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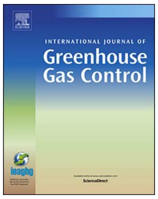

Reservoir-condition pore-scale imaging of dolomite reaction with supercritical CO_2 acidified brine: Effect of pore-structure on reaction rate using velocity distribution analysis

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ABSTRACT

To investigate the impact of rock heterogeneity and flowrate on reaction rates and dissolution dynamics, four millimetre-scale Silurian dolomite samples were pre-screened based on their physical heterogeneity, defined by the simulated velocity distributions characterising each flow field. Two pairs of cores with similar heterogeneity were flooded with supercritical carbon-dioxide ($scCO_2$) saturated brine under reservoir conditions, 50 °C and 10 MPa, at a high (0.5 ml/min) and low (0.1 ml/min) flowrate. Changes to the pore structure brought about by dissolution were captured *in situ* using X-ray microtomography (micro-CT) imaging. Mass balance from effluent analysis showed a good agreement with calculations from imaging. Image calculated reaction rates (r_{eff}) were 5-38 times lower than the corresponding batch reaction rate under the same conditions of temperature and pressure but without mass transfer limitations. For both high (Péclet number = 2600-1200) and low (Péclet number = 420-300) flow rates, an impact of the initial rock heterogeneity was observed on both reaction rates and permeability-porosity relationships.

1. Introduction

Understanding reactive transport in subsurface formations is important in many applications including carbon capture and storage (CCS) (Bachu, 2000), well acidization (Wang et al., 1993), contaminant transport (Zheng and Bennett, 1995), and leaching (Lin et al., 2016b). In the context of CCS in carbonate rich aquifers, dissolution of minerals raises a concern regarding CO_2 storage security (Metz et al., 2005). Field-scale flow modelling that incorporates reaction processes between the CO_2, formation brine, and rock is a necessary precaution and may help control uncertainties which affect storage security (Sifuentes et al., 2009). However this task proves challenging as there are large variations in reported values for parameters, resulting in predicted reaction rates that span orders of magnitude (Black et al., 2015). Therefore, in such models, a fundamental pore-scale understanding is key in accurately representing the behaviour of different length-scale heterogeneities and forms the basis upon which field-scale models are built (Li et al., 2008; Steefel et al., 2015; Steefel and Lasaga, 1994; Steefel and Maher, 2009). It is common to use a power law to predict permeability-porosity relationships, calibrated by its exponent − denoted in this work by m (Carman, 1937; Kozeny, 1927). This relationship is needed to characterize the effect of dissolution on averaged flow properties as input into field-scale models. (Luquot and Gouze, 2009; Menke et al., 2016, 2015; Noiriel et al., 2004; Smith et al., 2017, 2013). Pore-scale observations can help explain the mismatch between laboratory and field scale reaction rates (Li et al., 2006; Moore et al., 2012; Noiriel et al., 2004; Swoboda-Colberg and Drever, 1993; White and Brantley, 2003) and help elucidate the relationship between permeability and porosity for different initial pore structures.

Carbonate reservoirs, most susceptible to dissolution, are complex heterogeneous systems with mixed mineralogies, each having different reaction rates and characteristics (Black et al., 2015). Rock heterogeneities, fluid transport and dissolution kinetics are all factors which influence macroscopic dissolution patterns (Noiriel et al., 2009; Steefel and Lasaga, 1990). In recent years, direct pore-scale visual observations of geologic rocks, including dissolution, have been made possible by the use of X-ray imaging (Al-Khulaifi et al., 2017; Gharbi et al., 2013; Gouze and Luquot, 2011; Lin et al., 2016a; Lin et al., 2017; Luquot and Gouze, 2009; Menke et al., 2016, 2015; Noiriel et al., 2009, 2005, 2004). The way in which rock property alterations develop from dissolution is dependent on mineralogy, reservoir conditions, and pore structure (Al-Khulaifi et al., 2017; Noiriel et al., 2005; Wang et al.,

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1993). A systematic way to study reactive transport in carbonates is to start with reaction in pure minerals and then characterise dissolution dynamics in more complex mixtures. In single mineral systems, dissolution-induced changes in dynamic properties have been shown to be dependent on initial pore structure (Maheshwari et al., 2013; Menke et al., 2016; Smith et al., 2017). Thus far, most single-mineral imaging of dissolution by CO_2 acidic brine have featured calcite bearing limestones (Gharbi et al., 2013; Gouze and Luquot, 2011; Luquot and Gouze, 2009; Menke et al., 2016, 2015; Noiriel et al., 2005, 2004). They observe dissolution regimes that vary depending on the influences of transport limitation, reaction kinetics, pore and surface heterogeneities. In the works of Noiriel et al. (2004), (2005), the dissolution of a mm-scale limestone core by flowing ambient condition CO_2-enriched brine was captured with micro-CT imaging and chemical effluent monitoring. The intent was to identify the inherent relationship between fluid chemistry, hydrodynamic and structural properties by assessing porosity and reactive surface changes in parallel to permeability changes. This new type of experimentation enables the documentation of permeability-porosity evolution and its relation to structural modification. The study's main conclusions were that the initially large increase in permeability was observed by imaging and was attributed to the removal of fine grain calcite particles. Following this, the permeability increased with porosity at a lower rate because of an observable decrease in wall roughness and increase in pore connectivity. Finally, a higher flow rate gave a higher dissolution rate due to transport-limited conditions that accelerate dissolution in narrow pore pathways. In another work, Luquot and Gouze (2009) conducted a series of reservoir condition core flooding experiments on a limestone reservoir rock using reactive brine with different partial pressures of CO_2 to observe the effect of CO_2 injection away from an injection well. Non-uniform dissolution was reported for transport-controlled reaction while lower saturations of CO_2, seen farther away from the injection well, exhibited reaction-controlled uniform dissolution. Luquot and Gouze (2009) also reported an initial pore structure memory effect the loss of which offsets the power law relationship between permeability and porosity.

Fewer studies have looked at a slower reacting dolomite (Smith et al., 2017) despite the fact that dolomite is the second most abundant carbonate mineral (Ahr, 2008), and features as the main mineral in some prominent hydrocarbon reservoirs (Al-Siddiqi and Dawe, 1999). Smith et al. (2017) conducted reactive transport type experiments on dolomite samples to constrain 3D models that predict the evolution of porosity and permeability for CO_2 storage. The work compared the experimentally determined power law exponent of the permeability-porosity relationship and that from a model.

The approach in this work allows for the quantification of heterogeneity enabling direct comparison of its effects on dissolution patterns and perceived reaction rates. Therefore, the impact of pore structure on reaction rates and dissolution patterns in Silurian dolomite reacting with CO_2 acidified brine at reservoir conditions will be examined.

The general kinetics of any acidic brine-rock interactions at the pore scale are dictated by the interplay between hydrodynamic transport of reactants to fluid-rock the interface, reaction at the interface, and the transport of reactants away from the interface (Golfier et al., 2002; Lasaga, 1984). Studying the impact of pore structure heterogeneity for both single and mixed mineralogy systems is also possible using micro-CT imaging (Al-Khulaifi et al., 2017; Smith et al., 2013). Al-Khulaifi et al. (2017) imaged the dissolution of a millimetre-scale composite core made of Ketton calcite and Silurian dolomite arranged in series. The aim was to examine the effect of physical and chemical heterogeneity on dissolution regime and effective reaction rate; the average reaction rate of dolomite under similar conditions to those presented later in this work and a Péclet range of 3000-1000 was 6.46×10^{-6} mol/m^{2}s. Menke et al. (2016) injected super-critical CO_2 saturated brine at 50 °C and 10 MPa into millimetre-scale calcite cores (Portland and Estaillades, > 97.2% calcite), with variations of physical heterogeneity between the samples and imaged the pore space changes resulting from dissolution. In more heterogeneous rock it was observed that dissolution occurs along preferential flow pathways leading to channel growth. On the other hand, homogeneous pore structures gave rise to a uniform dissolution *i.e.* an even growth of all flow pathways.

Dolomite exhibits a reaction rate one order of magnitude lower than that of calcite (Peng et al., 2016). In the context of CO_2 storage, Luhmann et al. (2014) performed core-scale (centimetre-scale) dissolution experiments in dolomite core plugs to investigate the effect of varying flowrate; a faster increase of permeability was observed at high rates. In a more recent study, Smith et al. (2017) recognized the importance of pore-scale observations and imaged the dissolution of dolomite cores with different permeability and physical heterogeneity at 43 μm resolution to calibrate a continuum-scale reactive transport model. It has been reported that physical heterogeneity drives the dissolution front (Carroll et al., 2013; Hao et al., 2013; Kalia and Balakotaiah, 2009; Maheshwari et al., 2013; Smith et al., 2013) that determines the porosity-permeability relationship and effective reaction rate.

The approach in this paper is to characterize reactive transport in dolomite for CO_2 storage by combining pore-scale experimental observation and modelling. We provide micro-scale observations at an image resolution of 5.2 μm to provide insights into coupled reactive phenomena unresolvable at larger scales. To make direct observations of the effect of physical heterogeneity and flow conditions on reaction rates and patterns, a pre-screening method for characterizing the rock heterogeneity prior to conducting the reaction experiments is introduced. First, dry scans of the core samples are performed. Then, on these images, direct numerical simulations using a Navier-Stokes flow solver are run (Bijeljic et al., 2013; Raeini et al., 2012) to obtain velocity fields as their intrinsic heterogeneity characteristics. Using this analysis, four dolomite samples are classified into two heterogeneity groups A and B, based on their pore-scale velocity distributions. Next, dynamic reactive transport experiments are performed to obtain effective reaction rates and examine the impact of pore structure and initial flow field heterogeneity at two flowrates. Reactive transport experiments are then analysed by again employing direct flow simulation on time-lapsed pore-space dissolution images acquired during experimentation to provide (a) the porosity-permeability relationship, and (b) dynamic changes in flow heterogeneity characteristics from reaction-induced alterations in pore velocity distributions. Finally, there will be a discussion the origin of the effects of flowrate and initial rock heterogeneity on dissolution rates and patterns.

2. Materials and methods

The Silurian dolomite (> 99% dolomite) used in the reaction experiments was from the Thornton formation deposited between 443–416 million years ago (Al-Khulaifi et al., 2017). Silurian is homogeneous in chemical composition but spatially has a very heterogeneous pore structure even at the scale of sample size chosen for this work, 4.8 mm long by 4.8 mm diameter. As a pre-screening step, 8 samples were cored out of a single block of Silurian dolomite with the length of the cores being parallel to the bedding of the rock. After imaging the 8 samples at a resolution of 5.2 μm, flow simulation was performed directly on their segmented pore spaces (detailed description of flow modelling in Section 2.5). Characterizing the intrinsic flow heterogeneity of each sample was achieved by observing the probability density functions (PDFs) of velocities calculated in each pore voxel from the simulation. Two pairs were chosen for experimentation based on the shape of their velocity distributions reflecting their structural heterogeneity. Each individual pair has samples of matching heterogeneity (heterogeneity A and heterogeneity B) and within each pair, a low (0.1 ml/min) and high (0.5 ml/min) rate dissolution experiment was performed, giving a total of four experiments.