Kinetics of calcite dissolution in CO_2-saturated water at temperatures between (323 and 373) K and pressures up to 13.8 MPa

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ABSTRACT

We report measurements of the calcite dissolution rate in CO_2-saturated water at pressures ranging from (6.0 to 13.8) MPa and temperatures from (323 to 373) K. The rate of calcite dissolution in HCl(aq) at temperatures from (298 to 353) K was also measured at ambient pressure with pH between 2.0 and 3.3. A specially-designed batch reactor system, implementing a rotating disc technique, was used to obtain the dissolution rate at the solid/liquid interface of a single crystal, free of mass transfer effects. We used vertical scanning interferometry to examine the texture of the calcite surface produced by the experiment and the results suggested that at far-from-equilibrium conditions, the measured calcite dissolution rate was independent of the initial defect density due to the development of a dynamic dissolution pattern which became steady-state shortly after the onset of dissolution. The results of this study indicate that the calcite dissolution rate under surface-reaction-controlled conditions increases with the increase of temperature from (323 to 373) K and CO_2 partial pressure from (6.0 to 13.8) MPa. Fitting the conventional first order transition state kinetic model to the observed rate suggested that, although sufficient to describe calcite dissolution in CO_2-free HCl(aq), this model clearly underestimate the calcite dissolution rate in the (CO_2 + H_2O) system over the range of conditions studied. A kinetic model incorporating both pH and the activity of CO_2(aq) has been developed to represent the dissolution rates found in this study. We report correlations for the corresponding reaction rate coefficients based on the Arrhenius equation and compare the apparent activation energies with values from the literature. The results of this study should facilitate more rigorous modelling of mineral dissolution in deep saline aquifers used for CO_2 storage.

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1. Introduction

In recent years, carbon capture and storage (CCS) has emerged as a key technology for limiting anthropogenic CO_2 emissions while allowing the continued utilisation of fossil fuels. Potential CO_2 storage sites include active and depleted hydrocarbon reservoirs, un-mineable coal seams and deep saline aquifers (Blunt, 2010). Of these, the most promising geological formations for safe CO_2 storage are deep saline aquifers because the capacity, integrity and injection economics are most favourable, and the environmental impact can be minimal (Bachu, 2000; Anthonsen et al., 2013). Many physical and chemical processes are known to occur both during and after CO_2 injection in saline aquifers, including diagenetic chemical reactions and associated permeability changes (Grigg et al., 2005). The coupling of physical and chemical processes occurs in various situations, ranging from the near-well-bore region to far in the reservoir, and has consequences for the long-term viability of CO_2 storage (Egermann et al., 2005). Therefore, it is essential to have a fundamental understanding of the physical and chemical properties of the fluids and minerals, and of the rock–fluid

interactions, before implementing CO_2 storage in saline aquifers. Since carbonate minerals are abundant in sedimentary rocks, one of the requirements is to characterise the reactivity of carbonate minerals in aqueous solutions at reservoir conditions (Al-Siddiqi and Dawe, 1999).

The importance of carbonate dissolution in the (CO_2 + H_2O) system can be understood in terms of its impact on the integrity and stability of both the formation rocks and cap rocks (Koide et al., 1997; Kaszuba et al., 2003). The chemical interactions between CO_2-acidified brines and the reservoir minerals can influence the porosity and permeability of the formations, resulting in changes in the transport processes occurring during CO_2 storage. Typical examples reported in the literature include formation damage near the injection well and destabilisation of carbonate cements due to the presence of CO_2, either of which could result in premature termination of CO_2-storage operations (Mohamed et al., 2011). Furthermore, literature suggests that mineralisation of CO_2 occurs by a similar mechanism to the reverse process of carbonate dissolution. Hence, information derived from carbonate dissolution studies may be applied to enhance understanding of all aspects of CO_2 storage operations at a given site (Reddy et al., 1981; Druckenmiller and Maroto-Valer, 2005).

Calcite and dolomite are the major carbonate minerals in sedimentary rocks, and calcite is by far the most abundant carbonate mineral in

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deep-sea sediments (Morse and Arvidson, 2002). Numerous studies have been performed to understand calcite dissolution rates under various conditions of temperature, pressure and salinity (Berner and Morse, 1974; Plummer and Wigley, 1976; Sjöberg, 1976; Plummer et al., 1978; Morse et al., 1979; Wollast, 1990; MacInnis and Brantley, 1992; Rosenberg et al., 2012). Some of these studies were focused on the more acidic environment, such as acid fracturing for enhanced oil/gas extraction (Hung et al., 1989; Tinker, 1989). However, most were performed to evaluate sedimentary–rock and ocean–water chemistry. For CO_2-acidified aqueous systems, the chemical reactions involved during carbonate dissolution have usually been described in terms of up to three parallel reactions occurring at the solid–fluid interface as follows (Sjöberg, 1976; Plummer et al., 1978; Wollast, 1990; Brantley, 2008):

$$MCO_3 + H^+ \xrightarrow{k_1} M^{2+} + HCO_3^- \tag{1}$$

$$MCO_3 + H_2CO_3^* \xrightarrow{k_2} M^{2+} + 2HCO_3^- \tag{2}$$

$$MCO_3 \xrightarrow{k_3} M^{2+} + CO_3^{2-}. \tag{3}$$

Here, M represents a divalent metal ion (Ca in the present work), $H_2CO_3^*$ is the sum of dissolved molecular $CO_2(aq)$ and H_2CO_3 in the aqueous system, and k_1, k_2 and k_3 are rate coefficients. Plummer et al. (1978) suggest that the kinetics of calcite dissolution in the ($CO_2 + H_2O$) system can be divided into three regimes. In regime 1, dissolution is independent of CO_2 pressure per se, dominated by reaction (1) and hence dependent on the system pH only. In regime 2, dissolution is dependent on both pH and the partial pressure of CO_2 while in regime 3, calcium precipitation begins to play a role. Therefore, the overall carbonate dissolution rate can be described by:

$$r = k_1\alpha_{H^+} + k_2\alpha_{H_2CO_3^*} + k_3, \tag{4}$$

where α_X is activity of species X. This model has been used in several reservoir simulators; nevertheless, uncertainty remains concerning both the validity of this description and the values of the rate constants that appear in it under the conditions of pressure, temperature, pH and ionic strength pertaining to CO_2 storage. One reason for this is the limited amount of literature relating to such conditions. It has also been noted that the high solubility of CO_2 at reservoir conditions could result in significant changes to the activities of reactants and products participating in the dissolution process and alteration of the elementary steps responsible for rate control (Morse and Arvidson, 2002). Another complexity in many experimental studies of calcite dissolution kinetics is the distinction between the reaction-controlled and mass-transfer-controlled regimes. For the experiments conducted in batch or mixed flow reactors in which only overall reaction rate can be measured, the calcite dissolution rate may be primarily controlled by the hydrodynamic conditions that influence the thickness of the stagnant boundary layer. As a consequence, the observed reaction rates can be very different due to the varying influence of mass transfer resistance. Different values of the rate constants k_1, k_2 and k_3 have therefore been reported in the literature for different temperature and pH conditions and a fairly wide range of activation energies have been derived (Plummer et al., 1978; Chou et al., 1989; Compton et al., 1989). Since the rate Eq. (4) is phenomenological, the coefficients and any derived activations energies are best considered as apparent values.

Despite a significant number of studies on calcite dissolution in aqueous solutions, very few experiments have been conducted at high-temperature high-pressure conditions. Pokrovsky et al. (2005, 2009) have measured the dissolution of calcite, dolomite and magnesite at temperatures up to 423 K with pressures up to 5.5 MPa. However, typical CO_2 storage aquifers at depths of 1000 m will have pressures of around 10 MPa which may further increase to (12 to 15) MPa with the continuous injection of CO_2 (Blunt, 2010). To our knowledge, no

experimental data have been reported at such reservoir-like conditions. Additionally, calcite dissolution in low pH conditions (pH < 4) have often been studied under mass transfer limited conditions where hydrodynamics are highly influential and the data may not reflect the fluid transport conditions within the porous structure of the saline formation. Furthermore, the review by Morse et al. (2007) has suggested that much fundamental knowledge is lacking in understanding surface-controlled calcite dissolution reactions. The calcite dissolution data reported by Pokrovsky et al. (2005, 2009) were affected by mass transfer limitations even at the highest speed available in their rotating-disc reactor. Little is known about the influences of temperature and pressure on the calcite dissolution in the surface-reaction-controlled regime. The surface reaction controlled dissolution kinetics can be critical when advection is dominant during reactive transport processes and is the key parameter to be implemented into reactive transport modelling for CO_2 storage simulation. In summary, very few experiments have been conducted at high-pressure and high-temperature reservoir-like conditions that are applicable to CO_2 storage. Furthermore, most of the available data appear to be affected by mass-transfer resistance at the solid–liquid interface and experimental calcite dissolution data in the ($CO_2 + H_2O$) system under surface-reaction-controlled regime are scattered.

The impact of mass-transfer resistance on the overall dissolution rate can be reduced or eliminated using the rotating disc technique (Levitch, 1962). The transport rate constant (k_t) for the rotating-disc reactor at finite disc rotation speeds is given by

$$k_t = D/\delta, \tag{5}$$

where D is the diffusion coefficient of CO_2 and δ is the diffusion boundary layer thickness (stagnant boundary layer thickness) which in laminar flow is given approximately by the following relation (Gregory and Riddiford, 1956; Levitch, 1962; Alkattan et al., 1997):

$$\delta = 1.61(D/\nu)^{1/3}(\nu/\omega)^{1/2}. \tag{6}$$

Here, ν is the kinematic viscosity of the fluid and ω is the angular velocity of the disc. Thus, the thickness of the stagnant boundary layer reduces with the increase of the rotational speed, resulting in an increase of the flux of solute to the surface for a given concentration gradient. At a sufficiently-high angular velocity, surface reaction becomes the rate determining step and the overall reaction rate obtained experimentally will be free of mass transfer effects. The technique has also been applied to vary the concentration of the reactants and products on the solid surface in a controlled manner and to evaluate the reaction rate, ion diffusion coefficient and the order of reaction (Lund et al., 1975; Fredd and Scott Fogler, 1998).

Surface area is another key variable that influences the measured calcite dissolution rate and alternations of surface morphology may result in significant changes of dissolution rate. Berner and Holdren (1979) proposed that defect-sites, such as dislocation and fractures, have a higher tendency to dissolve due to the existence of excess surface energy compared to a smooth surface. These observations were subsequently verified with the advent of atomic-scale topographic techniques, such as atomic force microscopy (AFM) and vertical scanning interferometry (VSI) (Duckworth and Martin, 2004; Lüttge, 2006; Fischer et al., 2012; Xu et al., 2012). Calcite dissolution rate can be directly calculated from the real-time observation of the topographic changes by using step-retreat velocities and the step densities (Duckworth and Martin, 2003). Models describing the calcite dissolution kinetics based on those microscopic observations were subsequently proposed to account for the various dissolution rates at different defect sites. However, issues were raised after comparing the macroscopic and microscopic results since, in some cases, both dissolution rates agree whereas, in other cases, orders of magnitude differences were observed (Arvidson et al., 2003; Fischer et al., 2012; Schott et al.,