

We Ses 09

Dolomite Dissolution Rates at Conditions Relevant to CO₂ Sequestration in the Rotliegend Gas Fields in NE Netherlands

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SUMMARY

The kinetics of dolomite dissolution have been investigated in experiments conducted at conditions characteristic of the Rotliegend gas fields in the northeast of the Netherlands (Temperature 100 °C, Brine ionic strength $I > 6.4\text{M}$, $\text{pH} = 2-5$). Experiments were performed in closed, stirred, batch reactors at far from equilibrium conditions, with dolomite powders of different diameter fractions: 20-25 microns, 75-100 microns, and 300-350 microns, with respective geometric surface areas: 935 cm²/g, 225 cm²/g and 65 cm²/g. Dissolution experiments were also conducted in deionized water for the largest grain size to determine the effect of solution composition on dolomite kinetics. The rates were deduced from the change in the amount of Mg²⁺ released in brine with time and were normalized by the surface area of the minerals at each time interval.

Dolomite dissolution rates were faster in brine than in deionized water by almost a factor of 2, which was not anticipated in such high salinity brine. Ionic strength and ion pairing overshadow the common ion effect, thus enhancing dissolution. In this work, smaller grains exhibited faster rates after normalization for surface area.

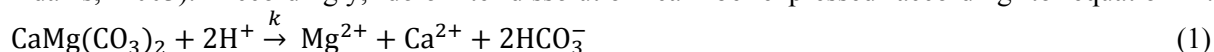
Introduction

The extent and security of carbon dioxide (CO₂) storage in geological formations is determined by a combination of physical (structural and residual) and chemical (solubility and mineral) trapping mechanisms that depend on the formation type. Amongst these mechanisms, mineral trapping is more likely to secure the integrity of CO₂ storage (Allen and Brent, 2010). This is because CO₂ can react with the host rock minerals through the aqueous phase and become chemically bound in stable carbonates at large time scales (Johnson et al., 2004; Lackner and Brenann, 2009). The extent of CO₂ mineral trapping depends on the kinetics of mineral-brine interactions. The mineral dissolution kinetics can be determined through laboratory experiments and extrapolated at reservoir scale and for longer time periods through geochemical models. Numerous studies have investigated the kinetics of mineral dissolution under various conditions. For example, Zhang et al. (2007) investigated the dissolution of dolomite as a function of particle size (grain surface area: 0.5-0.8 m²/g), at constant temperature within the range 25-250°C, constant pressure of 12.07 MPa and in neutral pH in deionized water. Pokrovsky et al. (2005) studied the dissolution of carbonate minerals as a function of salinity (0.001M ≤ [NaCl] ≤ 1M) and partial CO₂ pressure (0-5 MPa) in acidic solutions (pH=3-4) at 25°C. However, mineral dissolution data at in situ conditions (temperature, mineralogical characteristics, salinity and solution composition, pressure, and pH) are not common in literature. Especially experiments in high salinity brines of variable composition like those often encountered in hydrocarbon reservoirs are very scarce. One such study is from Gledhill and Morse (2005) who examined the kinetics of calcite pertinent to reservoir conditions (pH= 5-6.5; T=25-82.5 °C; and pCO₂ < 0.1 MPa) using concentrated brines (50-200 g/L). They found that calcite dissolution and precipitation rates are composition dependent and that increasing ionic strength led to inhibition of the dissolution rates.

In the current study we quantified dolomite dissolution kinetic rates at conditions relevant to the Rotliegend gas fields in northeast Netherlands, which are possible candidates for CO₂ sequestration. Dolomite forms 2 % of the Rotliegend reservoir mineralogy, which makes it the most pronounced form of carbonate (Bolourinejad et al., 2014). The reservoir is characterized by pressures around 30 MPa and a temperature of 100°C, and salinity of 300 g/L (ionic strength > 6.4 M), which is the highest ionic strength encountered in literature so far. First we provide an overview of the reaction kinetics and the experimental methods used and then we present the results illustrating the effect of different parameters on the dissolution rates.

Reaction kinetics

Mineral trapping initiates after CO₂ is injected in the reservoir and dissolved in brine, producing carbonic acid, which increases the acidity of the brine triggering mineral dissolution (Bachu and Adams, 2003). Accordingly, dolomite dissolution can be expressed according to equation 1:



Following this and according to the transition state theory (TST) the proton (H⁺) promoted dissolution rate in acidic environments (pH<5) can be expressed by equation 2:

$$r = k a_{\text{H}^+}^n \quad (2)$$

where k is the kinetic rate coefficient of reactions and a_{H⁺} is the activity of the protons (H⁺). The order of reaction n and kinetic rate coefficient k can be calculated by least squares regression on the logarithm of the rates (logr) as a function of pH.

Experimental methods

For the experiments, dolomite was obtained from Gerolstein (Germany), which was crushed into powders and sieved through screens of different sizes. Note that it is often assumed that the dissolution rates scale with the geometric surface area. Hence, the rates after normalisation for surface

area should be equal amongst different grain sizes of the same mineral. In this work we examined the validity of this assumption by comparing the rates, normalized by surface area, at different grain sizes. Most experiments were conducted in synthetic brine with a composition derived from actual local well data. For comparison, one experiment was also conducted in deionized water. The number and type of experiments is presented in Figure 1.

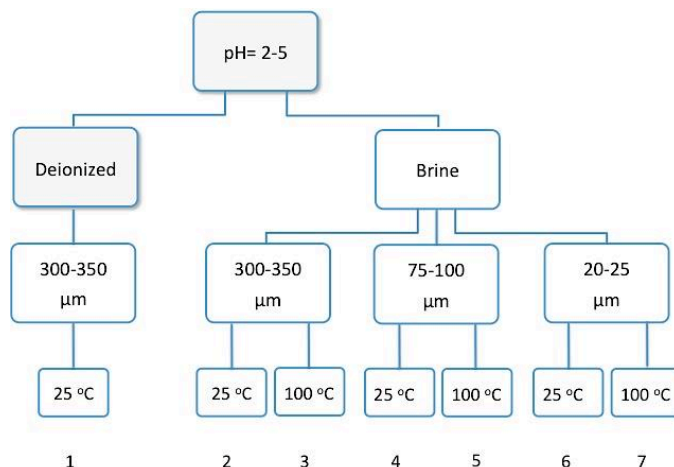


Figure 1 Schematic representation of the number and type of experiments in acidic solutions. Experiments with smaller grains at higher temperatures (5-7) produced fewer data in the acidic region at far from equilibrium.

Dolomite dissolution rates

The elemental release from dolomite dissolution (Ca^{2+} and Mg^{2+}), as measured by Induced Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), exhibited a linear trend with time at far from equilibrium conditions. Contrary to what was anticipated in view of the high initial concentration of Ca^{2+} and Mg^{2+} in the brine (common ion effect), we found that the elemental release in brine was higher and more rapid than in deionized water (Figure 2). Note that the high initial Ca^{2+} concentration of the brine (25200ppm) complicated the measurements of Ca^{2+} release in this case. Hence the calculation of dissolution rates in brine is based on the measured Mg^{2+} concentrations only.

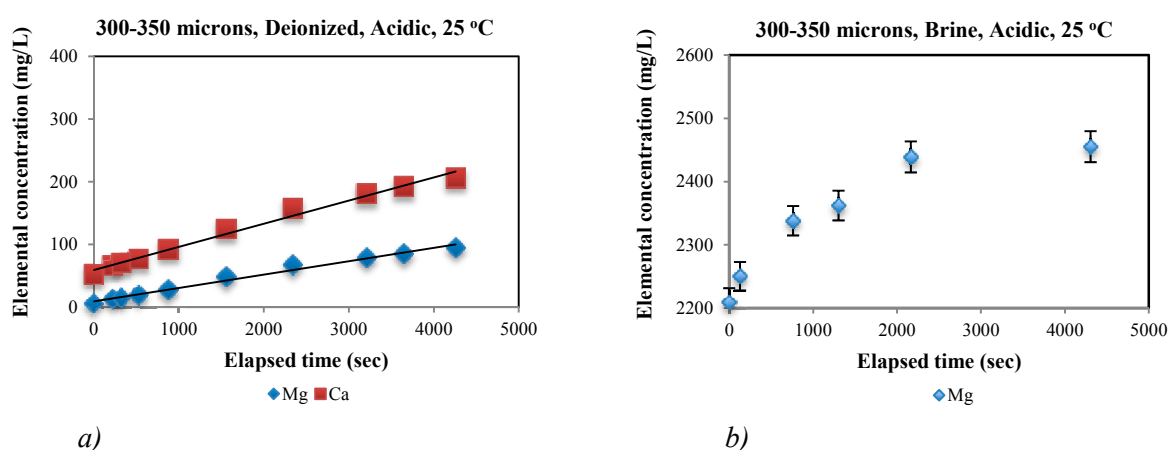


Figure 2 Elemental concentration (mg/L) as a function of elapsed time for the 300-350μm dolomite grains: a) Mg^{2+} and Ca^{2+} in deionized water, at 25 °C (experiment 1); a) Mg^{2+} in brine, at 25 °C (experiment 2). Note: The scale is the same in both graphs to allow for comparison in elemental release. In deionized water, the reactor or sample tube might have contained a small amount of salts, hence the initial Ca^{2+} concentration is not zero. The error bars of data points in a) coincide with the symbol size.

The dissolution rates ($\text{mol}/(\text{cm}^2 \cdot \text{s})$) were calculated as a function of the measured composition change with time using equation 3:

$$r = \frac{2 \cdot V}{A \cdot (m_i + m_{i-1})} \cdot \frac{d[\text{Me}^{2+}] \cdot 10^{-6}}{M_{\text{Me}} \cdot dt} \quad (3)$$

where $V(\text{L})$ is the volume of water in the reactor between two samplings, $A(\text{cm}^2/\text{g})$ is the specific surface area of the mineral, $m(\text{g})$ is the mass of the mineral, and $[\text{Me}^{2+}](\text{mg/L})$ is the concentration of the metal present in the solution (mg/L), either Ca^{2+} or Mg^{2+} , $M_{\text{Me}}(\text{g/mol})$ is the molar mass of Ca^{2+} or Mg^{2+} accordingly, m_i and $m_{i-1}(\text{g})$ is the mass of unreacted dolomite at the i^{th} and $(i-1)^{\text{th}}$ samplings respectively. From post-experimental SEM analysis of the recovered dolomite we found that the change in surface area was significant especially in the experiments with the largest grains where a reduction to 20% of the initial grain diameter was measured. The change was attributed to both the dissolution and stirring effect with time and was accounted for in the rates computation. The rates in brine are almost a factor 2 higher than those in deionized water. The respective plots of $\log r$ against pH are presented for deionized water and brine and for the largest and smallest grain sizes. The intercept with the vertical axis ($\log r$) produces the kinetic rate coefficient k , and the slope of the line indicates the order of reaction n .

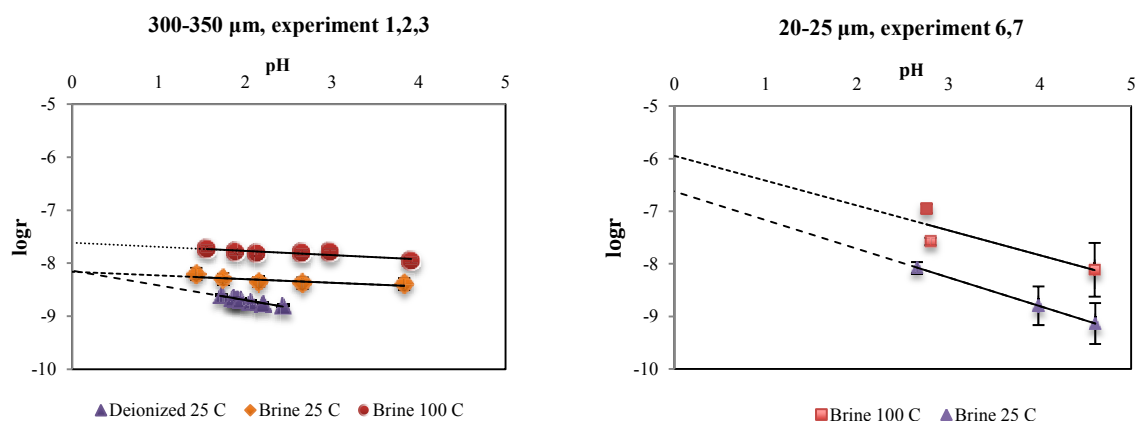


Figure 3 Plots of $\log r$ against pH for a) the 300-350 microns grains in brine and deionized water; and b) 20-25 microns grains, respectively. The error bars that do not show coincide with the symbol size.

The reaction rate coefficients in brine as calculated from the $\log r$ -pH intercepts (Figure 3) are $\log k_{\text{Mg}} = -8.16 \pm 0.06$ at 25°C and $\log k_{\text{Mg}} = -7.61 \pm 0.05$ at 100°C for the 300-350 microns grains in brine. For grain sizes of 20-25 microns the resulting coefficients in brine are $\log k_{\text{Mg}} = -6.6 \pm 0.5$ at 25°C , and $\log k_{\text{Mg}} = -5.9 \pm 1.0$ at 100°C .

Conclusions

We found that dolomite dissolution rates are higher in high salinity brine than in deionized water. We conclude that this is the result of competing mechanisms that are likely to occur in a highly concentrated brine. Ion pairing seems to overshadow the common ion effect, causing the ions in the solution to behave as if they were present at lower concentrations than their actual ones. Furthermore, dissolution is enhanced by ionic strength causing different ions to polarize the mineral surface, facilitating ion detachment.

The rates also exhibit a dependency on grain size. The smaller grains exhibit faster rates, when normalized by surface area.

Mineral dissolution studies are prone to uncertainties and considering the highly site specific nature of these studies, geochemical modelling of mineral trapping should be based on actual well data.

We believe that this study provides new information on the effect of different parameters on dolomite kinetics, a mineral that is not widely studied and the results can be used for geochemical modeling of mineral trapping in the Rotliegend reservoirs.

Acknowledgements

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