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Convective mixing fingers and chemistry interaction in carbon storage

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ABSTRACT

Dissolution of carbon-dioxide into formation fluids during carbon capture and storage (CCS) can generate an instability with a denser CO_2-rich fluid located above the less dense native aquifer fluid. This instability promotes convective mixing, enhancing CO_2 dissolution and favouring the storage safety. Convective mixing has been extensively analysed in the context of CCS over the last decade, however the interaction between convective mixing and geochemistry has been insufficiently addressed. This relation is explored using a fully coupled model taking into account the porosity and permeability variations due to dissolution-precipitation reactions in a realistic geochemical system based on the Hontomín (Spain) potential CCS site project. This system, located in a calcite, dolomite, and gypsum bearing host rock, has been analysed for a variety of Rayleigh and Damköhler values. Results show that chemical reactions tend to enhance CO_2 dissolution. The model illustrates the first stages of porosity channel development, demonstrating the significance of fluid mixing in the development of porosity patterns. The influence of non-carbon species on CO_2 dissolution shown in this study demonstrates the needs for realistic chemical and kinetic models to ensure the precision of physical models to accurately represent the carbon-dioxide injection process.

1. Introduction

Carbon capture and storage (CCS) may be the most promising measure for mitigating anthropogenic greenhouse gas emissions (Boot-Handford et al., 2014; Chu, 2009; Edenhofer et al., 2014; Haszeldine, 2009; Lackner, 2003; Metz et al., 2005; Oelkers and Cole, 2008). A likely storage host for much of this CO_2 is deep saline aquifers, as they are widely distributed around the globe and have a large potential storage capacity (Bachu, 2003; Bradshaw et al., 2007; Firoozabadi and Cheng, 2010; Metz et al., 2005; Michael et al., 2010; Orr, 2009; Szulczewski et al., 2012).

The target formations for subsurface geological storage are usually selected to preserve CO_2 in a supercritical state. Supercritical carbon dioxide is commonly less dense and viscous than the surrounding native formation fluid and migrates upwards until it reaches an impervious caprock. Once at this caprock, supercritical CO_2 spreads laterally. During its migration, some CO_2 will dissolve into the fluid creating a transition zone. This CO_2-rich aqueous fluid is approximately 1% denser than the native formation fluid (Ennis-King and Paterson, 2003; Garcia, 2001) and an instability arises, with a denser fluid located above the less dense native fluid. This instability promotes convection that carries the CO_2-rich aqueous fluid downwards generating finger shape CO_2-concentration profiles (Ennis-King and Paterson, 2003; Hidalgo et al., 2013; Kneafsey and Pruess, 2010).

CO_2 dissolution is a key process for carbon storage. It increases storage safety by decreasing the CO_2 fugacity, lowering the pressure of the supercritical CO_2 and, thus, limiting the gas migration and pressure build up. Furthermore, dissolved CO_2 promotes water-rock interaction that could mineralize the carbon, further increasing the stability of the carbon storage. As local thermodynamic equilibrium is rapidly attained between supercritical CO_2 and the native formation fluid, its dissolution is controlled by the fluid renewal rate. Fluid convection, therefore, can increase dramatically the CO_2 dissolution rate.

Recently, field evidence of these processes have been observed (Sathaye et al., 2014). Emami-Meybodi et al. (2015) reviewed recent advances in CO_2 convective dissolution in saline aquifers through experiments, and theoretical and numerical models. Numerous studies have focused on the physical aspects of convection includ-

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Table 1
Chemistry of the two end-member fluids at 80 °C. Concentrations are given in mmol $\mathrm{kg_w}^{-1}$. Density is given in kg m^{-3}.

	Density	pH	C	B	Br	Ca	Cl	F	K	Mg	Na	S
Native fluid	1024.5	6.98	0.263	1.465	1.036	53.51	547.1	0.19	14.34	2.623	470.7	24.31
CO_2-rich fluid	1035.9	3.35	652.3	1.465	1.036	53.51	547.1	0.19	14.34	2.623	470.7	24.31

ing the onset of instability and convection, effects of permeability variability, capillarity or aquifers natural flow (Emami-Meybodi et al., 2015; Hassanzadeh et al., 2007; Hidalgo et al., 2012; Hidalgo and Carrera, 2009; MacMinn et al., 2012; Meybodi and Hassanzadeh, 2013; Neufeld et al., 2010; Pau et al., 2010; Rapaka et al., 2008; Riaz et al., 2006; Slim and Ramakrishnan, 2010; Slim, 2014; Szulczewski and Juanes, 2013). However, much less is known about the interaction between convective mixing and geochemistry.

Although slow mineral-fluid reactions have little impact on gravitational instability, significant impact could be expected for fast reactions (Ennis-King and Paterson, 2007). A number of numerical analysis have assessed the effect of second order (Ghesmat et al., 2011) and first order (Andres and Cardoso, 2012, 2011) mineral carbonation reactions on convection in aquifers. Such reactions typically stabilize the system; Andres and Cardoso (2012, 2011) determined a Damköhler-Rayleigh ratio above which convective mixing is not possible. Such behaviour has been studied in a steady-state regime (Ward et al., 2014), and extended to 1) anisotropic media (Hill and Morad, 2014), 2) a transient nonlinear case (Kim and Choi, 2014) and 3) using a Darcy–Brinkman formulation (Kim and Kim, 2015).

In a previous study, Cardoso and Andres (2014) showed theoretically and experimentally that natural convection can be retarded, or even inhibited, by chemical reactions in silicate-rich aquifers. In contrast, Loodts et al. (2014) found theoretically that the impact of chemical reactions on convection depends on the monotonicity of the density-concentration profile in the system and showed experimentally that convective mixing is enhanced by the reaction of dissolved CO_2 with NaOH. These contrasting results emphasize the need to introduce realistic geochemical kinetics to accurately model the temporal evolution of carbon injection sites.

Alteration of the solid matrix due to mineral precipitation and dissolution may vary porosity, thereby altering the flow within an aquifer (Hewitt et al., 2013; Hidalgo et al., 2012). Fu et al. (2015) and Hidalgo et al. (2015) studied such interactions based on a mixing-limited reaction, assuming chemical equilibrium, and found that dissolution occurs in areas of high fluid mixing. Such effects are especially significant at flow stagnation points where the mixing layer is compressed and the transition between fluids with distinct compositions is shorter (Hidalgo et al., 2015).

This study explores numerically the interplay between geochemistry and convective mixing and its effect on CO_2 solubility trapping in a potential industrial CCS project in northern Spain. A pilot CO_2 geological storage project in deep saline aquifer is being coordinated by CIUDEN (CIUDad de la ENergía Foundation). The injection site is located in Hontomín (Burgos, Spain) within a carbonate-hosted aquifer, initially equilibrated with calcite, dolomite and gypsum. Calcite dissolution is assumed to follow a kinetic rate equation, whereas gypsum is assumed to react at local equilibrium. These reactions will alter fluid density, porosity, and permeability, and therefore the fluid flow patterns. This study builds upon similar efforts by Fu et al. (2015) and Hidalgo et al. (2015) by adding a more complex chemical system and showing the degree to which convective mixing can be enhanced by chemical reactions. Most notably, this study illuminates the effect of non-carbonate mineral reactions on CO_2 dissolution in carbon storage. It demonstrates the need for a site specific geochemical assessment of potential CCS sites and the need to take specific account of all potential mineral-fluid reactions that may occur within the subsurface carbon storage system. The influence of Damköhler and Rayleigh numbers is illustrated, allowing the application of computed results to numerous other geologic storage sites.

2. Model description

2.1. Physical governing equations

The equations governing the hydrodynamic system are the conservative solute transport and the continuity equation of groundwater flow. The computational model uses the convective form of the solute transport equation, derived from the divergence form of the transport equation by subtracting fluid mass balance multiplied by solute concentration (Galeati and Gambolati, 1989; Goode, 1992; Saaltink et al., 2004) such that:

$$\omega \frac{\partial \boldsymbol{c}}{\partial t} = -\psi \boldsymbol{q} \nabla \boldsymbol{c} + \nabla \cdot \left(\psi \boldsymbol{D} \nabla \boldsymbol{c} \right) - \boldsymbol{c} \nabla \cdot \rho \boldsymbol{D} \nabla \omega^{w}, \tag{1}$$

$$-\nabla \cdot (\rho \boldsymbol{q}) = \rho S_s \frac{\partial p}{\partial t}, \tag{2}$$

where $\omega = \phi \rho \omega^w$ and $\psi = \rho \omega^w$, $\boldsymbol{c}$ refers to the concentration vector of all species, ϕ denotes the porosity, ρ represents the liquid density, ω^w stands for the mass fraction of pure water in the liquid, $\boldsymbol{q}$ signifies the Darcy flow vector, $\boldsymbol{D}$ corresponds to the effective diffusion/dispersion tensor, which is assumed to be identical for all aqueous species, and S_s designates the specific pressure storativity. Note that as $\boldsymbol{D}$ is assumed identical for all aqueous species, charge balance is preserved in the system.

Darcy flow is defined as:

$$\boldsymbol{q} = -\frac{\kappa}{\mu} \left(\nabla p - \rho \boldsymbol{g} \right), \tag{3}$$

where κ stands for the intrinsic permeability of the medium, μ denotes the dynamic viscosity, p refers to the liquid pressure and $\boldsymbol{g}$ is the gravity acceleration.

The model is coupled in two-ways; chemistry affects fluid flow and hydrodynamics influence chemical reactions. In our system the effect of non-carbon species on fluid density is negligible compared to that of dissolved inorganic carbon (C^T) (Yang and Gu, 2006). Density can be assumed, therefore, to be a linear function of local dissolved carbon concentration (considering all of the carbon aqueous species: $CO_2^{(aq)}$, HCO_3^- and CO_3^{-2}) with an initial density (ρ_0) and a compressibility factor (β) in accord with

$$\rho = \rho_0 + \beta C^T, \tag{4}$$

The compressibility factor is based on that reported by Yang and Gu (2006) (Table 2) and results in a density difference between a CO_2-free and a CO_2-saturated fluid of 1% in accordance with previous studies (Garcia, 2001). Porosity depends on the mineral volumes of the media in accord with

$$\phi = 1 - \phi_{inert} - \sum_{i}^{N_m} V_{m,i} c_{m,i}, \tag{5}$$

where ϕ_{inert} stands for the volume fraction of non-reactive minerals, V_m refers to the molar volume of reactive mineral, and c_m denotes the mineral concentration, expressed as moles of mineral per volume of porous medium, of each reactive mineral present in