

1 **The role of advection and dispersion in the rock matrix on the transport of leaking CO<sub>2</sub>-**  
2 **saturated brine along a fractured zone**

3 Nawaz Ahmad<sup>a, b,\*</sup>, Anders Wörman<sup>a</sup>, Xavier Sanchez-Vila<sup>c</sup>, and Andrea Bottacin-  
4 Busolin<sup>d</sup>

5 <sup>a</sup> Department of Civil and Architectural Engineering, KTH Royal Institute of Technology,  
6 Brinellvägen 23, 10044, Stockholm, Sweden

7 <sup>b</sup> Policy Wing, Ministry of Petroleum and Natural Resources, Government of Pakistan,  
8 Pakistan

9 <sup>c</sup> Hydrogeology Group, Department of Geotechnical Engineering and Geosciences,  
10 Universitat Politècnica de Catalunya, UPC-BarcelonaTech, 08034 Barcelona, Spain

11 <sup>d</sup> School of Mechanical, Aerospace and Civil Engineering, University of Manchester, United  
12 Kingdom

13 \*Correspondence author at: Department of Civil and Architectural Engineering, KTH Royal  
14 Institute of Technology, Brinellvägen 23, 10044, Stockholm, Sweden.

15 E-mail address: [nawaza@kth.se](mailto:nawaza@kth.se)

16 **Running Title:** Reactive transport of CO<sub>2</sub>-saturated brine along a fractured zone

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<sup>1</sup> COMSOL code is available upon request from the author.

20 **Abstract:** CO<sub>2</sub> that is injected into a storage reservoir can leak in dissolved form because of  
21 brine displacement from the reservoir, which is caused by large-scale groundwater motion.  
22 Simulations of the reactive transport of leaking CO<sub>2aq</sub> along a conducting fracture in a clay-  
23 rich caprock are conducted to analyze the effect of various physical and geochemical  
24 processes. Whilst several modelling transport studies along rock fractures have considered  
25 diffusion as the only transport process in the surrounding rock matrix (diffusive transport),  
26 this study analyzes the combined role of advection and dispersion in the rock matrix in  
27 addition to diffusion (advection-dominated transport) on the migration of CO<sub>2aq</sub> along a  
28 leakage pathway and its conversion in geochemical reactions. A sensitivity analysis is  
29 performed to quantify the effect of fluid velocity and dispersivity. Variations in the porosity  
30 and permeability of the medium are observed in response to calcite dissolution and  
31 precipitation along the leakage pathway. We observe that advection and dispersion in the rock  
32 matrix play a significant role in the overall transport process. For the parameters that were  
33 used in this study, advection-dominated transport increased the leakage of CO<sub>2aq</sub> from the  
34 reservoir by nearly 305%, caused faster transport and increased the mass conversion of CO<sub>2aq</sub>  
35 in geochemical reactions along the transport pathway by approximately 12.20% compared to  
36 diffusive transport.

37

38 **Keywords:** Reactive transport, Advection dominated transport, Diffusive transport, CO<sub>2</sub>-  
39 saturated brine leakage, Transport in fractures, Rock matrix, Calcite kinetic reaction

40

## 41 **1. Introduction**

42 CO<sub>2</sub> storage in geological formations is a method to slow the atmospheric  
43 accumulation of greenhouse gases (Holloway, 2005; Middleton et al., 2012).  
44 Environmental hazards that are related to geological CO<sub>2</sub> storage are associated with  
45 its potential leakage from storage reservoirs (Stone et al., 2009; Haugan and Joos,  
46 2004). The leakage risk is the greatest when the injected CO<sub>2</sub> remains as a supercritical  
47 free-phase (CO<sub>2</sub>) in the reservoir because of its lower density than the resident fluid (Pruess,  
48 2006a, 2006b). However, the leakage risk diminishes with time because of the progressive  
49 dissolution of supercritical CO<sub>2</sub> in the formation fluid (IPCC, 2005). Upon the complete  
50 dissolution of CO<sub>2</sub> in the formation fluid (over 10,000 years), the leakage risk is only  
51 associated with the dissolved phase (CO<sub>2aq</sub>) (Bachu et al., 1994).

52 Recently, a relatively safer method of CO<sub>2</sub> geological sequestration has been  
53 investigated, in which brine that carries CO<sub>2aq</sub> is injected into the reservoir rather than  
54 supercritical CO<sub>2</sub> (Aradóttir et al., 2012; Gislason and Oelkers, 2014). The downward  
55 movement of this brine that carries CO<sub>2aq</sub> is expected because the injected fluid is  
56 denser than the resident one. This mode of sequestration exhibits relatively faster and  
57 higher consumption of CO<sub>2aq</sub> through mineral trapping (Aradóttir et al., 2012).  
58 However, large-scale groundwater motion may displace the brine from the reservoir,  
59 creating an associated risk of CO<sub>2aq</sub> leakage (Bachu et al., 1994; IPCC, 2005; Gaus,  
60 2010).

61 The transport of CO<sub>2aq</sub> may occur through a combination of processes, including advection,  
62 dispersion, and diffusion (Bachu et al., 1994). In some cases, fractures or faults may serve as  
63 the main leakage pathways (Grisak and Pickens, 2007). Leaking CO<sub>2aq</sub> may undergo various  
64 physical and geochemical interactions with the rock formation. Mass exchange between the  
65 conducting fracture and the rock matrix, sorption, and geochemical reactions may immobilize

66 solute species in the fractured rocks (Neretnieks, 1980; Cvetkovic et al., 1999; Xu et al., 2001;  
67 Bodin et al., 2003). Low-pH brine that carries  $\text{CO}_{2\text{aq}}$  may potentially undergo various  
68 geochemical reactions with its associated conversion through calcite dissolution or  
69 precipitation reactions (Dreybrodt et al., 1996; Kaufmann and Dreybrodt, 2007; Dreybrodt et  
70 al., 1997). Variations in the medium's porosity and permeability may result from mineral  
71 dissolution or precipitation because of geochemical interactions with leaking  $\text{CO}_2$ -saturated  
72 brine. For example, the fast dissolution of carbonate minerals may widen the existing flow  
73 paths (Andreani et al., 2008; Gaus, 2010; Ellis et al., 2011(a, b)).

74 Gherardi et al. (2007) analyzed the geochemical interactions of leaking  $\text{CO}_2$  and associated  
75 brine that carries  $\text{CO}_{2\text{aq}}$  by means of numerical studies and reported porosity variations near  
76 the reservoir-caprock interface, which are mainly related to calcite mineral reactions. In an  
77 experimental study, Andreani et al. (2008) reported a 50% increase in the medium's porosity  
78 in close proximity of the fracture because of calcite dissolution from cyclic flows of  $\text{CO}_2$  and  
79  $\text{CO}_2$ -saturated brine. Noiriél et al. (2007) examined the effects of acidic water in a flow-  
80 through experiment and reported the faster dissolution of carbonate minerals compared to clay  
81 minerals in the fracture. Ellis et al. (2011a) performed a seven-day experiment to study the  
82 geochemical evolution of flow pathway in fractured carbonate caprock because of leaking  
83  $\text{CO}_{2\text{aq}}$ -carrying brine. These authors reported an increase in fracture apertures because of the  
84 preferential dissolution of calcite mineral. Ellis et al. (2011b) reported a flow-through  
85 experiment of acidic brine in fractured carbonate caprock (over 90% of the bulk rock  
86 composed of calcite and dolomite), which increased the fracture apertures close to the inlet  
87 boundary because of preferential calcite dissolution.

88 Peters et al. (2014) suggested including the complex geochemical interactions of  $\text{CO}_2$ -  
89 saturated brine with mineral calcite in reactive transport models to investigate the  
90 permeability evolution of flow pathways in caprock. Nogues et al. (2013) suggested

91 disregarding minerals such as kaolinite, anorthite, and albite in geochemical models that  
92 involve the fate of CO<sub>2</sub>-saturated water whenever carbonate minerals are abundant. Several  
93 authors conceptualized solute transport in a fracture-matrix system as a dual-domain model;  
94 transport in fractures occurs through advection, dispersion and diffusion, whereas diffusion  
95 alone is considered in the matrix (Steefel and Lichtner, 1998a, 1998b; Novak, 1993, 1996;  
96 Ahmad et al., 2015).

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

## 111 **2. Model description**

112 The formulation of the reactive transport problem involves a series of mass balance  
113 and momentum equations combined with constitutive thermodynamic relationships.  
114 The reactions that are considered in the study are displayed in Table 1. Reactions (R0)-

115 (R4) were considered to be fast and modelled as in equilibrium, whereas the calcite  
 116 mineral reaction (R5) was considered a slow (kinetically controlled), reversible  
 117 reaction. Reaction (R0) represents the equilibrium between supercritical CO<sub>2</sub> and  
 118 CO<sub>2aq</sub> and was only included in the batch geochemical models but excluded in the  
 119 subsequent reactive transport modelling. The solubility of CO<sub>2</sub> in the fluid (reaction  
 120 (R0)) was based on the relationships that were developed by Duan and Sun (2003) and  
 121 later modified by Duan et al. (2006). This solubility model is valid for a wide range of  
 122 pressures, temperatures, and ionic strengths. The equilibrium constants for remaining  
 123 reactions (R1)-(R5) were obtained from the LLNL thermo database (Delany and  
 124 Lundeen, 1990), the default thermodynamic database for The Geochemist's  
 125 Workbench<sup>®</sup> (GWB), an integrated geochemical modelling package. Linear  
 126 interpolation was used to compute the equilibrium constants of the reactions at the  
 127 temperature that was used in the study. The activity coefficient of CO<sub>2aq</sub> was computed  
 128 from the model that was presented by Duan and Sun (2003). The B-dot model, an  
 129 extension of the Debye-Hückel equation, was used to compute the activity coefficients  
 130 of the involved aqueous species (Bethke, 2008).

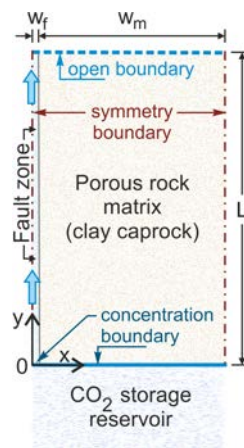
131 **Table 1.** Chemical reactions that were considered for the CaCO<sub>3</sub>-H<sub>2</sub>O-CO<sub>2</sub> system.

No.	Reaction
(R0)	$\text{CO}_{2\text{g}} \leftrightarrow \text{CO}_{2\text{aq}}$
(R1)	$\text{H}_2\text{O} + \text{CO}_{2\text{aq}} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$
(R2)	$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$
(R3)	$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$
(R4)	$\text{Na}^+ + \text{HCO}_3^- \leftrightarrow \text{NaHCO}_{3\text{aq}}$
(R5)	$\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$

132

133 2.1. Model domain

134 Fig. 1 presents the schematic of a CO<sub>2</sub> storage reservoir that is overlain by a clay-rich  
 135 caprock with a vertical conducting fracture. The domain involves a conducting fracture  
 136 that is surrounded by a less-permeable rock matrix.  $W_f$  is the half-width of the fracture  
 137 (taken as 1 mm),  $W_m$  is the half-width of the rock matrix (50 m), and  $L$  is the caprock  
 138 length (100 m). The fracture is assumed to be partially filled with porous material  
 139 (Wealthall et al., 2001; Wu et al., 2010; Laubach et al., 2010; Liu et al., 2013) and has  
 140 an initial porosity of 0.60. The porosity of the rock matrix is taken as 0.12. The lower  
 141 boundary of the caprock, and thus the upper boundary of the reservoir, is assumed to  
 142 be at a depth of 1040 m below the land surface. The leaking CO<sub>2</sub>-saturated brine from  
 143 the reservoir enters the transport domain from the bottom inflow boundary, which  
 144 comprises a fracture and rock matrix, and exits through the top (open) boundary.  
 145 Continuity conditions for the solute and fluid mass are applied at the fracture-matrix  
 146 interface. Symmetry with no-flow conditions are assumed at the left (center of the  
 147 fracture) and right (center of rock matrix) boundaries.



148

149 Figure 1. Schematic of the transport domain (clay-rich caprock with a vertical conducting  
 150 fracture) that overlies the CO<sub>2</sub> storage reservoir.

151

152 2.2. Reactive transport of aqueous species

153 The transport of aqueous species is defined by the following system of equations, which are  
 154 written in terms of the chemical component species (COMSOL; Ahmad et al., 2015):

$$155 \quad \mathbf{R}_f \theta \frac{\partial \mathbf{u}}{\partial t} + (1 - \mathbf{K}_d \rho_p) \mathbf{u} \frac{\partial \theta}{\partial t} - \nabla \cdot [(\mathbf{D}_D + \mathbf{D}_e) \nabla \mathbf{u}] + \nabla \cdot (\mathbf{v} \mathbf{u}) = \theta \mathbf{r}_{kin} \quad (1)$$

$$156 \quad \mathbf{R}_f = 1 + \frac{\rho_{bulk}}{\theta} \mathbf{K}_d \quad (1b)$$

157 where  $\mathbf{u}$  (x,y,t) is the vector of the concentration [mol/(kg water)] of the component  
 158 species;  $\mathbf{R}_f$  (x,y,t) is a diagonal matrix of the retardation factor, which considers  
 159 sorption on the surface of the immobile mineral phases;  $\mathbf{K}_d$  (x,y,t) is a diagonal matrix  
 160 where the elements include the sorption partition coefficients of the component species  
 161 [m<sup>3</sup>/kg];  $\rho_{bulk} = (1 - \theta) \rho_p$  is the bulk density [kg/m<sup>3</sup>] of the porous media;  $\theta$ (x,y,t) is  
 162 the spatially and temporally varying porosity of the medium;  $\rho_p$ (x,y,t) is the particle  
 163 density [kg/m<sup>3</sup>];  $\mathbf{D}_D$  is the dispersion tensor [m<sup>2</sup>/s];  $\mathbf{D}_e = \theta D_b \mathbf{I}$  is the effective  
 164 diffusion diagonal tensor [m<sup>2</sup>/s] with  $\mathbf{I}$  as the identity tensor;  $D_b$  is the diffusion  
 165 coefficient of CO<sub>2aq</sub> in brine;  $\mathbf{v}$  (x,y,t) is the specific flux [m/s], which is updated in  
 166 space and time; and  $\mathbf{r}_{kin}$  (x,y,t) [mol/(s·kg water)] is the reaction term, which considers  
 167 the consumption or production of component species from geochemical reactions  
 168 ((R1)-(R5) in Table 1). The diffusion coefficient of CO<sub>2aq</sub> in brine is computed at the  
 169 pressure and temperature conditions that are used in this study from the relationships  
 170 by Al-Rawajfeh (2004) and Hassanzadeh et al. (2008). The computed diffusion  
 171 coefficient of CO<sub>2aq</sub> in brine ( $3.05 \times 10^{-9}$  m<sup>2</sup>/s) is considered for all the component  
 172 species (Gherardi et al., 2007). The dispersion tensor in Eq. (1) is defined as a function  
 173 of the dispersivity and the components of the fluid velocity by the following  
 174 relationships (Bear, 1972):



$$\left\{ \begin{array}{l} D_{Dxx} = \alpha_L \frac{v_x^2}{|v|} + \alpha_T \frac{v_y^2}{|v|} \\ D_{Dyy} = \alpha_L \frac{v_y^2}{|v|} + \alpha_T \frac{v_x^2}{|v|} \\ D_{Dxy} = D_{Dyx} = (\alpha_L - \alpha_T) \frac{v_x v_y}{|v|} \end{array} \right. \quad (2)$$

175 where  $\alpha_L$  and  $\alpha_T$  are the longitudinal and transverse dispersivity, respectively.

176 The transport Eq. (1) is written in terms of the component species ( $\mathbf{u}$ ), which are linear  
 177 combinations of aqueous species that are unaffected by equilibrium reactions. The  
 178 methodology of Saaltink et al. (1998) allows us to express the mass conservation of  
 179 aqueous species and write the source/sink terms ( $\mathbf{r}_{\text{kin}}$ ) in terms of the chemical  
 180 components. The concentration of aqueous species at every node in the computational  
 181 domain is then computed by solving the algebraic equations that relate the components  
 182 and aqueous species (speciation process, see Appendix A). In this study, eight aqueous  
 183 chemical species in the reaction system ((R1) to (R5) in Table 1) are transformed into  
 184 four component species. Therefore,  $\mathbf{u}$  is a vector of size 4 and  $\mathbf{R}_f$  and  $\mathbf{K}_d$  are matrices  
 185 of size  $4 \times 4$ . Eq. (1) is a system of nonlinear partial differential equations in which the  
 186 variables  $\theta$ ,  $\rho_p$ , and  $\rho_{bulk}$ , the matrices  $\mathbf{R}_f$  and  $\mathbf{K}_d$  and the vector  $\mathbf{r}_{\text{kin}}$  are nonlinear  
 187 functions of the local concentration of the component species ( $u$ ).

### 188 2.3. Mass conservation of calcite mineral

189 The mass conservation of calcite mineral that undergoes kinetic reaction in the  
 190 transport domain (fracture and rock matrix) is modelled by using the following  
 191 ordinary differential equation (ODE):

$$192 \quad \frac{\partial c_{m,bulk}}{\partial t} = -\theta \rho_b r_m \quad (3)$$

193 where  $c_{m,bulk}$  (x, y, t) is the concentration of mineral calcite per unit bulk volume  
 194 [mol/m<sup>3</sup>], and the reaction term  $r_m$  (x, y, t) represents the consumption (dissolution) or  
 195 production (precipitation) of calcite [mol/(s·kg water)]. The initial mineral  
 196 concentration ( $c_{m,bulk}$ ) values are computed to be 3142.03 and 6912.46 mol/m<sup>3</sup> in the  
 197 fracture and the rock matrix, respectively, based on the corresponding initial volume  
 198 fraction of calcite (Table 2).

199 **Table 2.** Caprock mineralogical composition in the fracture and the rock matrix.

Mineral	Mineral volume fraction in unaltered rock (Gherardi et al., 2007)	Mineral volume fraction in the fracture for 0.60 porosity	Mineral volume fraction in the rock matrix for 0.12 porosity
Calcite	0.290	0.116	0.255
Dolomite	0.040	0.016	0.035
Quartz	0.200	0.080	0.176
Illite	0.020	0.008	0.018
K-feldspar	0	0	0
Chlorite	0.060	0.024	0.053
Albite	0	0	0
Kaolinite	0.050	0.020	0.044
Na-smectite	0.150	0.060	0.132
Muscovite	0.190	0.076	0.1672

200

#### 201 2.4. Mineral kinetic reaction

202 The mineral kinetic reaction ( $r_m$ ) in Eq. (3) is defined in terms of the species concentration  
 203 and mineral reactive surface area (Lasaga, 1994):

$$204 \quad r_m = k_m A_m [1 - \Omega_m] \quad (4)$$

205 where  $k_m$  is the temperature-dependent kinetic rate constant of the mineral [mol/(s·m<sup>2</sup>)] and  
 206  $A_m$  is the reactive surface area of the mineral [m<sup>2</sup>/(kg water)], which is updated in time and  
 207 space during the modeling process. The term  $\Omega_m = Q_m/K_{eq}$  is the saturation state of calcite,  
 208 where  $Q_m$  represents the calcite ion activity product, and  $K_{eq}$  is the equilibrium constant for

209 the mineral reaction. The mineral dissolves in the solution if the saturation state of the brine  
 210 solution with respect to the mineral is less than unity and precipitates if  $\Omega_m > 1$ . The  
 211 temperature dependence of the kinetic rate constant ( $k_m$ ) of the mineral is described by the  
 212 Arrhenius equation (Lasaga, 1984):

$$213 \quad k_m = k_{25} \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] \quad (5)$$

214 where  $R$  ( $= 8.314$  J/(mol-K)) is the gas constant;  $T$  is the temperature [K].  $E_a$  is the  
 215 activation energy of calcite, and  $k_{25}$  is a reaction constant, which are set to 41.87  
 216 KJ/mol and  $1.60 \times 10^{-9}$  mol/(s-m<sup>2</sup>), respectively, at 25°C (Svensson and Dreybrodt,  
 217 1992).

### 218 2.5. Mineral reactive surface area

219 The geometric approach is adopted to calculate the mineral reactive surface from the number  
 220 of mineral grains (Johnson et al., 2004; Marini, 2007). The initial mineral reactive surface  
 221 area ( $A_m$ ) values are calculated to be 3.52 and 38.67 m<sup>2</sup>/(kg water) in the fracture and rock  
 222 matrix, respectively, based on the initial volume fractions of calcite in Table 2. The mineral  
 223 kinetic reaction causes variations in the number of mineral grains and, thus, in the reactive  
 224 surface area. The following relationship models the variations in the reactive surface area of  
 225 the mineral:

$$226 \quad A_m = 0.1 \left( \frac{A_g}{\theta \rho_b V_g} \right) (MV c_{m,bulk}) \quad (6)$$

227 where  $A_g$  and  $V_g$  are the physical surface area and volume of a mineral grain, respectively  
 228 (assumed to be spherical with a radius of  $1.65 \times 10^{-5}$  m);  $MV$  is the molar volume of the  
 229 mineral; and  $c_{m,bulk}$  is the concentration of the mineral, which varies in time and space

230 because of the mineral kinetic reaction (3). The mineral reactive surface area is set to 10% of  
 231 its computed physical surface area (Johnson et al., 2004).

## 232 2.6. Velocity field for the transport system

233 The velocity field in the fracture and rock matrix is defined by the Brinkman equations,  
 234 where flow in porous media is described by a combination of the mass and momentum  
 235 balances:

$$236 \quad \frac{\partial(\theta\rho_b)}{\partial t} + \nabla \cdot (\rho_b \mathbf{v}) = 0 \quad (7)$$

$$237 \quad \frac{\rho_b}{\theta} \left[ \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \frac{\mathbf{v}}{\theta} \right] = -\nabla p + \nabla \cdot \left[ \frac{\mu_b}{\theta} \left\{ (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I} \right\} \right] - \left( \frac{\mu_b}{\kappa} \right) \mathbf{v} + \mathbf{F} \quad (8)$$

238 where  $\rho_b$  is the density [ $\text{kg}/\text{m}^3$ ] and  $\mu_b$  is the dynamic viscosity [ $\text{kg}/(\text{m}\cdot\text{s})$ ] of  $\text{CO}_2$ -  
 239 saturated brine;  $p$  is the pressure [Pa]; and  $\kappa$  is the permeability of the porous medium  
 240 [ $\text{m}^2$ ]. Gravity is included through the force term ( $\mathbf{F} = -\rho_b \mathbf{g}$ ), where  $\mathbf{g}$  is the  
 241 gravitational acceleration vector [ $9.81 \text{ m}/\text{s}^2$ ]. The brine density and viscosity are equal  
 242 to  $1000 \text{ kg}/\text{m}^3$  and  $6.27 \times 10^{-4} \text{ kg}/(\text{m}\cdot\text{s})$ , respectively. The viscosity of the brine is  
 243 computed from the model by Mao and Duan (2009) at  $45^\circ\text{C}$  and  $105 \times 10^5 \text{ Pa}$   
 244 (representing conditions at the lower boundary of the domain, which is assumed to be  
 245 at a depth of 1040 m below the surface). The Brinkman equations expand Darcy's law  
 246 by including an additional term that considers viscous transport in the momentum  
 247 equation while treating both the pressure gradient and flow velocity as independent  
 248 vectors. Popov et al. (2009) found that the Stokes-Brinkman equation can represent  
 249 porous media that is coupled to free flow regions such as fractures, vugs, and caves,  
 250 including material fill-in and suspended solid particles. The Brinkman equation is  
 251 numerically attractive because it defines the flow field in two regions (free flow and  
 252 porous media) by using only a single system of equations instead of a two-domain

253 approach (Gulbranson et al., 2010). The validity of the Brinkman equations in  
254 COMSOL for modelling flow in porous media has been reported in several works  
255 (e.g., Sajjadi et al., 2014; Chabonan et al., 2015; Golfier et al., 2015; Basirat et al.,  
256 2015).

## 257 2.7. Medium's porosity

258 The variations in the porosity of the porous medium from mineral dissolution and  
259 precipitation are modelled in time and space (in fracture and rock matrix) based on the  
260 updated volume fraction of the calcite mineral through the following relationship:

$$261 \quad \theta = 1 - VF_{rock,p} \quad (9)$$

262 where  $VF_{rock,p} = \sum_m VF_{m,p}$  is the summation of the volume fractions of all the minerals  
263 forming the rock, and  $VF_{m,p} = V_{m,p}/V_{rock,p}$  [-] represents the volume fraction (ratio of  
264 the mineral volume to the total bulk volume) of each mineral. Some numerical  
265 restrictions are applied (Xu et al., 2014): (i) the minimum threshold value of the  
266 mineral concentration is set to  $1 \times 10^{-7}$  mol/m<sup>3</sup> to avoid the complete dissolution and  
267 corresponding disappearance of the mineral from the domain, and (ii) the minimum  
268 porosity of the medium is set to  $1 \times 10^{-3}$  to stop any further mineral precipitation below  
269 this value.

## 270 2.8. Medium's permeability

271 The medium's initial permeability is calculated by using the Kozeny-Carman relationship  
272 (e.g., Bear and Chang, 2010):

$$273 \quad \kappa_0 = C \frac{\theta_0^3}{(1-\theta_0)^2 (A_{rock,SSAV})^2} \quad (10)$$

274 where  $A_{rock,SSAV}$  is the specific surface area of the solid rock per unit volume of the  
 275 solid rock [ $\text{m}^2/\text{m}^3$ ], which depends on the mineral composition of the porous media;  $C$   
 276 is a coefficient that equals 0.2; and  $\theta_0$  is the initial porosity of the medium. The initial  
 277 estimated permeability values are  $2.24 \times 10^{-10} \text{ m}^2$  in the conducting fracture and  
 278  $3.71 \times 10^{-13} \text{ m}^2$  in the rock matrix according to the initial porosities of 0.60 and 0.12 and  
 279 Eq. (10).

280 Mineral dissolution or precipitation changes the medium's porosity and permeability. The  
 281 medium's permeability is updated in time and space by using the Kozeny-Carman  
 282 relationship (Lai et al., 2014; Xu et al., 2014):

$$283 \quad \kappa = \kappa_0 \frac{(1-\theta_0)^2 \theta^3}{(1-\theta)^2 \theta_0^3} \quad (11)$$

#### 284 2.9. Sorption of mobile species

285 Different minerals have shown a capacity to adsorb  $\text{CO}_2$  (Santschi and Rossi, 2006; Fujii et  
 286 al., 2010; Tabrizy et al., 2013; Heller and Zoback, 2014). Santschi and Rossi (2006) reported  
 287 that dissolved  $\text{CO}_2$  adsorbs onto calcite mineral surfaces through the formation of an  
 288 intermediate species  $[\text{Ca}(\text{OH})(\text{HCO}_3)]$ , with a partition coefficient of  $6.6 \times 10^{-2} \text{ m}^3/\text{kg}$ . In their  
 289 experimental study, Fujii et al. (2010) observed the reversible nature of the sorption of  $\text{CO}_2$   
 290 onto rocks and minerals at pressure and temperature conditions that are relevant to  $\text{CO}_2$   
 291 geological storage. Heller and Zoback (2014) observed the lowest  $\text{CO}_2$  adsorption capacity for  
 292 “Eagle Ford 127” clay, which mainly consists of calcite (80%). From their study the values of  
 293 partition coefficient were deduced as  $7.39 \times 10^{-4} \text{ m}^3/\text{kg}$  and  $3.33 \times 10^{-3} \text{ m}^3/\text{kg}$  for “Eagle Ford  
 294 127” and “Montney” clay types respectively at a pressure of  $105 \times 10^5 \text{ Pa}$ .

295 In this study a value of  $2.50 \times 10^{-4} \text{ m}^3/\text{kg}$  was used as a partition coefficient that is lower than  
 296 the values reported by Santschi and Rossi (2006) and by Heller and Zoback (2014). The

297 reason is that these authors used crushed rock in their experiments, whereas this study deals  
298 with intact rock, thus with smaller reactive surface areas. Additionally, we use the same  
299 partition coefficient for all the mobile species because of the large uncertainty in the sorption  
300 properties and complex geochemical interactions of all the species and to simplify the  
301 analysis.

#### 302 *2.10. Initial and boundary values*

303 The initial pressure in the domain is defined as the hydrostatic pressure with a  
304 subsurface pressure gradient of  $1 \times 10^4$  Pa/m (Pruess, 2008). The pressures equal  
305  $105 \times 10^5$  Pa at the bottom and  $95 \times 10^5$  Pa at the top for this gradient and an atmospheric  
306 pressure of  $1 \times 10^5$  Pa, assuming that the domain is located at a depth of 1040 m below  
307 the land surface. In the base-case transport scenarios, an excess pressure of 71.63 Pa in  
308 addition to the prevailing hydrostatic pressure is applied at the bottom boundary to  
309 obtain fluid Darcy velocities of 10 and  $2 \times 10^{-2}$  m/year in the conducting fracture and  
310 rock matrix, respectively. These velocities show a combined Darcy velocity of 0.0202  
311 m/year for the fracture plus the matrix system. This velocity falls in the range for  
312 regional-scale Darcy velocities of 1 to 10 cm/year, which are measured in a number of  
313 sedimentary basins (Bachu et al., 1994).

314 The initial water chemistry in the reservoir and transport domain (clay-rich caprock) is  
315 obtained from the background Batch Geochemical Modelling (BGM). The background BGM  
316 is performed at a temperature of 45°C and CO<sub>2</sub> partial pressure of  $1 \times 10^3$  Pa (Xu et al., 2005)  
317 and considers 0.5 M of NaCl solution until full equilibrium is reached (with respect to all the  
318 reactions in Table 1). The chemistry of the leaking CO<sub>2</sub>-saturated brine is obtained from CO<sub>2</sub>  
319 dissolution modelling that is performed at a temperature of 45°C and CO<sub>2</sub> partial pressure of  
320  $105 \times 10^5$  Pa (representing a depth of 1040 m below the surface) for a 0.5 M NaCl solution.

321 Table 3 displays the initial water chemistry in the reservoir and clay-rich caprock (column 2)  
 322 and that of the leaking CO<sub>2</sub>-saturated brine in the reservoir (column 3). The compositions of  
 323 the initial and boundary brines in the modelling process, written in terms of chemical  
 324 components, are presented in Table 4. The composition of leaking brine at the bottom inflow  
 325 boundary is set to remain constant during the entire simulation time, assuming that the brine  
 326 in the reservoir always stays in equilibrium with calcite.

327  
 328 **Table 3.** Initial prevailing water chemistry in the reservoir and clay-rich caprock (column 2)  
 329 and the chemistry of CO<sub>2</sub>-saturated brine in the reservoir (column 3).

Pressure and temperature	45°C and 1×10 <sup>3</sup> Pa	45°C and 105×10 <sup>5</sup> Pa
Aqueous species	c [mol/(kg water)]	c [mol/(kg water)]
HCO <sub>3</sub> <sup>-</sup>	3.33×10 <sup>-3</sup>	6.04×10 <sup>-2</sup>
Na <sup>+</sup>	4.99×10 <sup>-1</sup>	4.89×10 <sup>-1</sup>
Cl <sup>-</sup>	5.00×10 <sup>-1</sup>	5.00×10 <sup>-1</sup>
Ca <sup>2+</sup>	2.01×10 <sup>-3</sup>	3.58×10 <sup>-2</sup>
CO <sub>2aq</sub>	1.98×10 <sup>-4</sup>	1.08
H <sup>+</sup>	5.44×10 <sup>-8</sup>	1.67×10 <sup>-5</sup>
OH <sup>-</sup>	1.29×10 <sup>-6</sup>	4.25×10 <sup>-9</sup>
CO <sub>3</sub> <sup>2-</sup>	1.43×10 <sup>-5</sup>	8.85×10 <sup>-7</sup>
NaHCO <sub>3aq</sub>	6.63×10 <sup>-4</sup>	1.13×10 <sup>-2</sup>
pH	7.26	4.78

330

331 **Table 4.** Initial (sub-index 0) and boundary conditions (sub-index bc) in terms of the chemical  
 332 components. The translation of aqueous species to component species and viceversa can be  
 333 seen in Appendix A.

Component species	Concentration [mol/(kg water)]	Component species	Concentration [mol/(kg water)]
u <sub>HCO<sub>3,0</sub></sub>	4.02×10 <sup>-3</sup>	u <sub>HCO<sub>3,bc</sub></sub>	7.17×10 <sup>-2</sup>
u <sub>Na<sub>0</sub></sub>	5.00×10 <sup>-1</sup>	u <sub>Na<sub>bc</sub></sub>	5.00×10 <sup>-1</sup>
u <sub>Ca<sub>0</sub></sub>	2.01×10 <sup>-3</sup>	u <sub>Ca<sub>bc</sub></sub>	3.58×10 <sup>-2</sup>
u <sub>CO<sub>2,0</sub></sub>	1.82×10 <sup>-4</sup>	u <sub>CO<sub>2,bc</sub></sub>	1.08

334



335 *2.11. Various reactive transport scenarios*

336 Various reactive transport scenarios (Table 5) for leaking CO<sub>2</sub>-saturated brine are  
337 performed to analyze the effects of different transport processes on the mobility and  
338 retention of CO<sub>2aq</sub>, as well as the variations in the medium's porosity and permeability  
339 along the leakage pathway driven by geochemical reactions. The transport modelling  
340 of leaking CO<sub>2</sub>-saturated brine is performed for a period of 500 years.

341 *2.11.1. Base-case transport scenarios*

342 We denote scenarios 1, 2, 3 and 4 as the base cases, aimed at investigating the roles of  
343 advection and dispersion in the rock matrix (advection-dominated transport) compared  
344 to diffusion alone (diffusive transport). In all cases, advection, diffusion and dispersion  
345 are considered to occur in the fracture. In scenarios 1 and 3, the mass transport in the  
346 rock matrix is modelled by considering that the only active transport process is  
347 diffusion, while scenarios 2 and 4 include advection and dispersion alongside diffusion  
348 in the rock matrix. Sorption is included in scenarios 3 and 4. The longitudinal and  
349 transverse dispersivity values for transport scenarios 1 and 3 are 10 m and 1 m,  
350 respectively, in the fracture and zero in the rock matrix. The same longitudinal and  
351 transverse dispersivity values are used in transport scenarios 2 and 4, but now both in  
352 the fracture and the rock matrix. The dispersivity values are related to the length scale  
353 of the transport domain, as reported by Gelhar et al. (1992).

354

355

356

357

358 Table 5. Various base-case reactive transport scenarios (1, 2, 3 and 4) and the reactive  
 359 transport scenarios (5, 6, 7 and 8) in the sensitivity analysis.

Reactive transport scenario	Partition coefficient [m <sup>3</sup> /kg]	Initial velocity [m/year]	Longitudinal dispersivity in fracture / matrix [m]	Advection in the matrix	Excess pressure at the bottom [Pa]
1	0	10	10 / 0	N	71.625
2	0	10	10 / 10	Y	71.625
3	2.5×10 <sup>-4</sup>	10	10 / 0	N	71.625
4	2.5×10 <sup>-4</sup>	10	10 / 10	Y	71.625
5	0	5	10 / 10	Y	20.750
6	0	15	10 / 10	Y	122.50
7	0	10	20 / 20	Y	71.625
8	0	10	30 / 30	Y	71.625

360

361 *2.11.2. Sensitivity analysis*

362 Sensitivity analysis is performed to investigate the roles of fluid velocity and  
 363 dispersivity on the reactive transport of CO<sub>2aq</sub> along the leakage pathway. Thus, we  
 364 perform additional reactive transport scenarios 5, 6, 7 and 8 (Table 5). Scenarios 5 and  
 365 6 involve, respectively, maximum fluid velocities of nearly 5 m/year and 15 m/year at  
 366 the bottom (inlet) of the fracture, matching the regional-scale Darcy velocities that are  
 367 characteristic of deep sedimentary basins (Bachu et al., 1994). These velocities are achieved  
 368 by applying an excess pressure of 20.75 Pa and 122.50 Pa, respectively, in addition to the  
 369 prevailing hydrostatic pressure at the bottom boundary. Pressures are kept constant in time, so  
 370 that velocities vary in space and time driven by changes in porosity and permeability caused  
 371 by mineral reaction. The longitudinal dispersivity values in scenarios 7 and 8 are 20 m  
 372 and 30 m, respectively, in both the fracture and the rock matrix. A transverse  
 373 dispersivity of 1 m is used in both the fracture and the rock matrix for transport  
 374 scenarios 5 to 8 (sensitivity not tested).

375 *2.12. Methodology of calculating the mass conversion of CO<sub>2aq</sub> in geochemical reactions*

376 The mass conversion of CO<sub>2aq</sub> in geochemical reactions in each reactive transport  
377 scenario (Table 5) is calculated by comparing the mass balances with those from  
378 conservative transport scenarios (thus neglecting all the geochemical reactions in Table  
379 1). The mass balance of CO<sub>2aq</sub> in each scenario is calculated by considering the  
380 cumulative mass that enters the transport domain through the bottom inflow boundary,  
381 the mass that leaves through the top open boundary, and the mass that is stored in the  
382 aqueous and adsorbed states in the transport domain over time. The mass conversion of  
383 CO<sub>2aq</sub> in geochemical reactions is presented in each reactive transport scenario as a  
384 percentage of the mass inflow as  $\% m_{con} = \frac{m_{con}}{m_{in}} 100$ , that is, the ratio between the  
385 cumulative mass conversion of CO<sub>2aq</sub> in geochemical reactions ( $m_{con}$ ) and its  
386 cumulative mass inflow ( $m_{in}$ ) over time.

387 *2.13. Numerical solution technique*

388 The reactive transport coupled system of equations ((1)-(11)) with the corresponding  
389 initial and boundary conditions is modelled in COMSOL Multiphysics<sup>®</sup>. The flow and  
390 transport are modelled by adopting a one-domain approach with a single set of  
391 transport equations for the entire domain (fracture plus rock matrix) (Goyeau et al.,  
392 2003; Jamet et al., 2009; Tao et al., 2013; Basirat et al., 2015). In this study, we solve  
393 the non-linear system of equations that arises from coupled reactive transport  
394 modelling by using a segregated approach, which sequentially solves the various  
395 physics that are involved. Thus, the solution includes segregated solution steps with  
396 individual custom damping and tolerance. A damped version of Newton's method is  
397 used in all steps, with damping factors that equal unity. The flow problem (pressure  
398 and velocity field) is solved first (segregated step 1), the transport problem for

399 conservative species (components) is next (step 2), followed by the speciation problem  
400 (finding the aqueous species as a function of transport component species) in step 3;  
401 finally, the mass conservation equation of kinetic mineral calcite is solved in step 4. An  
402 implicit non-linear solver that is based on the backward differentiation formula (BDF)  
403 is used for time marching. The Jacobian matrix is updated every iteration to make the  
404 solver more stable. A structured mesh with quadrilateral elements is used as the  
405 numerical grid in the transport domain (fracture plus rock matrix). The mesh is refined  
406 in and near the fracture and towards the bottom inlet boundary (supplementary  
407 material). The complete mesh consists of 16560 quadrilateral elements. A total of  
408 269509 degrees of freedom (DOF) are solved. The average time for solving each of the  
409 reactive transport scenarios is nearly 12 hours on an Intel(R) Core(TM)2 Quad CPU  
410 with RAM of 16 GB.

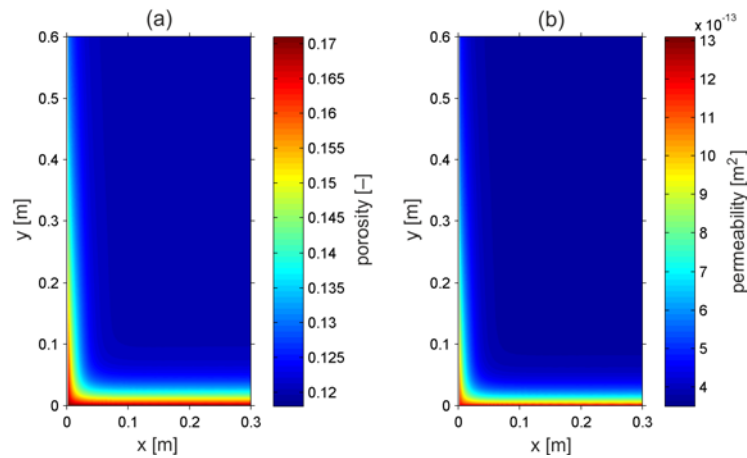
### 411 **3. Results**

412 The mixing of leaking CO<sub>2</sub>-saturated brine with the resident pore waters in the  
413 transport domain (both the fracture and rock matrix in the clay-rich caprock) created a  
414 fluid under-saturated with respect to calcite, thus initiating calcite dissolution near the  
415 bottom inflow boundary. Calcite within the transport domain might dissolve or  
416 precipitate depending on the evolving geochemical conditions during the simulation.

#### 417 *3.1. Base-case reactive transport scenarios*

418 The calcite dissolution and precipitation reactions, which are driven by leaking CO<sub>2</sub>-  
419 saturated brine, caused variations in the medium's porosity and permeability in space  
420 and time along the transport pathway. Fig. 2a and 2b show the variations in the  
421 porosity and permeability in the rock matrix for the reactive transport scenario 2 after a  
422 simulation time of 500 years. The rock matrix's porosity increased by nearly 42% from

423 the initial value of 0.12 to a value of 0.17, whereas the permeability attained a value of  
 424  $1.337 \times 10^{-12} \text{ m}^2$  from its initial value of  $3.71 \times 10^{-13} \text{ m}^2$ . This increase was mostly  
 425 concentrated near the bottom inflow boundary because of continued calcite dissolution,  
 426 which was driven by leaking  $\text{CO}_2$ -saturated brine. A negligible decrease in porosity  
 427 and permeability was observed towards the top of the transport domain along the  
 428 conducting fracture, which indicates a small amount of calcite precipitation.



429

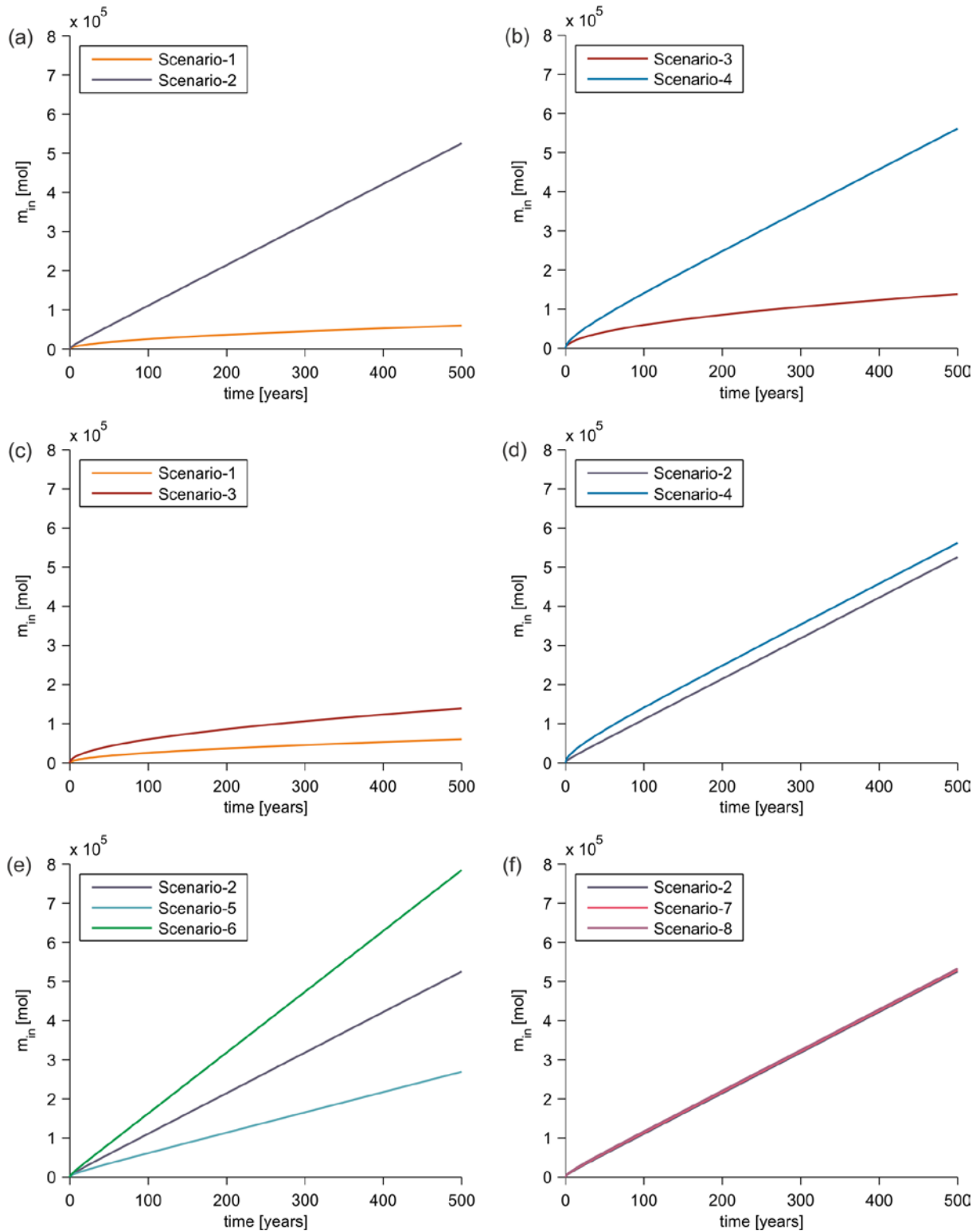
430 Figure 2. Variations in the porosity (a) and permeability (b) of the rock matrix in the base-  
 431 case reactive transport scenario 2 after 500 years.

432

433 *3.1.1. Role of advection and dispersion in the rock matrix*

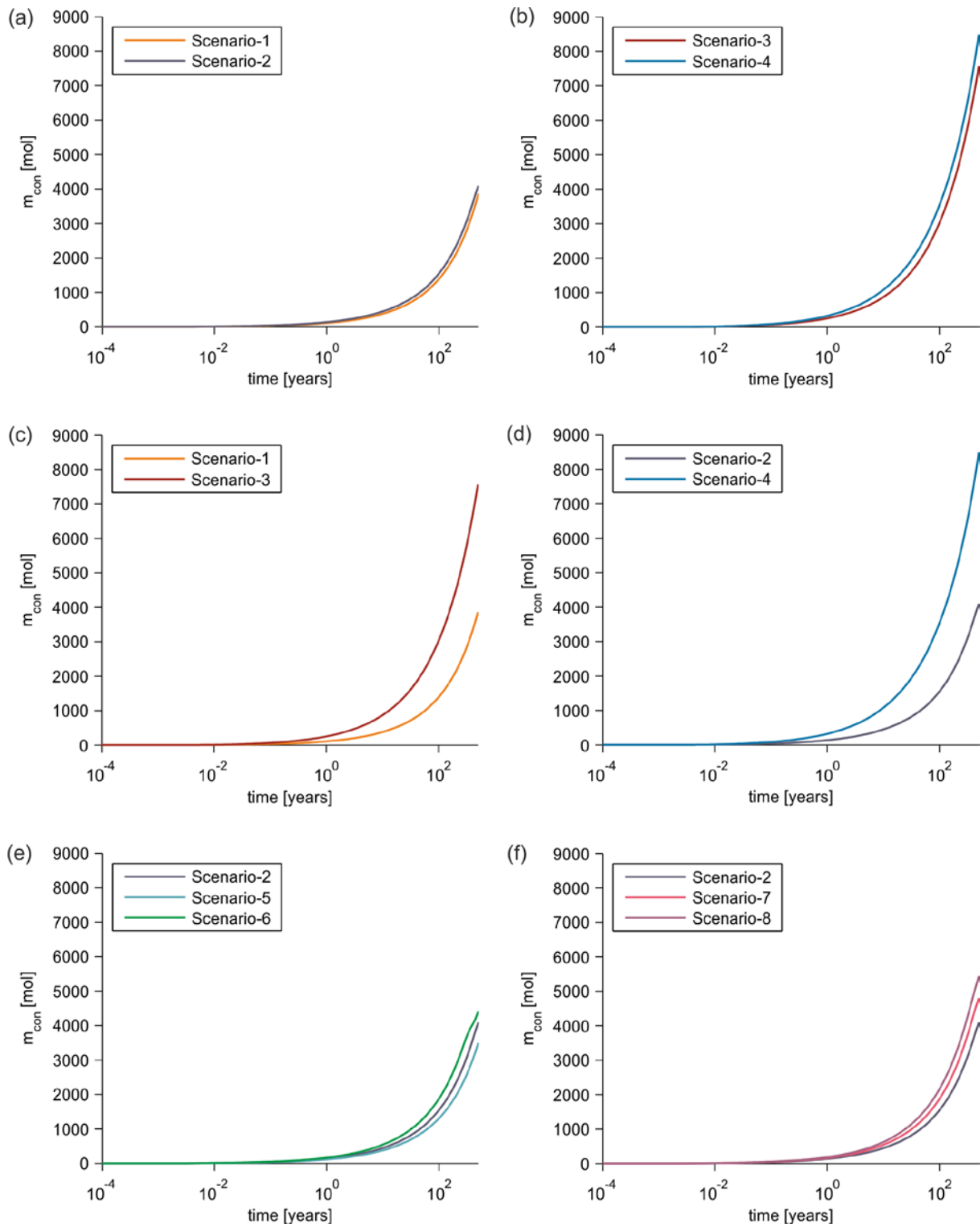
434 Figs. 3, 4 and 5 present the mass of  $\text{CO}_{2\text{aq}}$  that entered the transport domain from the reservoir  
 435 through the inflow boundary, its mass conversion in geochemical reactions and percent mass  
 436 conversion, respectively, in the various studied reactive transport scenarios. In the advection-  
 437 dominated transport scenarios 2 and 4, the combination of advection, dispersion and diffusion  
 438 transport processes increased the leakage of  $\text{CO}_{2\text{aq}}$  from the reservoir (Fig. 3a, 3b) and mass  
 439 conversion during the geochemical reactions (Fig. 4a, 4b) along the transport domain  
 440 compared to the corresponding values in diffusive transport scenarios 1 and 3.

441 The mass balances of  $\text{CO}_{2\text{aq}}$  in the transport domain in the base-case reactive transport  
442 scenarios 1, 2, 3 and 4 after 500 years are reported in Table 6. This table lists the  $\text{CO}_{2\text{aq}}$  mass  
443 inflows from the reservoir, the mass that was stored in aqueous and adsorbed states, the mass  
444 that was converted in geochemical reactions, and the mass that left the transport domain  
445 through the top open boundary.



446

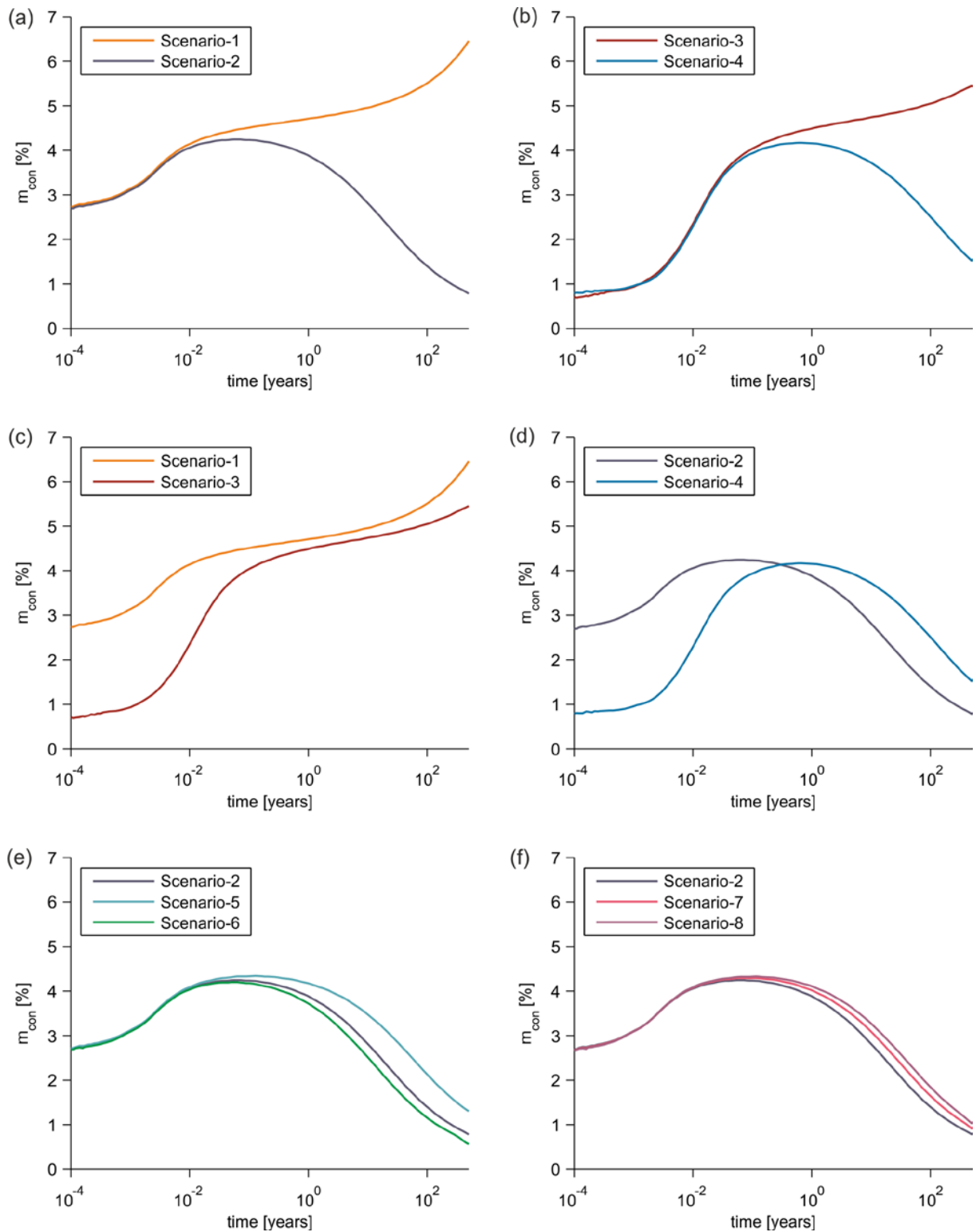
447 Figure 3. Mass inflow of  $\text{CO}_{2\text{aq}}$  through the bottom inflow boundary in various reactive  
 448 transport scenarios over time: (a) scenarios 1 and 2; (b) scenarios 3 and 4; (c) scenarios 1 and  
 449 3; (d) scenarios 2 and 4; (e) scenarios 2, 5 and 6; and (f) scenarios 2, 7 and 8.



450

451 Figure 4. Mass conversion of  $\text{CO}_{2\text{aq}}$  in various reactive transport scenarios over time: (a)  
 452 scenarios 1 and 2; (b) scenarios 3 and 4; (c) scenarios 1 and 3; (d) scenarios 2 and 4; (e)  
 453 scenarios 2, 5 and 6; and (f) scenarios 2, 7 and 8.





454

455 Figure 5. Percentage mass conversion of  $\text{CO}_{2\text{aq}}$  in various reactive transport scenarios over  
 456 time; (a) scenarios 1 and 2; (b) scenarios 3 and 4; (c) scenarios 1 and 3; (d) scenarios 2 and 4;  
 457 (e) scenarios 2, 5 and 6; and (f) scenarios 2, 7 and 8.  
 458

459 The total mass inflow was split in terms of advective, dispersive and diffusive fluxes  
 460 through the bottom inflow boundary both at the fracture and in the rock matrix. The  
 461 highest mass inflow, mass that was stored in an aqueous state and mass conversion of  
 462 CO<sub>2aq</sub> were associated with the advection-dominated transport scenarios 2 and 4  
 463 compared to the values in the corresponding diffusive transport scenarios 1 and 3.  
 464 Higher stored mass in an adsorbed state can also be observed in the advection-  
 465 dominated transport scenario 4 compared to the corresponding diffusive transport  
 466 scenario 3. The mass balance errors were less than 0.1% in all the scenarios.

467 **Table 6.** CO<sub>2aq</sub> mass balance [mol] in the base-case reactive transport scenarios 1, 2, 3, and 4  
 468 after 500 years.

Reactive transport scenarios	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Total mass that entered the domain	$5.98 \times 10^4$	$5.26 \times 10^5$	$1.39 \times 10^5$	$5.62 \times 10^5$
Mass that entered from advection (fracture)	$5.70 \times 10^3$	$5.56 \times 10^3$	$6.04 \times 10^3$	$5.78 \times 10^3$
Mass that entered from diffusion (fracture)	$1.79 \times 10^0$	$2.94 \times 10^{-1}$	$3.85 \times 10^0$	$1.68 \times 10^0$
Mass that entered from dispersion (fracture)	$3.19 \times 10^3$	$5.12 \times 10^2$	$7.21 \times 10^3$	$3.02 \times 10^3$
Mass that entered from advection (matrix)	0	$5.12 \times 10^5$	0	$5.12 \times 10^5$
Mass that entered from diffusion (matrix)	$5.09 \times 10^4$	$4.86 \times 10^3$	$1.26 \times 10^5$	$2.49 \times 10^4$
Mass that entered from dispersion (matrix)	0	$3.12 \times 10^3$	0	$1.60 \times 10^4$
Mass that left the domain (fracture)	$9.24 \times 10^{-1}$	$1.69 \times 10^2$	$9.14 \times 10^{-1}$	$9.14 \times 10^{-1}$
Mass that left the domain (matrix)	$0.00 \times 10^0$	$3.32 \times 10^3$	$0.00 \times 10^0$	$8.65 \times 10^1$
Mass stored in an aqueous state	$5.59 \times 10^4$	$5.19 \times 10^5$	$2.22 \times 10^4$	$9.31 \times 10^4$
Mass stored in an adsorbed state	$0.00 \times 10^0$	$0.00 \times 10^0$	$1.09 \times 10^5$	$4.60 \times 10^5$
Mass converted in the geochemical reactions	$3.86 \times 10^3$	$4.09 \times 10^3$	$7.57 \times 10^3$	$8.49 \times 10^3$
Mass conversion of CO <sub>2aq</sub> after 500 years (%)	$6.46 \times 10^0$	$7.79 \times 10^{-1}$	$5.45 \times 10^0$	$1.51 \times 10^0$
Error in the mass balance (%)	$1.82 \times 10^{-2}$	$-9.16 \times 10^{-2}$	$1.97 \times 10^{-2}$	$1.34 \times 10^{-2}$

469

470 The mass balance for mineral calcite and  $\text{Ca}^{2+}$  and the split for the mass of calcite [mol] and  
 471 pore volume [ $\text{m}^3$ ] in the fracture and rock matrix in the base-case transport scenarios 1, 2, 3  
 472 and 4 after 500 years are presented in Table 7. Calcite dissolution prevailed over precipitation  
 473 in the transport domain during the simulations, which implies a decrease in its mass and  
 474 increase in the overall pore volume in the fracture and rock matrix. Considering advection in  
 475 the rock matrix (scenarios 2 and 4) increased the calcite dissolution, pore volume and mass of  
 476  $\text{Ca}^{2+}$  compared to the corresponding diffusive transport scenarios 1 and 3. Moreover,  
 477 relatively higher calcite dissolution occurred in the fracture than in the rock matrix compared  
 478 to the initial mass of calcite in the fracture and rock matrix because of the higher advective  
 479 velocity in the former. Finally, the mass of produced  $\text{Ca}^{2+}$  was equal to the mass of dissolved  
 480 calcite (except for the mass balance errors of less than 0.14%).

481 **Table 7.** Mass balance [mol] of calcite and  $\text{Ca}^{2+}$  and increase in the pore volume [ $\text{m}^3$ ] in the  
 482 transport domain for the base-case reactive transport scenarios (1, 2, 3, and 4) after 500 years.

Reactive transport scenarios	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Mass of dissolved calcite in the fracture	$7.26 \times 10^0$	$7.33 \times 10^0$	$1.24 \times 10^1$	$1.36 \times 10^1$
Decrease in mass in the fracture (%)	$2.31 \times 10^0$	$2.33 \times 10^0$	$3.94 \times 10^0$	$4.33 \times 10^0$
Mass of dissolved calcite in the rock matrix	$3.81 \times 10^3$	$4.07 \times 10^3$	$7.58 \times 10^3$	$8.36 \times 10^3$
Decrease in mass in the rock matrix (%)	$1.10 \times 10^{-2}$	$1.18 \times 10^{-2}$	$2.19 \times 10^{-2}$	$2.42 \times 10^{-2}$
Total mass of dissolved calcite	$3.81 \times 10^3$	$4.08 \times 10^3$	$7.59 \times 10^3$	$8.38 \times 10^3$
Increase in pore volume in the fracture	$2.68 \times 10^{-4}$	$2.71 \times 10^{-4}$	$4.57 \times 10^{-4}$	$5.02 \times 10^{-4}$
Increase in pore volume in the rock matrix	$1.41 \times 10^{-1}$	$1.50 \times 10^{-1}$	$2.80 \times 10^{-1}$	$3.09 \times 10^{-1}$
Total increase in the pore volume	$1.41 \times 10^{-1}$	$1.51 \times 10^{-1}$	$2.80 \times 10^{-1}$	$3.09 \times 10^{-1}$
Mass of produced $\text{Ca}^{2+}$	$3.81 \times 10^3$	$4.08 \times 10^3$	$7.58 \times 10^3$	$8.37 \times 10^3$
Error in the mass balance (%)	$-1.03 \times 10^{-1}$	$-4.75 \times 10^{-2}$	$1.42 \times 10^{-1}$	$4.40 \times 10^{-2}$

483

484 Sorption in the transport scenarios 3 and 4 increased the  $\text{CO}_{2\text{aq}}$  leakage from the reservoir  
 485 (Fig. 3c, 3d) and mass conversion of  $\text{CO}_{2\text{aq}}$  in the geochemical reactions (Fig. 4c, 4d) in the  
 486 transport domain compared to the transport scenarios 1 and 2, which did not consider  
 487 sorption. Comparing the sorption scenario-3 with the corresponding no-sorption scenario 1  
 488 and the sorption scenario 4 with the no-sorption scenario 2 indicates that sorption almost

489 doubled the mass conversion of  $\text{CO}_{2\text{aq}}$  in the geochemical reactions (row 13 of Table 6);  
490 calcite dissolution (row 6 of Table 7), with an associated increase in pore volume (row 9 of  
491 Table 7); and production of  $\text{Ca}^{2+}$  (row 10 of Table 7).

492 Although the advection-dominated transport scenarios 2 and 4 increased the conversion of  
493  $\text{CO}_{2\text{aq}}$  mass [mol] in the geochemical reactions compared to the corresponding diffusive  
494 transport scenarios 1 and 3, decreasing trends in the percentage mass conversion were  
495 observed (Fig. 4a vs Fig. 5a and Fig. 4b vs Fig. 5b). Similarly, higher  $\text{CO}_{2\text{aq}}$  mass conversion  
496 occurred in the sorption transport scenarios 3 and 4 compared to the corresponding no-  
497 sorption transport scenarios 1 and 2, yet decreasing trends were observed for the percent mass  
498 conversion in these scenarios (Fig. 4c vs Fig. 5c and Fig. 4d vs Fig. 5d). This result can be  
499 explained by the variability in the  $\text{CO}_{2\text{aq}}$  mass inflows.

## 500 3.2. Sensitivity analysis

### 501 3.2.1. Role of velocity magnitude

502 Different initial fluid velocities prevailed in the fracture and rock matrix because of different  
503 excess pressure at the bottom boundary of the transport domain in scenarios 2, 5, and 6;  
504 velocities then changed during the simulation time due to variations in porosity and  
505 permeability. Mass inflows (Fig. 3e) and  $\text{CO}_{2\text{aq}}$  mass conversion in the reactions (Fig. 4e)  
506 increased with the initial fluid velocity in the transport pathway. However, the percentage of  
507 mass conversion of  $\text{CO}_{2\text{aq}}$  decreased with increasing fluid velocity (Fig. 5e). The mass  
508 conservation indicated that the mass inflow and mass conversion of  $\text{CO}_{2\text{aq}}$  in the geochemical  
509 reactions increased with increasing fluid velocity in the transport domain (Table 6 and 8).  
510 Additionally, the mass of dissolved calcite, the pore volume and the mass production of  $\text{Ca}^{2+}$   
511 increased with increasing fluid velocity in scenarios 2, 5 and 6.

512

513 **Table 8.** CO<sub>2aq</sub> mass balance [mol] for the different reactive transport scenarios 5, 6, 7, and 8  
 514 after 500 years.

Reactive transport scenarios	Scenario 5	Scenario 6	Scenario 7	Scenario 8
Total mass that entered the domain	$2.69 \times 10^5$	$7.85 \times 10^5$	$5.29 \times 10^5$	$5.33 \times 10^5$
Mass that entered from advection (fracture)	$2.77 \times 10^3$	$8.31 \times 10^3$	$5.60 \times 10^3$	$5.61 \times 10^3$
Mass that entered from diffusion (fracture)	$6.23 \times 10^{-1}$	$1.89 \times 10^{-1}$	$3.14 \times 10^{-1}$	$3.24 \times 10^{-1}$
Mass that entered from dispersion (fracture)	$5.42 \times 10^2$	$4.95 \times 10^2$	$1.10 \times 10^3$	$1.70 \times 10^3$
Mass that entered from advection (matrix)	$2.55 \times 10^5$	$7.68 \times 10^5$	$5.12 \times 10^5$	$5.12 \times 10^5$
Mass that entered from diffusion (matrix)	$9.03 \times 10^3$	$3.38 \times 10^3$	$4.75 \times 10^3$	$4.68 \times 10^3$
Mass that entered from dispersion (matrix)	$1.45 \times 10^3$	$4.85 \times 10^3$	$6.11 \times 10^3$	$9.04 \times 10^3$
Mass that left the domain (fracture)	$4.74 \times 10^{-1}$	$2.03 \times 10^3$	$2.92 \times 10^2$	$4.03 \times 10^2$
Mass that left the domain (matrix)	$4.32 \times 10^1$	$1.35 \times 10^5$	$6.26 \times 10^3$	$9.40 \times 10^3$
Mass stored in an aqueous state	$2.66 \times 10^5$	$6.42 \times 10^5$	$5.18 \times 10^5$	$5.18 \times 10^5$
Mass stored in an adsorbed state	0	0	0	0
Mass converted in the geochemical reactions	$3.50 \times 10^3$	$4.42 \times 10^3$	$4.81 \times 10^3$	$5.43 \times 10^3$
Mass conversion of CO <sub>2aq</sub> after 500 years (%)	$1.30 \times 10^0$	$5.63 \times 10^{-1}$	$9.10 \times 10^{-1}$	$1.02 \times 10^0$
Error in the mass balance (%)	$5.47 \times 10^{-3}$	$4.83 \times 10^{-2}$	$-1.01 \times 10^{-1}$	$-1.03 \times 10^{-1}$

515 **Table 9.** Mass balance [mol] of calcite and Ca<sup>2+</sup> and increase in the pore volume [m<sup>3</sup>] in the  
 516 transport domain for the different transport scenarios 5, 6, 7, and 8 after 500 years.  
 517

Reactive transport scenarios	Scenario 5	Scenario 6	Scenario 7	Scenario 8
Mass of dissolved calcite in the fracture	$4.65 \times 10^0$	$4.88 \times 10^0$	$7.43 \times 10^0$	$8.54 \times 10^0$
Decrease in mass in the fracture (%)	$1.48 \times 10^0$	$1.55 \times 10^0$	$2.36 \times 10^0$	$2.72 \times 10^0$
Mass of dissolved calcite in the rock matrix	$3.48 \times 10^3$	$4.43 \times 10^3$	$4.80 \times 10^3$	$5.40 \times 10^3$
Decrease in mass in the rock zone	$1.01 \times 10^{-2}$	$1.28 \times 10^{-2}$	$1.39 \times 10^{-2}$	$1.56 \times 10^{-2}$
Total mass of dissolved calcite	$3.49 \times 10^3$	$4.43 \times 10^3$	$4.80 \times 10^3$	$5.41 \times 10^3$
Increase in pore volume in the fracture	$1.72 \times 10^{-4}$	$1.80 \times 10^{-4}$	$2.74 \times 10^{-4}$	$3.15 \times 10^{-4}$
Increase in pore volume in the rock matrix	$1.29 \times 10^{-1}$	$1.63 \times 10^{-1}$	$1.77 \times 10^{-1}$	$1.99 \times 10^{-1}$
Total increase in the pore volume	$1.29 \times 10^{-1}$	$1.64 \times 10^{-1}$	$1.77 \times 10^{-1}$	$2.00 \times 10^{-1}$
Mass of produced Ca <sup>2+</sup>	$3.49 \times 10^3$	$4.43 \times 10^3$	$4.81 \times 10^3$	$5.41 \times 10^3$
Error in the mass balance (%)	$6.16 \times 10^{-3}$	$5.32 \times 10^{-2}$	$-1.07 \times 10^{-1}$	$-1.13 \times 10^{-1}$

518

519

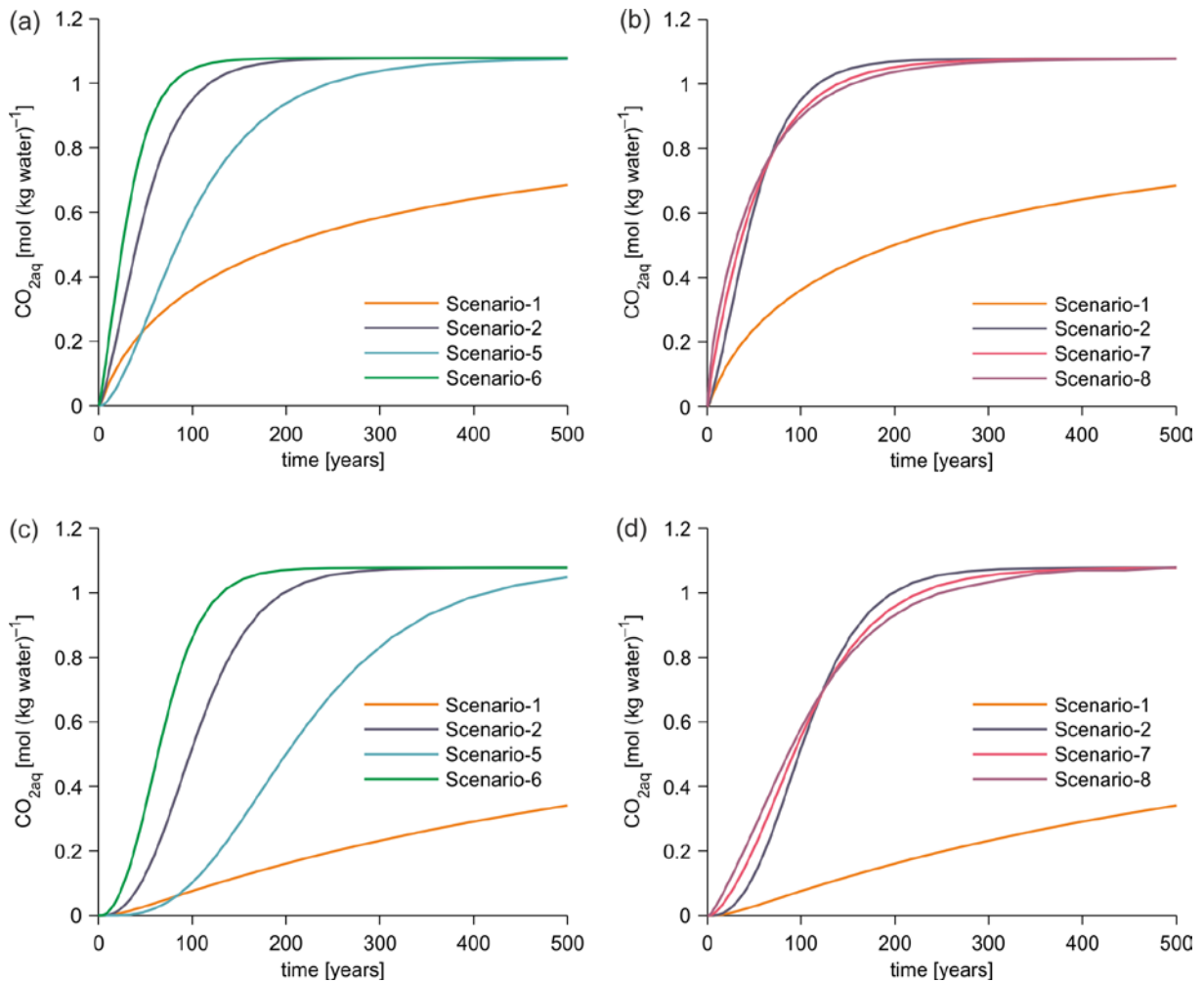
520 *3.2.2. Role of longitudinal dispersivity*

521 The higher longitudinal dispersivity very slightly increased the mass inflow ( $5.26 \times 10^5$ ,  
522  $5.29 \times 10^5$  and  $5.33 \times 10^5$  mol in scenarios 2, 7 and 8, respectively) (Figs. 3f and 4f; Tables 6  
523 and 8). However, the mass conversion of  $\text{CO}_{2\text{aq}}$  in the geochemical reactions (Fig. 4f) and  
524 percent mass conversion (Fig. 5f) increased with increasing dispersivity. In these scenarios,  
525 the higher quantities of  $\text{CO}_{2\text{aq}}$  that were converted in the geochemical reactions for almost the  
526 same mass inflows resulted in similar trends for  $\text{CO}_{2\text{aq}}$  mass conversion and its percentage of  
527 mass conversion (Figs. 4f and 5f; Table 8). For a given fluid velocity, the mass of dissolved  
528 calcite, the mass of produced  $\text{Ca}^{2+}$ , and the pore volume increased with the longitudinal  
529 dispersivity (Tables 7 and 9).

530 *3.3. Breakthrough curves of leaking  $\text{CO}_{2\text{aq}}$*

531 The effects of advection and dispersion in the rock matrix on the transport of leaking  $\text{CO}_{2\text{aq}}$   
532 are presented in the form of breakthrough curves, which represent its concentration at 10 and  
533 20 m locations from the bottom inlet boundary along the conducting fracture over time (Fig.  
534 6). Fast migration of  $\text{CO}_{2\text{aq}}$  along the leakage pathway was observed in the advection-  
535 dominated transport scenarios compared to the diffusive transport scenarios. Fast transport  
536 that was mainly driven by advection increased the  $\text{CO}_{2\text{aq}}$  concentration in the advection-  
537 dominated transport scenario 2 compared to the diffusive transport scenario 1 after a travel  
538 distance of 10 and 20 m along the conducting fracture. Additionally, the highest velocity in  
539 scenario 6 resulted in the highest concentration of  $\text{CO}_{2\text{aq}}$  (Fig. 6a and 6c). During earlier  
540 times, the higher dispersivity in scenario 8 increased the concentration of  $\text{CO}_{2\text{aq}}$  (Fig. 6b and  
541 6d). However, the lowest dispersivity value used in scenario 2 resulted in the highest  $\text{CO}_{2\text{aq}}$   
542 concentration after 67 and 135 years for the 10- and 20-m locations, respectively. This result

543 occurred because of the fast spreading and dilution of species concentration that was caused  
544 by higher dispersion along the transport pathway over time in scenario 8.



545  
546 Figure 6. Breakthrough curves for  $\text{CO}_{2\text{aq}}$  for various reactive transport scenarios at various  
547 locations along the fracture over time; (a) scenarios 1, 2, 5, and 6 at 10 m from the inflow  
548 boundary; (b) scenarios 1, 2, 7, and 8 at 10 m; (c) scenarios 1, 2, 5, and 6 at 20 m from the  
549 inflow boundary; and (d) scenarios 1, 2, 7, and 8 at 20 m.  
550

#### 551 4. Discussion

552 The role of calcite kinetics in contact with  $\text{CO}_2$ -saturated brine in the reservoir in the presence  
553 of free-phase  $\text{CO}_2$  in the reservoir has been investigated. For the purpose, two sets of  $\text{CO}_2$   
554 dissolution modelling have been performed for elevated values of  $\text{CO}_{2\text{aq}}$  in the presence of  
555 free-phase  $\text{CO}_2$  in the reservoir for calcite was (i) reactive and (ii) non-reactive. The presence

556 of calcite kinetics provided buffer and kept pH at a higher value of 4.78 whereas pH settled at  
557 3.56 in the absence of calcite reaction. This added alkalinity caused by calcite dissolution may  
558 shift  $\text{CO}_{2\text{aq}}$  into other ions in solution along the transport domain. Calcite dissolution in the  
559 reactive transport scenarios mainly occurred in close vicinity to the bottom inflow boundary  
560 (Gherardi et al., 2007; Andreani et al., 2008; Ellis et al., 2011b), resulting in the simultaneous  
561 production of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , which brought the brine solution closer to calcite saturation  
562 away from the inflow boundary. The resulting saturation conditions with respect to calcite  
563 stopped any significant calcite dissolution in the rock matrix beyond 0.1 m from the inflow  
564 boundary, and caused mineral precipitation towards the top of the transport domain, mainly  
565 close to the conducting fracture. However, calcite precipitation was too low to have any  
566 significant effect on the decrease in porosity and permeability in the fracture and rock matrix.

567 In scenario 6, the rock matrix's porosity attained a value of 0.17 after 500 years at the inflow  
568 boundary but reached a value of 0.15 (the initial one was 0.12) approximately 0.01 m from the  
569 boundary. However, the rock matrix's porosity close to the fracture was higher than 0.15 up  
570 to a distance of 0.25 m from the inflow boundary in scenario 6. This result can be explained  
571 by the fast transport along the fracture, which caused calcite dissolution to occur over a  
572 relatively longer distance.

573 Declining trends in the percent mass conversion after some initial times that were observed in  
574 Fig. 5d as compared to Fig. 5c, are related to additional advection in the rock matrix in the  
575 advection-dominated transport scenarios 2 and 4. The percent mass conversion in scenarios 2  
576 and 4 fell off after  $2.01 \times 10^6$  s and  $1.89 \times 10^7$  s, respectively (Fig. 5a, 5b, and 5d) but continued  
577 to increase in scenarios 1 and 3 (Fig. 5a, 5b, and 5c). Advection in scenarios 2 and 4 increased  
578 the mass inflows at an almost constant rate, whereas the mass inflow decreased with time in  
579 scenarios 1 and 3 due to the decreasing diffusive fluxes across the inflow boundary. Although  
580 the concentration gradients across the inflow boundary kept decreasing over time in all these



581 transport scenarios, the diffusive fluxes were the only transport process across the inflow  
582 boundary in the diffusive transport scenarios 1 and 3, which decreased the mass inflow  
583 compared to the corresponding inflows in the advection-dominated transport scenarios 2 and  
584 4. Thus, the higher mass inflow in scenarios 2 and 4 with time created declining trends in  
585 percent mass conversion (Fig. 5a, 5b, and 5d).

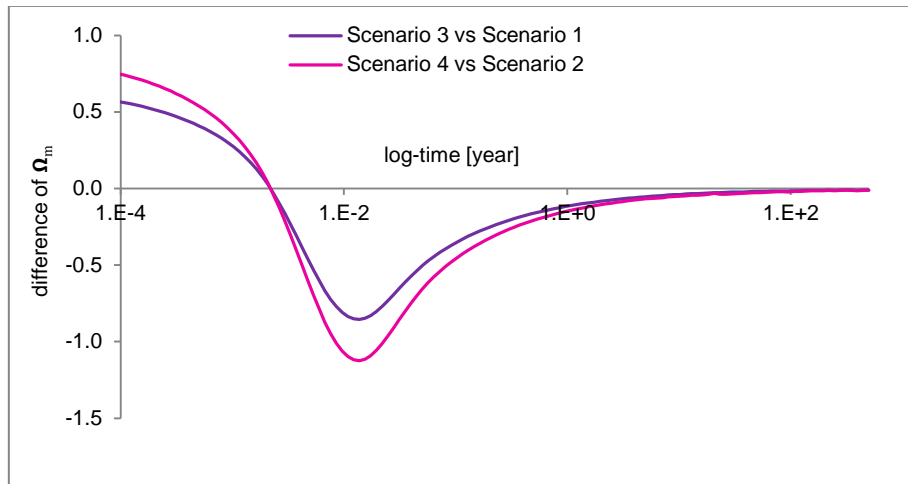
586 The higher observed mass conversion of  $\text{CO}_{2\text{aq}}$  in the geochemical reactions in sorption  
587 scenarios 3 and 4 compared to the corresponding no-sorption scenarios 1 and 2 (Fig. 4c and  
588 4d) were mainly related to (i) the higher mass inflows through the inflow boundary induced  
589 by sorption and, to a lesser extent, (ii) the lower saturation state of calcite in the transport  
590 domain when sorption was included in the simulations. Over time, relatively lower saturation  
591 of calcite (mineral) prevailed in the transport domain in the sorption scenarios 3 and 4  
592 compared to the no-sorption scenarios 1 and 2. The sorption process fixed the mass of  $\text{Ca}^{2+}$   
593 and  $\text{HCO}_3^-$  onto the rock surfaces and lowered the concentration of these species in an  
594 aqueous state. This process lowered the saturation state of calcite in the sorption scenarios 3  
595 and 4, promoting calcite dissolution and thus contributing towards the overall higher  $\text{CO}_{2\text{aq}}$   
596 mass conversion in the geochemical reactions in these scenarios.

597 Higher percent mass conversion occurred during earlier times in the no-sorption scenarios 1  
598 and 2 compared to the corresponding sorption scenarios 3 and 4 (Fig. 5c and 5d). This result  
599 mainly occurred because sorption (scenarios 3 and 4) induced relatively higher concentration  
600 gradients across the inflow boundary; thus, higher diffusive fluxes resulted in higher mass  
601 inflows. Sorption fixed the species' masses in an adsorbed state and reduced their  
602 concentrations in an aqueous state, increasing the concentration gradients and mass inflows  
603 and decreasing the percent mass conversion during these earlier times.

604 This study shows that pH distribution along the transport pathway alone cannot fully predict  
605 the calcite reaction kinetics and the related conversion of  $\text{CO}_{2\text{aq}}$  into other ions; instead the  
606 reactive process is mostly controlled by the saturation state of calcite. As an example, at a pH  
607 of 7.26, the brine was at saturation with respect to calcite and thus no reaction occurred in the  
608 transport domain before leakage of  $\text{CO}_2$ -saturated brine started taking place. On the other  
609 hand, leaking  $\text{CO}_2$ -saturated brine was at a pH of 4.78, and also saturated with respect to  
610 calcite, so again no reaction was driven. It was only the mixing of the two fluids (one  
611 prevailing in the transport pathway and the other one leaking from the reservoir) that brought  
612 the saturation state of calcite below one and caused calcite dissolution, concentrated initially  
613 in the vicinity of the lower leaking boundary. Over time, the calcite reaction zone advanced in  
614 the transport domain; however, due to the increase in  $\text{Ca}^{+2}$  and  $\text{HCO}_3^-$  as a result of calcite  
615 dissolution, the saturation state started increasing away from the lower leaking boundary.  
616 Eventually geochemical conditions evolved when saturation state with respect to calcite  
617 reached one; as a consequence, calcite dissolution ceased even though the pH value was 4.78  
618 (representing leaking  $\text{CO}_2$ -saturated brine), much lower than the initial value of 7.26  
619 prevailing in the transport pathway. This shows that the fall in the pH value along the  
620 transport pathway did not fully predict the calcite reaction regimes; instead calcite reactivity  
621 and related conversion of  $\text{CO}_{2\text{aq}}$  was found related to saturation state of calcite in the transport  
622 domain for the modelled leakage scenarios.

623 We computed the saturation state of calcite in the full domain (fracture plus rock matrix) in  
624 the no-sorption scenarios 1 and 2 and the corresponding sorption scenarios 3 and 4 over a  
625 simulation time of 500 years to further illustrate the role of sorption in maintaining a  
626 relatively lower saturation state of calcite, inducing dissolution. The saturation state of calcite  
627 was computed as its integral over the entire domain and simulation time. Fig. 7 presents the  
628 difference of the saturation state of calcite between the sorption scenarios and the

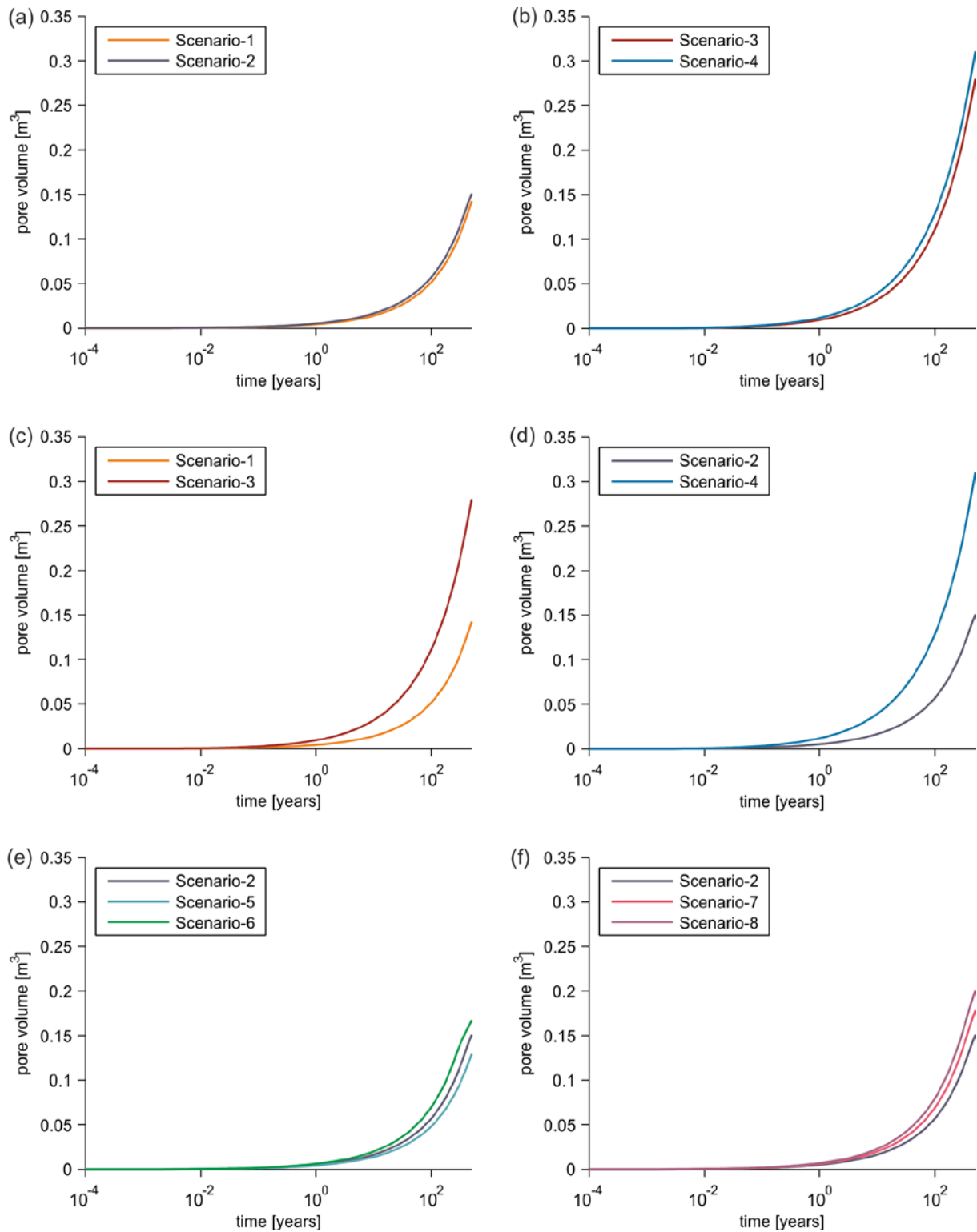
629 corresponding no-sorption scenarios. Except for the very early times ( $2.34 \times 10^{-3}$  year), the  
 630 saturation state of calcite remained lower in the sorption scenarios 3 and 4 compared to the  
 631 corresponding no-sorption scenarios 1 and 2. The resulting low saturation state of calcite from  
 632 sorption increased the conversion of  $\text{CO}_2$  through the higher dissolution of calcite.



633

634 Figure 7. Difference of the saturation state of calcite ( $\Omega_m$ ) in the transport domain over time:  
 635 between the sorption scenario 3 and the corresponding no-sorption scenario 1; and between the  
 636 sorption scenario 4 and the corresponding no-sorption scenario 2.  
 637

638 The steep observed gradients of the percent mass conversion of  $\text{CO}_{2\text{aq}}$  during the early times  
 639 in all the reactive transport scenarios are related to the prevailing higher calcite dissolution  
 640 reaction rate and associated higher mass conversion of  $\text{CO}_{2\text{aq}}$  relative to the mass inflow  
 641 through the bottom inflow boundary. During the earlier times, leaking  $\text{CO}_2$ -saturated brine  
 642 induced the lowest saturation of calcite and, thus, the highest calcite dissolution reaction rate  
 643 and  $\text{CO}_{2\text{aq}}$  mass conversion. Furthermore, the mass conversion of  $\text{CO}_{2\text{aq}}$  in the geochemical  
 644 reactions for all the reactive transport scenarios was well correlated with the calcite  
 645 dissolution and associated increase in pore volume in the transport domain over time (Fig. 4  
 646 vs Fig. 8).



647

648 Figure 8. Increase in pore volume within the transport domain from calcite dissolution in  
 649 various reactive transport scenarios over time: (a) scenarios 1 and 2; (b) scenarios 3 and 4; (c)  
 650 scenarios 1 and 3; (d) scenarios 2 and 4; (e) scenarios 2, 5 and 6; and (f) scenarios 2, 7 and 8.  
 651

652 For the same initial fluid velocity at the bottom boundary of the fracture, the highest  $\text{CO}_{2\text{aq}}$   
653 concentration along the fracture in the advection-dominated transport scenario 2 indicates  
654 lower mass transfer from the conducting fracture into the rock matrix, when compared to that  
655 in the diffusive transport scenario 1 (Fig. 6a, 6b). The fast transport of  $\text{CO}_{2\text{aq}}$  from advection  
656 in the rock matrix in the advection-dominated transport scenario 2 created low concentration  
657 gradients across the fracture-matrix interface that, in turn, decreased the diffusive mass  
658 transfer from the conducting fracture into the rock matrix.

## 659 **5. Conclusions**

660 This work presents the results of reactive transport simulations of  $\text{CO}_2$ -saturated brine  
661 that leaks along a conducting fracture and a surrounding rock matrix in clay-rich  
662 caprock. The model that was developed here considered the effects of advection,  
663 dispersion and diffusion in both the fracture and rock matrix on the quantities of leaked  
664  $\text{CO}_{2\text{aq}}$ , the evolution of the medium's porosity and permeability because of  
665 geochemical reactions, and the conversion of  $\text{CO}_{2\text{aq}}$  in geochemical reactions along the  
666 leakage pathway.

667 Advection and dispersion in addition to diffusion in the rock matrix increased the  
668 leakage of  $\text{CO}_{2\text{aq}}$  from the reservoir and its transport speed along the leakage pathway  
669 (arriving faster and further) as compared to the scenarios where transport occurred only  
670 by diffusion in the rock matrix. The amount of  $\text{CO}_{2\text{aq}}$  that leaked from the reservoir  
671 was also found to increase with fluid velocity along the leakage pathway. The mass  
672 conversion of  $\text{CO}_{2\text{aq}}$  in the geochemical reactions was found to increase with the fluid  
673 velocity and dispersion for the same set of hydraulic and geochemical parameters. The  
674 observed increase in  $\text{CO}_{2\text{aq}}$  leakage from the reservoir and the amount that was  
675 consumed in the geochemical reactions implies that advection and dispersion in the

676 rock matrix are important transport processes that must be considered in addition to  
 677 diffusion when modelling the leakage of  $\text{CO}_{2\text{aq}}$  along a fractured pathway.

678

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685

686

## APPENDIX

687 **Appendix A: Writing the chemical component species from the aqueous species involved**  
 688 **in the equilibrium and mineral kinetic reactions for the reactive transport system**

689 A total of eight aqueous species ( $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{CO}_{2\text{aq}}$ ,  $\text{Ca}^{2+}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{NaHCO}_{3\text{aq}}$ )  
 690 are involved in four of the equilibrium reactions (R1) to (R4) and the mineral kinetic reaction  
 691 (R5), which are presented in Table 1. Following the formulation by Saaltink et al. (1998),  
 692 these eight aqueous species can be converted into four chemical components and written in

693 vector form:  $\mathbf{u}^T = \left( u_{\text{HCO}_3}, u_{\text{Na}}, u_{\text{CO}_2}, u_{\text{Ca}} \right)^T$ , with the components defined as

$$\begin{cases}
 u_{\text{HCO}_3} = c_{\text{HCO}_3^-} - c_{\text{H}^+} + c_{\text{OH}^-} + 2c_{\text{CO}_3^{2-}} + c_{\text{NaHCO}_{3\text{aq}}} \\
 u_{\text{Na}} = c_{\text{Na}^+} + c_{\text{NaHCO}_{3\text{aq}}} \\
 u_{\text{CO}_2} = c_{\text{CO}_{2\text{aq}}} + c_{\text{H}^+} - c_{\text{OH}^-} - c_{\text{CO}_3^{2-}} \\
 u_{\text{Ca}} = c_{\text{Ca}^{2+}}
 \end{cases} \quad (\text{A.1})$$

694

695 By transforming all the aqueous species in the reactions into the component species,  
 696 the required number of transport equations decreases to four (number of chemical  
 697 component species) from the original eight (number of aqueous species). The  
 698 source/sink term in transport equation (1) takes the following form:

$$699 \quad \mathbf{r}_{\mathbf{kin}} = \begin{cases} r_{u\text{HCO}_3} = 2r_m \\ r_{u\text{Na}} = 0 \\ r_{u\text{CO}_2} = -r_m \\ r_{u\text{Ca}} = r_m \end{cases} \quad (\text{A.2})$$

700 Thus, the source/sink term ( $\mathbf{r}_{\mathbf{kin}}$ ) provides information regarding the changes in the chemical  
 701 component species that are driven by the combined effects of equilibrium and mineral kinetic  
 702 reactions in the reactive transport equation (1). The term ( $r_m$ ) represents the kinetic reaction  
 703 (dissolution or precipitation) of mineral calcite, which was defined in equation (4). From  
 704 (A.2) it is immediately seen that  $\mathbf{r}_{\mathbf{kin}}$  is only a function of the kinetic reaction; this means  
 705 that components are independent of the equilibrium reaction (which is actually the  
 706 definition).

## 707 A.2 Speciation modelling

708 The transport of component species by equation (1) requires calculating the aqueous species  
 709 concentration at every node of the computational domain. The concentration of aqueous  
 710 species is obtained from the solution of the following eight algebraic equations (A.3 through  
 711 A.10), which result from four of the equilibrium reactions (R1) to (R4) and the mineral kinetic  
 712 reaction (R5):

$$713 \quad \left( c_{\text{H}^+} \gamma_{\text{H}^+} c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} \right) - \left( c_{\text{CO}_2\text{aq}} \gamma_{\text{CO}_2\text{aq}} K_{\text{CO}_2\text{aq}} \right) = 0 \quad (\text{A.3})$$

714 
$$\left(c_{\text{H}^+} \gamma_{\text{H}^+} c_{\text{OH}^-} \gamma_{\text{OH}^-}\right) - (K_{\text{H}_2\text{O}}) = 0 \quad (\text{A.4})$$

715 
$$\left(c_{\text{H}^+} \gamma_{\text{H}^+} c_{\text{CO}_3^{2-}} \gamma_{\text{CO}_3^{2-}}\right) - \left(c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} K_{\text{HCO}_3^-}\right) = 0 \quad (\text{A.5})$$

716 
$$\left(c_{\text{NaHCO}_3\text{aq}} \gamma_{\text{NaHCO}_3\text{aq}}\right) - \left(c_{\text{Na}^+} \gamma_{\text{Na}^+} c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} K_{\text{Na}^+}\right) = 0 \quad (\text{A.6})$$

717 
$$u_{\text{HCO}_3^-} - \left(c_{\text{HCO}_3^-} - c_{\text{H}^+} + c_{\text{OH}^-} + 2c_{\text{CO}_3^{2-}} + c_{\text{NaHCO}_3\text{aq}}\right) = 0 \quad (\text{A.7})$$

718 
$$u_{\text{Na}} - \left(c_{\text{Na}^+} + c_{\text{NaHCO}_3\text{aq}}\right) = 0 \quad (\text{A.8})$$

719 
$$u_{\text{CO}_2} - \left(c_{\text{CO}_2\text{aq}} + c_{\text{H}^+} - c_{\text{OH}^-} - c_{\text{CO}_3^{2-}}\right) = 0 \quad (\text{A.9})$$

720 
$$c_{\text{Ca}^{2+}} = u_{\text{Ca}} \quad (\text{A.10})$$

721



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