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Kinetics of dolomite dissolution in a packed bed by acidified desalinated water

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HIGHLIGHTS

- Critical review of published data on dolomite dissolution by acidified water
- Theoretical modeling and experimental confirmation of dolomite acid dissolution
- Acid strength found to be also a parameter governing the dissolution mass transfer coefficient
- Dolomite dissolution is a viable process for re-mineralization of desalinated water.

ARTICLE INFO

ABSTRACT

A post treatment process commonly applied in water desalination practice serves to introduce calcium and carbonate alkalinity to the water in order to protect the distribution system from corrosion damage. Addition of magnesium ions also is currently under consideration. Dolomite is a double salt of $CaCO_3$ and $MgCO_3$ and its dissolution by acidified desalinated water is of interest as this could serve to provide calcium, magnesium and carbonate alkalinity in a single re-mineralization operation. A critical literature review highlights the limitations of published data on dolomite dissolution and in particular their inadequacy for predicting dissolution in industrial equipment. The present study examines the kinetics of re-mineralization of acidified desalinated water in continuous flow over a packed bed of dolomite grains. A kinetic model based on mass transfer control is presented and shown to be in excellent agreement with experimental data. Results of this study indicate that dolomite dissolution is a viable process for re-mineralization of desalinated water.

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1. Introduction

A post treatment process commonly applied in water desalination practice serves to introduce calcium and carbonate alkalinity to the water in order to protect the distribution system from corrosion damage. Currently, the two most widely used processes for introducing calcium and carbonate alkalinity to desalinated water are dissolution of either calcite or lime by acidified desalinated water. According to a WHO report [1] there is need to consider dosage of magnesium ions in addition to calcium ions. Dolomite is a double salt of $CaCO_3$ and $MgCO_3$ and its dissolution by acidified desalinated water is of interest as this could serve to provide calcium, magnesium and carbonate alkalinity in a single re-mineralization operation.

Re-mineralization of desalinated water by dolomite dissolution has been considered but discarded on the basis of slow dissolution kinetics and high treatment costs [2,3]. The most likely reason for the neglect of

dolomite re-mineralization is the lack of adequate technical information and in particular, design data.

The objective of the present study was to investigate the kinetics of re-mineralization of acidified desalinated water flowing over a bed of dolomite grains and to develop a design model for packed bed dissolution.

2. Dolomite dissolution studies

Most of the extensive literature on dissolution and precipitation of carbonate minerals in CO_2 systems originates from interest in the role of these reactions in a variety geological processes. Examples are diagenesis of calcareous deep-sea sediments and formation of karst regions [4,5]. The kinetics and rate-limiting mechanism of dolomite dissolution have been far less extensively studied than those of calcite dissolution. The few published dolomite dissolution studies consider dissolution systems remote from that commonly encountered in industrial equipment, viz. flow of acidified water on a fixed bed of particles [6–11].

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In one of the earliest studies, Lund et al. [6] investigated dissolution of dolomite by HCl with using a rotating disk system. The main objective was to delineate conditions where dissolution is surface reaction controlled and where it is mass transfer controlled. Analysis of the data was based on the following crude kinetic model equating the mass transfer step with the surface reaction step:

$$-R = k[C_o - C_i] = k_s \cdot C_i^n \tag{1}$$

where R is the dissolution rate, k — the rotating disk mass transfer coefficient, C_o — the solution HCl concentration, C_i — the HCl concentration on the dolomite surface, k_s — the surface reaction coefficient and n — a temperature dependent empirical exponent. Values of the rotating disk mass transfer coefficients were determined from the following literature correlation:

$$\frac{1}{k} = 1.612 \cdot \frac{Sc^{-2/3}}{\sqrt{\Omega v}} \cdot \left(1 + 0.298Sc^{-1/3} + 0.145Sc^{-2/3}\right) \tag{2}$$

where Ω is the angular rotating speed of the disk, Sc — the solution Schmidt number and v — the solution kinematic viscosity.

Using calculated values of k, experimental data were used to determine the magnitudes of k_s and n. The value of n varied from 0.44 at 25 °C to 0.83 at 100 °C. The dissolution was found to be reaction limited at 25 and 50 °C even at the lowest rotation speed. At 100 °C the dissolution exhibited some diffusion limitations even at the highest rotation speed.

Results of the above study are hardly relevant to the dissolution of dolomite in industrial fixed bed systems where flow is in the laminar region at very low Reynolds numbers. The highly empirical nature of the model is also problematical.

In a major study performed by Busenberg and Plummer [7] dolomite dissolution by CO_2 was measured by a weight loss method on single cleavage crystals. The experimental data were correlated by the following empirical equation:

$$-R = k_1(a_{H^+})^n + k_2\left(a_{H_2CO_3^*}\right)^n + k_3(a_{H_2O})^n - k_4(a_{HCO_3^-})^n \tag{3}$$

where a_i denotes activity of species i and k_j are rate coefficients.

The value of the exponent n was 0.5 at temperatures below 45 °C and increased progressively with temperature reaching a value of 0.85 at 100 °C. Since stirring rates had no effect it was concluded that dolomite dissolution is controlled by heterogeneous chemical reactions. The mechanism invoked to interpret the result described by Eq. (3) was that the initial dissolution step involved a relatively rapid reaction of the $CaCO_3$ component of dolomite with the solution H^+ and H_2CO_3 species followed by a slow rate limiting reaction of the $MgCO_3$ component of dolomite with these species.

Chou et al. [8] investigated CO_2 dissolution of micronized dolomite particles of 100 to 200 μm in a continuous fluidized bed at a temperature of 25 °C. The experimental data were in general agreement with the results reported by Busenberg and Plummer [7]. However, correlation of the fluidized bed data according to Eq. (3) yielded the value $n = 0.75$. Also, dissolution rates at low pH values were higher than those measured by Busenberg and Plummer [7].

Pokrovsky et al. [10,11] measured dissolution rates of dolomite at temperatures of 25 to 150 °C, pH levels of 3 to 6, $NaHCO_3$ concentrations of 10^{-5} to 10^{-1} and CO_2 partial pressures of 10^{-5} to 55 atm. Experiments on dolomite crystal planes dissolution were performed in a batch reactor using the rotating disk technique. The dissolution data were interpreted within the framework of a surface complexation model [12] representing surface chemical reactions with a set of quasi thermodynamic constants which are independent of changes in solution conditions. A problematical feature of surface complexation theory is the existence of several competing models and that published equilibrium adsorption equilibria constants are often not self-consistent [13].

Liu and Dreybrodt [14] investigated dolomite dissolution at 20 °C in a continuous flow system by the rotating disk technique. The CO_2 partial pressure was varied in the range of 30 Pa to 1 bar. These authors criticized the lack of consideration of mass transfer aspects in many published dolomite dissolution studies since at low reactant concentrations mass transfer resistance is high and can affect significantly the dissolution rate. They illustrated this point with their experimental data by demonstrating that results conformed to the Busenberg and Plummer correlation only in runs performed at relatively high CO_2 partial pressures where mass transfer resistance was negligible.

In conclusion, the literature review reveals many gaps in available information on dolomite dissolution and that a unified generally accepted kinetic model has yet to be developed. It is evident that prediction of dolomite grains dissolution in a continuous flow packed bed system requires a dedicated investigation.

3. Dolomite dissolution models

Limestone dissolution fixed bed contactors which are used for neutralizing acid waters and re-mineralizing desalinated water are operated at low acid concentrations. Typical inlet CO_2 concentrations are of the order of 1 to 5 mm [15–18] compared to CO_2 concentrations reaching 30 mm in the major dissolution study of Busenberg and Plummer [7]. The likelihood of mass transfer control is evident.

Two independent investigations authored by Yamauchi et al. [15] and Letterman et al. [19] indeed showed that the kinetics of dissolution of calcite grains by acidified desalinated water in a fixed bed system is very well described by a mass transfer control model. This approach has been applied in this study to the more complex system of dolomite which involves dissolution of a double salt.

For pure dolomite $CaMg(CO_3)_2$ the Ca:Mg molar ratio is unity and the fractional calcium ratio is: $x = \frac{[Ca^{+2}]}{[Mg^{+2}]+[Ca^{+2}]} = \frac{1}{2}$. In natural dolomite $Ca_{2x}Mg_{2(1-x)}(CO_3)_2$ the Ca:Mg molar ratio differs from unity and varies from $x = 0.665$ for slightly calcitic dolomite to $x = 0.375$ for slightly magnesian dolomite [20].

3.1. Rate equations

Consider first the case of the single salt calcite dissolution under mass transfer control conditions. The basic rate equation [15,19,21] is described by the difference between the calcium solution concentration $[Ca^{+2}]$ and the equilibrium calcium concentration $[Ca^{+2}]_e$ on the solution-calcite interface:

$$-R = \frac{Q \cdot d[Ca^{+2}]}{dS_p} = k\left\{[Ca^{+2}]_e - [Ca^{+2}]\right\} \tag{4}$$

where Q is the volumetric solution flow rate (L/min), S_p — the calcium grains surface area (cm^2), and k — the mass transfer coefficient — MTC (cm/min).

Expressing the particles area in terms of the average particles diameter D_p (cm) and integrating Eq. (4), the rate of dissolution of calcite grains along a bed of length L (cm) is given by:

$$\ln \frac{[Ca^{+2}]_e - [Ca^{+2}]_L}{[Ca^{+2}]_e - [Ca^{+2}]_0} = -k \cdot \frac{6(1-\varepsilon)}{D_p\phi} \cdot \frac{L}{u} \tag{5}$$