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Theoretical and experimental study of micronized dolomite dissolution

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ABSTRACT

Based on corrosion control and health requirement considerations, there is universal agreement on the need to remineralize desalinated water with calcium ions. Growing voices calling for supplementary addition of magnesium ions from health considerations have led to increasing searches of viable magnesium remineralization processes. Dolomite remineralization has a marked advantage because this mineral is a double salt composed of $CaCO_3$ and $MgCO_3$, and its dissolution can provide both calcium and magnesium ions in a single process. The objective of this work was to enable application of the newly developed process of remineralization of desalinated water by micronized calcite powder dissolution to remineralization by micronized dolomite dissolution. Design models were developed and experimentally verified.

Keywords: Post-treatment; Desalination; Remineralization; Kinetics; Dolomite; Dissolution

1. Introduction

Because desalinated water is devoid of chemicals, it is commonly remineralized by post-treatment intended to protect the water distribution system from corrosion and to meet drinking water health requirements. There is wide agreement on the need to remineralize desalinated water with calcium ions within the concentrations range of 50–120 mg/L as $CaCO_3$ and with carbonate alkalinity within the range of 50–150 mg/L as $CaCO_3$ [1,2]. Large-scale desalination plants, worldwide, introduce calcium ions and carbonate alkalinity to the water by dissolution of limestone grains using carbon dioxide or sulfuric acid [3,4].

Concern has been raised on the magnesium deficiency of desalinated water [5,6]. Though the need to add magnesium to the water is controversial, this issue has evoked searches for viable magnesium dosage processes that might be sought at some future date [7–11]. Possible processes for magnesium ions addition include blending desalinated water with a magnesium-rich water source, dosage of a magnesium salt solution, an ion-exchange process [7], magnesia pellets dissolution in a packed bed [8,9], and dolomite grains dissolution in a packed bed [10,11].

The last mentioned possibility seems to be the most attractive alternative. Because dolomite is a mineral composed of both $CaCO_3$ and $MgCO_3$, the calcite in existing remineralization columns could be simply replaced by dolomite, and its dissolution by acidified desalinated water would add both Ca and Mg in a single process. Dolomite minerals differing in their calcium to magnesium contents are available enabling control of a desired calcium to magnesium ratio in the remineralized water. The work of Greiserman et al. [11] provides experimentally verified kinetic models enabling design of dolomite dissolution in packed beds by desalinated water acidified with either carbonic or sulfuric acid.

Currently, there is interest in a recently developed alternate remineralization technique in which calcite dissolution is achieved by slurry flow of acidified desalinated water with micron-size calcite particles [12–15]. The advantage of the slurry flow technique is the very high increase in the dissolution rate of micron-size calcite particles compared with

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that of millimeter-size calcite grains in fixed bed systems. However, while in a fixed bed process, the filtration capability of the calcite bed provides a turbidity-free remineralized water stream, the residual undissolved particles of the micronized slurry system require clarification. This can be adequately achieved by membrane ultrafiltration [15] or by threaded microfiber filtration [16]

Theoretical design models of water remineralization by micronized calcite slurry dissolution with carbonic and sulfuric acids were recently developed and shown to be in excellent agreement with experimental data [17]. In view of the abovementioned potential of dolomite dissolution to remineralize desalinated water with both calcium and magnesium, the micronized calcite slurry dissolution model was extended to the case of dolomite dissolution by either carbon dioxide or sulfuric acid. Experimental confirmation of the theoretical models is presented for both the simplified case of virtual equilibrium conditions and for the case of kinetics control.

2. Dissolution model

2.1. Equilibrium composition of acidified dolomite solutions

Pure dolomite $CaMg(CO_3)_2$ is characterized by a molar ratio of Ca:Mg = 1:1 whereas in natural dolomite the ratio differs from unity. The chemical formula of natural dolomite can be expressed by $Ca_{2x}Mg_{2(1-x)}(CO_3)_2$ indicating that the fractional molar contents of the Ca and Mg are given as follows:

$$\frac{\mathrm{Ca}}{\mathrm{Mg}+\mathrm{Ca}} = x \tag{1}$$

$$\frac{\mathrm{Mg}}{\mathrm{Mg}+\mathrm{Ca}} = 1 - x \tag{2}$$

The dolomite used in this study had the fractional molar calcium content of 0.52 representing a Ca:Mg molar ratio of 1.08. This is natural ratio, available in the market.

2.2. Solution equilibria in dolomite dissolution by CO_2

The most common expression describing the solubility product K_{sp} of natural dolomite is as follows:

$$K_{sp} = \left[\mathrm{Ca}^{2+}\right]_e^{2x} \cdot \left[\mathrm{Mg}^{2+}\right]_e^{2(1-x)} \cdot \left[\mathrm{CO}_3^{2-}\right]_e^2 \tag{3}$$

where the index *e* denotes equilibrium conditions. The value of K_{sp} at 25°C = $4.5 \cdot \times 10^{-22}$ $(\mathrm{mol/L})^4$.

Equilibrium concentration values of the various dissolved species ($[CO_2]_e$, $[Ca^{2+}]_e$, $[Mg^{2+}]_e$) in a dolomite slurry dosed with a carbon dioxide concentration $[CO_2]_0$ are given by the following equations derived elsewhere [11]:

$$\frac{K_{sp} \cdot K_1^{\,2}}{K_2^{\,2}} = \frac{16 \cdot x^{2x} \cdot (1-x)^{2(1-x)} \cdot \left([\mathrm{CO}_2]_0 - [\mathrm{CO}_2]_e\right)^6}{\left[\mathrm{CO}_2\right]_e^2} \tag{4}$$

$$[\mathrm{Ca}^{2+}]_e - x \cdot ([\mathrm{CO}_2]_0 - [\mathrm{CO}_2]_e) \tag{5}$$

$$[\mathrm{Mg}^{2+}]_e - (1-x) \cdot ([\mathrm{CO}_2]_0 - [\mathrm{CO}_2]_e) \tag{6}$$

where K_1 and K_2 are the first and second dissociation constants of carbonic acid.

2.3. Solution equilibria in dolomite dissolution by H_2SO_4

Equilibrium concentrations values of the dissolved species ($[H^+]_e$, $[Ca^{2+}]_e$, $[Mg^{2+}]_e$) in a dolomite slurry dosed with a sulfuric acid concentration $[H_2SO_4]_0 \equiv [SO_4^{\,2-}]_e$ are given by the following equations derived elsewhere [11]:

$$K_{sp} - [\mathrm{Ca}^{2+}]_e^4 \cdot \alpha_2^{\,2} \cdot \left\{\frac{1-x}{x}\right\}^{2(1-x)} \left\{\frac{x^2+(1-x)^2}{x}\right\}^2 \tag{7}$$

$$\begin{aligned} &[\mathrm{Ca}^{2+}]_e \cdot \left\{\frac{2-(x^2+(1-x)^2)\cdot(\alpha_1+2\cdot\alpha_2)}{x}\right\} + [\mathrm{H}^+]_e \\ &\quad = 2 \cdot [\mathrm{SO}_4^{\,2-}]_e + \frac{K_w}{[\mathrm{H}^+]_e} \end{aligned} \tag{8}$$

where K_w is dissociation constant of water, and α_1 and α_2 are total carbon fractional values of the bicarbonate and carbonate ions, respectively:

$$\alpha_1 = \left\{1 + \frac{[\mathrm{H}^+]_e}{K_1} + \frac{K_2}{[\mathrm{H}^+]_e}\right\}^{-1} \tag{9}$$

$$\alpha_2 = \left\{1 + \frac{[\mathrm{H}^+]_e^2}{K_1 \cdot K_2} + \frac{[\mathrm{H}^+]_e}{K_2}\right\}^{-1} \tag{10}$$

Solution of Eqs. (7) and (8) gives the equilibrium concentrations $[H^+]_e$, $[Ca^{2+}]_e$. The equilibrium magnesium concentration is determined by Eq. (2).

2.4. Comparison of the composition of solutions acidified by CO_2 and H_2SO_4

Fig. 1 compares the equilibrium calcium and magnesium concentrations obtained from dissolution of the dolomite used in this study (Ca:Mg = 1.08:1) at various feed concentrations of the carbonic and sulfuric acids. As anticipated, the strong sulfuric acid provides significantly higher calcium and magnesium concentrations.

2.5. Basic dissolution equations

As in the case of micronized calcite dissolution [17], dolomite dissolution is mass transfer controlled and conforms to the following rate equation:

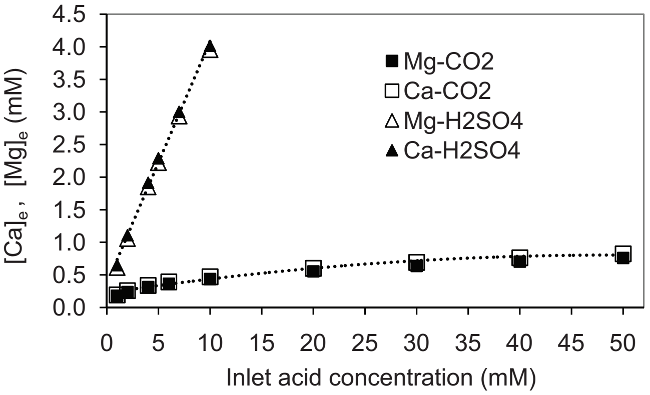

Fig. 1. Comparison of equilibrium concentrations of calcium and magnesium at varying inlet concentrations of CO_2 and H_2SO_4.

$$-\frac{d[Ca^{2+}+Mg^{2+}]}{dt}=\left\{\frac{6\cdot S}{d_p\cdot\rho}\right\}\cdot k_s\cdot\{[Ca^{2+}]_e+[Mg^{2+}]_e-[Ca^{2+}]-[Mg^{2+}]\} \tag{11}$$

where S is the instantaneous mass concentration of the particles, d_p the instantaneous average particle size, ρ is the dolomite density (g/cm³), and k_s is the dissolution mass transfer coefficient (cm/s).

Because dissolution causes simultaneous release of magnesium and calcium, Eq. (11) can be decomposed as follows:

$$-\frac{d[Ca^{2+}]}{dt}=\left\{\frac{6\cdot S}{d_p\cdot\rho}\right\}\cdot k_s\cdot\{[Ca^{2+}]_e-[Ca^{2+}]\} \tag{12}$$

$$-\frac{d[Mg^{2+}]}{dt}=\left\{\frac{6\cdot S}{d_p\cdot\rho}\right\}\cdot k_s\cdot\{[Mg^{2+}]_e-[Mg^{2+}]\} \tag{13}$$

For micron-size particles, the Froessling correlation indicates that the particles mass transfer coefficient can be closely approximated by the following relation:

$$\frac{k_s\cdot d_p}{D_v}=2 \tag{14}$$

where D_v is the diffusivity of dissolved $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ ions, which has the approximate value of 8.5×10^{-6} cm²/s (at 25°C).

The varying powder concentration S can be eliminated from Eqs. (12) and (13) using the following material balance equations:

$$[Ca^{2+}]-[Ca^{2+}]_0=\frac{x}{0.5}\cdot\left\{\frac{S_0-S}{M_W}\cdot1000\right\}=\frac{x}{0.5}\cdot S_0\cdot\frac{1000}{M_W}\cdot\left\{1-\frac{d_p^3}{d_{p_0}^3}\right\} \tag{15}$$

$$\begin{aligned}[Mg^{2+}]-[Mg^{2+}]_0&=\frac{1-x}{0.5}\cdot\left\{\frac{S_0-S}{M_W}\cdot1000\right\}\\&=\frac{1-x}{0.5}\cdot S_0\cdot\frac{1000}{M_W}\cdot\left\{1-\frac{d_p^3}{d_{p_0}^3}\right\}\end{aligned} \tag{16}$$

where M_w is the molecular weight of dolomite (188.4 g/mol).

Combining Eqs. (12)–(16) gives the final differential equations each containing only one time dependent variable:

$$\begin{aligned}\frac{d[Ca^{2+}]}{dt}&=A\cdot\{[Ca^{2+}]_e-[Ca^{2+}]\}\\&\cdot\left\{1-\frac{x}{0.5}\cdot\frac{([Ca^{2+}]-[Ca^{2+}]_0)}{1000\cdot S_0}\cdot M_w\right\}^{1/3}\end{aligned} \tag{17}$$

$$\begin{aligned}\frac{d[Mg^{2+}]}{dt}&=A\cdot\{[Mg^{2+}]_e-[Mg^{2+}]\}\\&\cdot\left\{1-\frac{1-x}{0.5}\cdot\frac{([Mg^{2+}]-[Mg^{2+}]_0)}{1000\cdot S_0}\cdot M_w\right\}^{1/3}\end{aligned} \tag{18}$$

where

$$A=\frac{12\cdot D_v\cdot S_0}{(d_{p0})^2\cdot\rho} \tag{19}$$

It may be noted that the same dissolution equations apply for remineralization with both carbonic acid and sulfuric acid the only modification being in the different values of the equilibrium solubility values.

2.6. Segregated dissolution equations

Efficient mixing of the acidified desalinated water with the micronized dolomite particles can be achieved by high recycle flow of the slurry. Although dissolution of the particles takes place in a back mix system, the dissolution reaction occurs under "segregated mixed flow conditions". The various particles react with the acid in the batch mode at different time periods according to the residence distribution of a backmix flow system [17,18]. For an ideal system, the residence time distribution of the various slurry elements is given by Levenspiel [18]:

$$E(t)=\frac{\exp(-t/\tau)}{\tau} \tag{20}$$

where $E(t)\cdot dt$ represents the fraction of the slurry residing in the reaction vessel in the time interval between t and $t+dt$. The average residence time τ is given by the following:

$$\tau=\frac{V}{Q} \tag{21}$$

where V is the reaction volume and Q is the flow rate. The exit concentration for segregated flow is as follows:

$$C_{\text{out}} = \int_0^\infty C_{\text{batch}}(t)\cdot E\cdot \mathrm{d}t \tag{22}$$

As in the case of micronized calcite dissolution [17], the exit calcium $[\mathrm{Ca}]_{\text{out}}$ and magnesium $[\mathrm{Mg}]_{\text{out}}$ concentrations resulting from dissolution of a concentrated dolomite slurry under segregated mixed flow conditions are given as follows:

$$\begin{aligned}\left[\mathrm{Ca}^{2+}\right]_{\text{out}} &= \frac{1}{\tau}\cdot\int_0^\infty\left\{\left[\mathrm{Ca}^{2+}\right]\cdot\exp(-t/\tau)\right\}\cdot\mathrm{d}t\\ &= \frac{1}{\tau}\cdot\int_0^{\left[\mathrm{Ca}^{2+}\right]_e}\left\{\frac{\left[\mathrm{Ca}^{2+}\right]\cdot\exp(-f_1(\mathrm{Ca}^{2+})/\tau)}{f_2(\mathrm{Ca}^{2+})}\right\}\cdot\mathrm{d}\left[\mathrm{Ca}^{2+}\right]\end{aligned} \tag{23}$$

$$\begin{aligned}\left[\mathrm{Mg}^{2+}\right]_{\text{out}} &= \frac{1}{\tau}\cdot\int_0^\infty\left\{\left[\mathrm{Mg}^{2+}\right]\cdot\exp(-t/\tau)\right\}\cdot\mathrm{d}t\\ &= \frac{1}{\tau}\cdot\int_0^{\left[\mathrm{Mg}^{2+}\right]_e}\left\{\frac{\left[\mathrm{Mg}^{2+}\right]\cdot\exp(-f_1(\mathrm{Mg}^{2+})/\tau)}{f_2(\mathrm{Mg}^{2+})}\right\}\cdot\mathrm{d}\left[\mathrm{Mg}^{2+}\right]\end{aligned} \tag{24}$$

where

$$f_1(\mathrm{Ca}^{2+}) = \int_0^{\mathrm{Ca}^{2+}(t)}\frac{\mathrm{d}\left[\mathrm{Ca}^{2+}\right]}{A\cdot\left\{[\mathrm{Ca}^{2+}]_e-\left[\mathrm{Ca}^{2+}\right]\right\}\cdot\left\{1-\frac{x}{0.5}\cdot\frac{\left([\mathrm{Ca}^{2+}]-[\mathrm{Ca}^{2+}]_0\right)}{1000\cdot S_0}\cdot M_W\right\}^{1/3}} = t \tag{25}$$

$$f_1(\mathrm{Mg}^{2+}) = \int_0^{\mathrm{Mg}^{2+}(t)}\frac{\mathrm{d}\left[\mathrm{Mg}^{2+}\right]}{A\cdot\left\{[\mathrm{Mg}^{2+}]_e-\left[\mathrm{Mg}^{2+}\right]\right\}\cdot\left\{1-\left(\frac{1-x}{0.5}\right)\cdot\frac{\left([\mathrm{Mg}^{2+}]-[\mathrm{Mg}^{2+}]_0\right)}{1000\cdot S_0}\cdot M_W\right\}^{1/3}} = t \tag{26}$$

and

$$f_2(\mathrm{Ca}) = \frac{\mathrm{d}[\mathrm{Ca}^{2+}]}{\mathrm{d}t} \tag{27}$$

$$f_2(\mathrm{Mg}) = \frac{\mathrm{d}[\mathrm{Mg}^{2+}]}{\mathrm{d}t} \tag{28}$$

3. Experimental setup

3.1. Experimental system

The experimental system (Fig. 2) used in the study of micronized calcite dissolution [17] served this work aiming to characterize micronized dolomite powder dissolution. Backmix flow was obtained by the high recycle rate (65 L/min) of the desalinated water fed at a flow rate of 3.7–11.5 L/min. The course of dissolution was followed by periodic analyses of the product water for calcium, magnesium, alkalinity, pH, turbidity, and temperature. Full steady state conditions were reached in about 7 retention times.

3.2. Analytical methods

Calcium and magnesium concentrations were determined by ethylenediaminetetraacetic acid titrations according to Standard Methods 2340C and 3500B [19]. The pH was measured with Consort C931 pH meter. Turbidity was determined by a HACH turbid meter model 2100P.

3.3. Dolomite properties

The calcium to magnesium ratio was determined by complete dissolution of the dolomite powder with 32% hydrochloric acid and analyzing the calcium and magnesium content by inductively coupled plasma. The measured Ca to Mg molar ratio was 1.08 indicating a fractional molar calcium content of x = 0.52. Analyses of the composition of equilibrated solutions of dolomite samples dissolved by both H_2SO_4 and CO_2 at 25°C gave the following solubility product result:

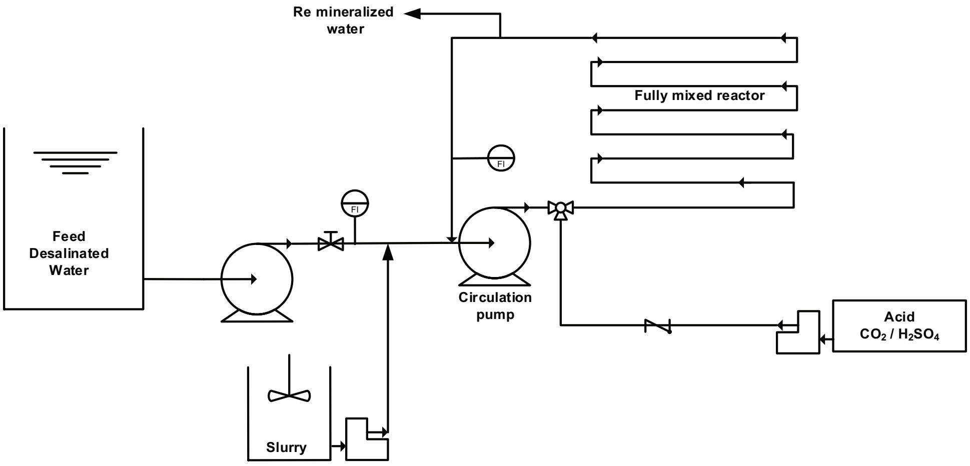

Fig. 2. Schematic diagram of the micronized dolomite dissolution system.

$$K_{sp} = \left[\mathrm{Ca}^{2+}\right]_e^{2x} \cdot \left[\mathrm{Mg}^{2+}\right]_e^{2(1-x)} \cdot \left[\mathrm{CO}_3^{2-}\right]_e^2 = 4.5\times10^{-22}\,(\mathrm{mol/L})^4$$

The dolomite powder mean particle diameter, measured by a particle size analyzer (Mastersizer 2000, Malvern, UK), was $D_{[3,2]}$ = 2.4 µm and its density, measured by a pycnometer, was 2.7 g/cm³.

3.4. Experimental program

Table 1 summarizes the experimental program. The micronized dissolution models were tested in three series of experiments conducted at: (i) dissolution levels sufficiently far from equilibrium conditions enabling verification of the kinetic model; (ii) dissolution levels sufficiently near equilibrium conditions enabling verification of the equilibrium solubility equation; and (iii) experiments designed to compare between micronized calcite and dolomite powders dissolution by sulfuric acid.

The experiments designed to compare between micronized calcite and dolomite powders dissolution were conducted at similar equilibrium calcium concentrations in the range of 1.14–2.28 mM, at S_0 = 2.5 mM, and τ = 10 min. The sulfuric acid concentration was varied from 0.7 to 1.4 mM in the calcite tests and from 2.0 to 4.9 mM in the dolomite tests.

4. Results

4.1. Validation of the dolomite kinetic model

Validation of the dolomite kinetic model was performed under relatively low dissolution driving forces, achieved by inlet slurry concentrations only slightly lower than the calcium and magnesium equilibrium solubilities. Inlet slurry feed concentration was S_0 = 0.06 mM, the inlet CO_2 and H_2SO_4 concentrations were 0.126 ($[Ca]_e$ = 0.0568 and $[Mg]_e$ = 0.0525 mM) and 0.043 mM ($[Ca]_e$ = 0.0457 and $[Mg]_e$ = 0.0421 mM), respectively. The retention time varied between 3.5 and 10.0 min. As seen in Fig. 3, good agreement between measured and predicted Ca and Mg concentrations within 10% was obtained for both acids. These results confirm the model predictions.

4.2. Verification of the equilibrium conditions model

The parameters determining product water composition are the inlet slurry and acid concentrations and the retention time. Verification of the model predicting solution composition at virtual equilibrium conditions with both acids was carried out at dissolution levels sufficiently near equilibrium conditions. Three series of experiments were performed in which two of the three parameters were kept constant, while the third parameter was varied (Table 1). Figs. 4–6 display the results showing the effects of inlet acid concentration, inlet slurry concentration, and retention time, respectively, on solution composition.

All effects were as anticipated. Increase of acid inlet concentration (Fig. 4) resulted in augmentation of the exit calcium and magnesium concentrations. Increase of the slurry concentration (Fig. 5) had no effect on the exit calcium and magnesium concentration because all runs were carried out at inlet slurry concentrations exceeding equilibrium compositions. Also, increase of the retention time (Fig. 6) had no effect on the exit calcium and magnesium concentration because the short minimum retention time of 3.6 min was sufficient to reach near equilibrium conditions. The predicted equilibrium curves in all runs are seen to virtually coincide with the

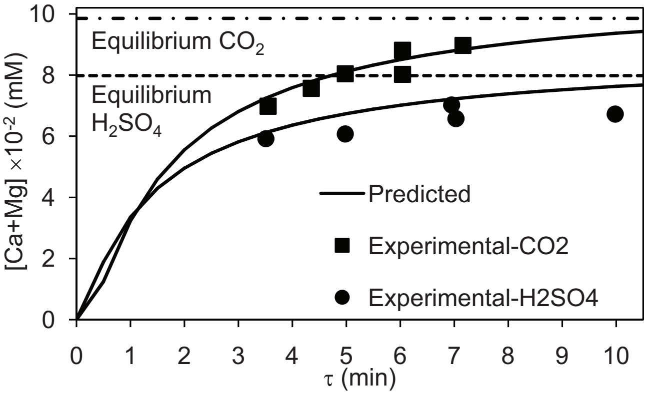

Fig. 3. Comparison of experimental and predicted values of Ca and Mg.

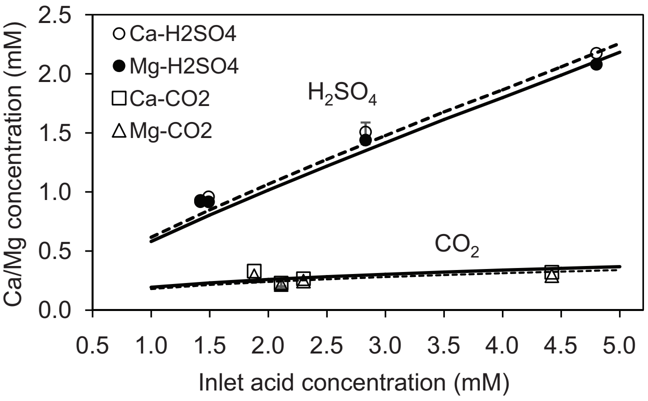

Fig. 4. Effect of inlet acid concentration on the Ca and Mg contents of the product water (solid lines—Mg equilibrium; dashed lines—Ca equilibrium).

Table 1
Experimental conditions

Parameter tested	Inlet acid concentration		Inlet slurry concentration		Retention time		Model verification	
Acid	CO_2	H_2SO_4	CO_2	H_2SO_4	CO_2	H_2SO_4	CO_2	H_2SO_4
S_0 (mM)	2.1	4.8	1.5–4.1	2.4–4.6	2.1	2.4	0.06	
$[Acid]_{in}$ (mM)	2.1–4.4	1.4–4.5	2.1	2.0	2.1	2.0	0.126	0.043
τ (min)	5.0	10.0	5.0		3.6–9.8		3.5–10.0	

experimental points indicating very good agreement with theory.

Dolomite ion recovery, by acid dissolution, is defined as the ratio of the ion solution concentration to its equilibrium concentration:

$$\text{Recovery}(\%) = \frac{[\text{Ca}]}{[\text{Ca}]_e} \cdot 100 = \frac{[\text{Mg}]}{[\text{Mg}]_e} \cdot 100 \tag{29}$$

The virtual agreement between measured and equilibrium concentrations indicates that 100% recovery can be achieved in dolomite dissolution under the experimental conditions of Figs. 4–6. It may also be noted that the measured average molar ratio of Ca to Mg in these experiments was 1.11:1 which is in close proximity to the 1.08:1 ratio of the dolomite powder (Section 3.3) lending confidence to the experimental measurements.

4.3. Comparison of dissolution by CO_2 with dissolution by H_2SO_4

The data presented in Fig. 1 showed that similar equilibrium concentrations of calcium and magnesium can be obtained with a much lower concentration of H_2SO_4 compared with CO_2. This indicates a clear advantage of using sulfuric acid as compared with carbon dioxide. Fig. 7 displays the significant reduction in acid consumption provided by sulfuric acid. For example, in order to obtain 0.69 and 0.64 mM of calcium and magnesium, respectively (total of 1.33 mM), a 26.5-fold higher concentration of CO_2 is required compared with sulfuric acid (1.13 and 30.00 mM, respectively). However, as indicated below, the required consumption of NaOH for neutralizing residual acidity is much higher with sulfuric acid.

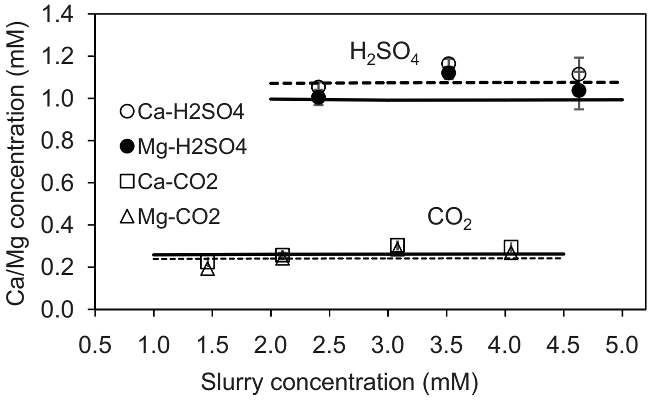

Fig. 5. Effect of slurry concentration on the Ca and Mg contents of the product water at inlet acid concentrations of 2 mM and a retention time of 5 min (solid lines—Mg equilibrium; dashed lines—Ca equilibrium).

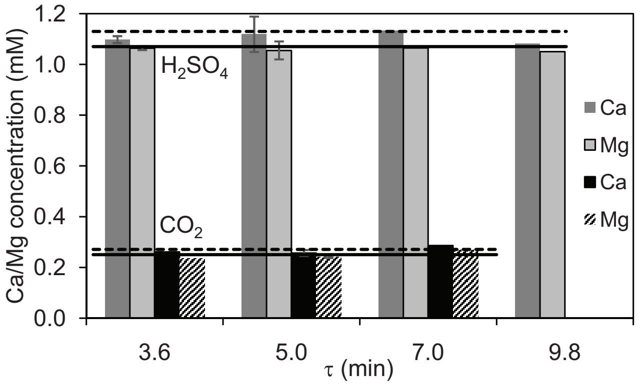

Fig. 6. Effect of slurry concentration on the Ca and Mg contents of the product water at inlet acid concentrations of 2 mM and slurry concentrations of 2.1–2.4 mM (solid lines—Mg equilibrium; dashed lines—Ca equilibrium).

Fig. 8 compares the pH of the product water obtained at various slurry concentrations at the same dosage of 2.1 mM of the two acids. As expected, the use of the stronger acid led to a lower pH of the product water in comparison with the weak acid. As the slurry concentration was increased, the product water pH was higher due to augmented residual undissolved dolomite powder.

4.4. Comparison of micronized calcite and dolomite dissolutions

Dolomite dissolution offers the alternative of remineralizing desalinated water with both calcium and magnesium instead of the prevalent approach of remineralization with

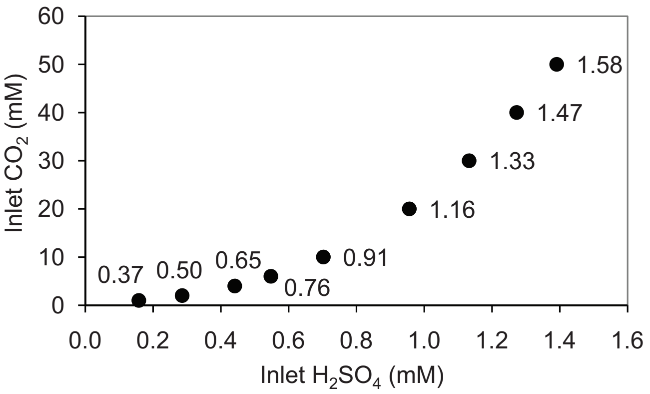

Fig. 7. Ratio of CO_2 to H_2SO_4 concentrations required to achieve similar outlet concentrations of Ca and Mg (sums of ([Ca]+[Mg]) in mM are labeled).

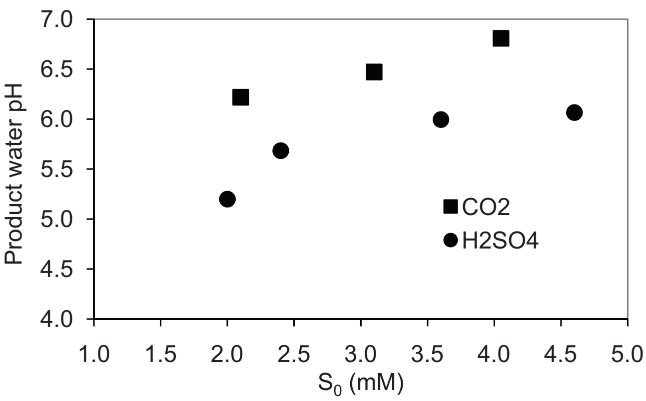

Fig. 8. Product water pH at varying dolomite slurry concentrations at inlet acid concentrations of 2.1 mM and a retention time of 10 min.

calcium only. It is therefore of interest to compare solution compositions obtained by dissolution of micronized calcite and micronized dolomite. Experiments were carried out comparing between calcite and dolomite dissolutions by H_2SO_4 at acid dosages providing the same equilibrium concentration of calcium, ranging from 1.14 to 2.28 mM. Slurry concentration was 2.5 mM, and retention time was 10 min. Results are summarized in Figs. 9 and 10.

As expected, similar calcium concentrations conforming to theory were obtained by both dolomite dissolution and calcite dissolution because in both cases slurry concentration, calcium equilibrium concentration, and retention time were the same. However, Fig. 9 shows that the acid concentration required to dissolve the dolomite was higher by more than a factor of 2. This is because in the case of dolomite, the acid releases both calcium and magnesium ions; for each 1.0 mM of calcium an additional 0.93 mM of magnesium is introduced into the desalinated water. Furthermore, the micronized dolomite powder solubility product ($K_{sp} = 4.5 \times 10^{-22}$ (mol/L)^4) is significantly lower than that solubility of calcite ($K_{sp} = 4.6 \times 10^{-9}$ (mol/L)^2).

Fig. 10 compares the product water pH obtained by the calcite and dolomite powder dissolutions of Fig. 9. As expected, the higher sulfuric acid dosages in dolomite dissolution led to lower pH levels of the water product. A pH level as low as 2.6 was obtained at the inlet H_2SO_4 concentration of 4.9 mM. Such low pH levels can have negative economic implications because the amount of neutralizing NaOH required to meet remineralized water pH standards is a major cost item [3].

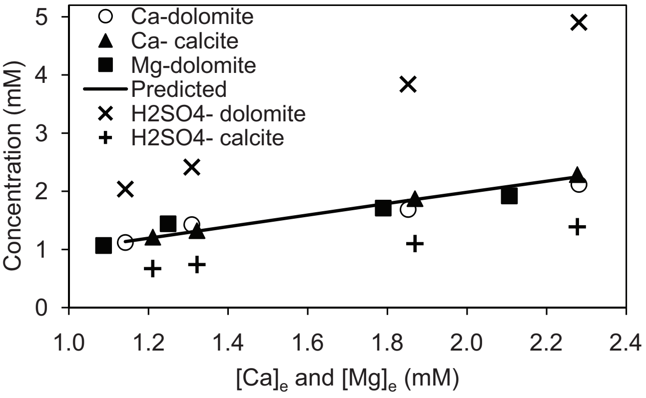

Fig. 9. Experimental and predicted exist Ca and Mg concentrations and inlet H_2SO_4 required to achieve the desired equilibrium concentrations (S_0 = 2.5 mM; τ = 10 min).

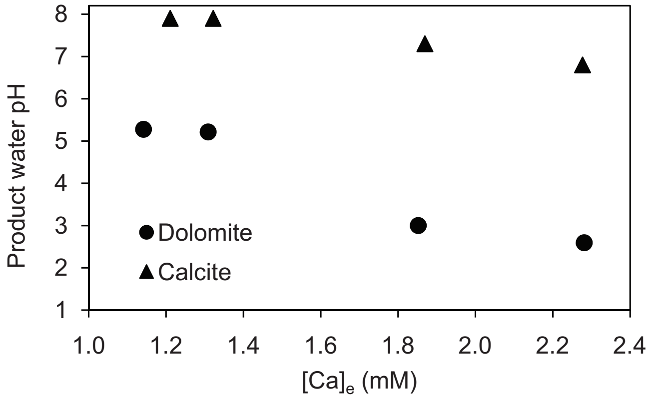

Fig. 10. Product water pH of calcite and dolomite dissolution by H_2SO_4 at varying Ca equilibrium concentrations (S_0 = 2.5 mM; H_2SO_4 = 0.7–4.9 mM; τ = 10 min).

5. Concluding remarks

The models developed in this study enable design of desalinated water remineralization by acid dissolution of micronized dolomite powder which has the advantage of introducing into the water both calcium and magnesium ions in a single process. The effects of the three major operating parameters inlet acid and dolomite slurry concentrations and retention time were systemically investigated and shown to be in full support with the theoretical models.

Dissolution with both carbon dioxide and sulfuric acid was examined. Acid consumption can be significantly reduced by use of sulfuric acid instead of carbon dioxide, but the required consumption of NaOH for neutralizing residual acidity is much higher with sulfuric acid. Clearly economic optimization calculation is called for.

Acknowledgment

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Nomenclature

A	—	Frequency factor, cm/min
[Ca]	—	Calcium concentration, mM
$[Ca]_0$	—	Calcium initial concentration, mM
$[Ca]_e$	—	Calcium equilibrium concentration, mM
$[CO_2]_0$	—	Carbon dioxide initial concentration, mM
$[CO_2]_e$	—	Carbon dioxide equilibrium concentration, mM
dp	—	Mean particle diameter, cm
dp_0	—	Initial mean particle diameter, cm
D_v	—	Diffusivity, cm^2/s
$[H^+]_e$	—	Equilibrium acidity
K_1	—	First carbonate equilibrium dissociation constant, mol/L
K_2	—	Second carbonate equilibrium dissociation constant, mol/L
k_s	—	Mass transfer coefficient, cm/min
K_{sp}	—	Dolomite solubility product, (mol/L)^4
K_w	—	Water dissociation constant, (mol/L)^2
[Mg]	—	Magnesium concentration, mM
$[Mg]_0$	—	Initial magnesium concentration, mM
$[Mg]_e$	—	Magnesium equilibrium concentration, mM
M_w	—	Molecular weight, g/mol
S	—	Slurry concentration, mM
S_0	—	Inlet slurry concentration, mM
Sh	—	Sherwood number
$[SO_4^{2-}]$	—	Sulfate concentration, mM
t	—	Time, min
x	—	Fractional molar calcium content in dolomite

Greeks

α_1 — HCO_3^- total carbon fraction
α_2 — CO_3^{2-} total carbon fraction
ρ — Density, g/cm^3
τ — Retention time, min

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