



Kinetics of carbonate dissolution in CO₂-saturated aqueous system at reservoir conditions

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In recent years, carbon capture and storage (CCS) has emerged as a key technology for limiting anthropogenic CO₂ emissions while allowing the continued utilisation of fossil fuels. The most promising geological storage sites are deep saline aquifers because the capacity, integrity and injection economics are most favourable, and the environmental impact can be minimal. Many rock-fluid chemical reactions are known to occur both during and after CO₂ injection in saline aquifers. The importance of rock-fluid reactions in the (CO₂ + H₂O) system can be understood in terms of their impact on the integrity and stability of both the formation rocks and cap rocks. The chemical interactions between CO₂-acidified brines and the reservoir minerals can influence the porosity and permeability of the formations, resulting in changes in the transport processes occurring during CO₂ storage. Since carbonate minerals are abundant in sedimentary rocks, one of the requirements to safely implement CO₂ storage in saline aquifers is to characterise the reactivity of carbonate minerals in aqueous solutions at reservoir conditions.

In this work, we reported measurements of the intrinsic rate of carbonate dissolution in CO₂-saturated water under high-temperature high-pressure reservoir conditions extending up to 373 K and 14 MPa. The rate of carbonate dissolution in CO₂-free HCl(aq) was also measured at ambient pressure at temperatures up to 353 K. Various pure minerals and reservoir rocks were investigated in this study, including single-crystals of calcite and magnesite, and samples of dolomite, chalks and sandstones. A specially-designed batch reactor system, implementing the rotating disc technique, was used to obtain the intrinsic reaction rate at the solid/liquid interface, free of mass transfer effects. The effective area and mineralogy of the exposed surface was determined by a combination of surface characterisation techniques including XRD, SEM, EDX and optical microscopy. The results of the study indicate that the rotating disc technique can allow accurate measurement of the carbonate dissolution rate under surface-reaction-controlled conditions, and that the carbonate dissolution rate typically increases with the increase of temperature, CO₂ partial pressure and solution acidity. The study shows that the dissolution of carbonate in CO₂-free acidic solutions can be described as a first order heterogeneous reaction; however, this model is not sufficient to describe the reaction kinetics of carbonate minerals in the (CO₂ + H₂O) system, particularly for high reactivity carbonates, such as calcite, at reservoir conditions. For these systems, both pH and the activity of CO₂(aq) influence the dissolution rate. Based on the experimental results, kinetic models have been developed and parameterised to describe the dissolution of different carbonate minerals. The results of this study should facilitate more rigorous modelling of mineral dissolution in deep saline aquifers used for CO₂ storage.

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