieks, 1980; Cvetkovic et al., 1999; Xu et al., 2001; Bodin et al., 2003). Low-pH brine that carries CO_{2aq} may potentially undergo various geochemical reactions with its associated conversion through calcite dissolution or precipitation reactions (Dreybrodt et al., 1996;

☆ COMSOL code is available upon request from the author.
* Corresponding author.
E-mail address: nawaza@kth.se (N. Ahmad).

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Kaufmann and Dreybrodt, 2007; Dreybrodt et al., 1997). Variations in the medium's porosity and permeability may result from mineral dissolution or precipitation because of geochemical interactions with leaking CO_2-saturated brine. For example, the fast dissolution of carbonate minerals may widen the existing flow paths (Andreani et al., 2008; Gaus, 2010; Ellis et al., 2011(a,b)).

Gherardi et al. (2007) analyzed the geochemical interactions of leaking CO_2 and associated brine that carries CO_{2aq} by means of numerical studies and reported porosity variations near the reservoir-caprock interface, which are mainly related to calcite mineral reactions. In an experimental study, Andreani et al. (2008) reported a 50% increase in the medium's porosity in close proximity of the fracture because of calcite dissolution from cyclic flows of CO_2 and CO_2-saturated brine. Noiriel et al. (2007) examined the effects of acidic water in a flow-through experiment and reported the faster dissolution of carbonate minerals compared to clay minerals in the fracture. Ellis et al. (2011a) performed a seven-day experiment to study the geochemical evolution of flow pathway in fractured carbonate caprock because of leaking CO_{2aq}-carrying brine. These authors reported an increase in fracture apertures because of the preferential dissolution of calcite mineral. Ellis et al. (2011b) reported a flow-through experiment of acidic brine in fractured carbonate caprock (over 90% of the bulk rock composed of calcite and dolomite), which increased the fracture apertures close to the inlet boundary because of preferential calcite dissolution.

Peters et al. (2014) suggested including the complex geochemical interactions of CO_2-saturated brine with mineral calcite in reactive transport models to investigate the permeability evolution of flow pathways in caprock. Nogues et al. (2013) suggested disregarding minerals such as kaolinite, anorthite, and albite in geochemical models that involve the fate of CO_2-saturated water whenever carbonate minerals are abundant. Several authors conceptualized solute transport in a fracture-matrix system as a dual-domain model; transport in fractures occurs through advection, dispersion and diffusion, whereas diffusion alone is considered in the matrix (Steefel and Lichtner, 1998(a,b); Novak, 1993,1996; Ahmad et al., 2015).

In this study, we consider the presence of an altered rock matrix zone (where advection and dispersion may not be negligible) that surrounds a fracture and how these processes affect the reactive transport of CO_2-saturated brine that is leaking along this fracture-matrix system. The velocity fields in the fracture and rock matrix are modeled by Brinkman equations while considering the time- and space-dependent variations in porosity and permeability that are caused by the dissolution and precipitation of calcite. Various transport scenarios are simulated for a period of 500 years to analyze the significance of adding advection and dispersion into the rock matrix compared to diffusion alone (diffusive transport) on the fate of leaking CO_{2aq} and its conversion in geochemical reactions along the leakage pathway. A comparative analysis between various reactive transport scenarios is presented in terms of variations in the medium's porosity, CO_{2aq} leakage fluxes from the reservoir, the retention of CO_{2aq} because of mass that is stored in aqueous and adsorbed states, and CO_{2aq} that is converted in geochemical reactions along the leakage pathway. A sensitivity analysis is also performed to determine the significance of the fluid velocity and dispersivity.

2. Model description

The formulation of the reactive transport problem involves a series of mass balance and momentum equations combined with constitutive thermodynamic relationships. The reactions that are considered in the study are displayed in Table 1. Reactions (R0)-(R4) were considered to be fast and modeled as in equilibrium, whereas the calcite mineral reaction (R5) was considered a slow (kinetically controlled), reversible reaction. Reaction (R0) represents the equilibrium between supercritical CO_2 and CO_{2aq} and was only included in the batch geochemical models but excluded in the subsequent reactive transport modeling. The solubility of CO_2 in the fluid (reaction (R0)) was based on the relationships that were developed by Duan and Sun (2003) and later modified by Duan et al. (2006). This solubility model is valid for a wide range of pressures, temperatures, and ionic strengths. The equilibrium constants for remaining reactions (R1)-(R5) were obtained from the LLNL thermo database (Delany and Lundeen, 1990), the default thermodynamic database for The Geochemist's Workbench®, 2016 (GWB), an integrated geochemical modeling package. Linear interpolation was used to compute the equilibrium constants of the reactions at the temperature that was used in the study. The activity coefficient of CO_{2aq} was computed from the model that was presented by Duan and Sun (2003). The B-dot model, an extension of the Debye-Hückel equation, was used to compute the activity coefficients of the involved aqueous species (Bethke, 2008).

Table 1
Chemical reactions that were considered for the $CaCO_3–H_2O–CO_2$ system.

No.	Reaction
(R0)	$CO_{2g} \leftrightarrow CO_{2aq}$
(R1)	$H_2O+CO_{2aq} \leftrightarrow H^+ + HCO_3^-$
(R2)	$H_2O \leftrightarrow H^+ + OH^-$
(R3)	$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$
(R4)	$Na^+ + HCO_3^- \leftrightarrow NaHCO_{3aq}$
(R5)	$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$

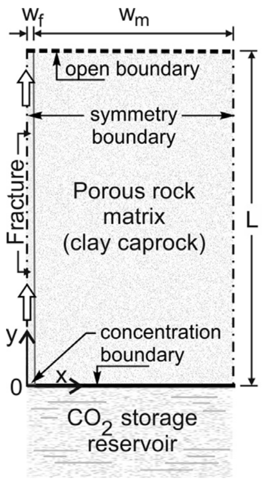

Fig. 1. Schematic of the transport domain (clay-rich caprock with a vertical conducting fracture) that overlies the CO_2 storage reservoir.

2.1. Model domain

Fig. 1 presents the schematic of a CO_2 storage reservoir that is overlain by a clay-rich caprock with a vertical conducting fracture. The domain involves a conducting fracture that is surrounded by a less-permeable rock matrix. W_f is the half-width of the fracture (taken as 1 mm), W_m is the half-width of the rock matrix (50 m), and L is the caprock length (100 m). The fracture is assumed to be partially filled with porous material (Wealthall et al., 2001; Wu et al., 2010; Laubach et al., 2010; Liu et al., 2013) and has an initial porosity of 0.60. The initial porosity of the rock matrix is taken as 0.12. The lower boundary of the caprock, and thus the upper boundary of the reservoir, is assumed to be at a depth of 1040 m below the land surface. The leaking CO_2-saturated brine from the reservoir enters the transport domain from the bottom