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Remineralization of desalinated water by limestone dissolution with carbon dioxide

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ABSTRACT

A commonly used remineralization process involves bringing CO_2-acidified desalinated water in contact with a bed of limestone. Dissolution of limestone provides two essential ingredients to the water: bicarbonate alkalinity and calcium content. The kinetics of limestone dissolution with CO_2 was studied as a function of inlet CO_2 concentration, water flow velocity, and temperature. The experimental data conformed very well to the Yamauchi model. Optimal design of a hardening column is discussed.

Keywords: Desalinated water; Hardening; Calcite dissolution; Kinetic model; Optimal design

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1. Introduction

Since desalinated water is devoid of minerals, a certain degree of remineralization is necessary in order to meet health requirements and to make the water palatable and non-corrosive. There are four main remineralization processes:

(1) Addition of $CaCl_2$ and $NaHCO_3$.
(2) Lime dissolution by carbon dioxide:

$$Ca(OH)_2 + 2CO_2 \rightarrow Ca^{2+} + 2HCO_3^- \tag{1}$$

(3) Limestone dissolution by carbon dioxide:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \tag{2}$$

(4) Calcite dissolution by sulfuric acid:

$$2CaCO_3 + H_2SO_4 \rightarrow Ca(HCO_3)_2 + CaSO_4 \tag{3}$$

Limestone dissolution is by far the simplest and most widely used process. Calcite pellets are commonly used. Design of a limestone packed bed column requires a reliable kinetic expression describing the dissolution of calcite pellets. Hasson and Bendrihem [1] examined several published kinetic expressions. Their experimental data were found to fit closely the Yamauchi et al. [2] model which is based on the assumption that the dissolution driving force is the difference between the bulk and equilibrium CO_2 concentrations ($[CO_2]_e$). The depletion of the dissolved CO_2 in the water percolating through the limestone column is then given by:

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$$\ln\frac{[\mathrm{CO_2}]_\mathrm{L} - [\mathrm{CO_2}]_\mathrm{e}}{[\mathrm{CO_2}]_0 - [\mathrm{CO_2}]_\mathrm{e}} = -k \cdot \frac{6(1-\varepsilon)}{d_\mathrm{p}\phi} \cdot \frac{L}{u} \tag{4}$$

where $[\mathrm{CO_2}]_0$, $[\mathrm{CO_2}]_\mathrm{L}$, $[\mathrm{CO_2}]_\mathrm{e}$ are the inlet, outlet and equilibrium concentrations of the carbon dioxide respectively, k is the dissolution reaction rate coefficient, u is the superficial flow velocity, ε is the fractional bed porosity, L is the bed height, d_p is the pellet equivalent diameter, and ϕ is the pellet shape factor.

Material balance relations show that Eq. 4 also holds for concentration changes in the calcium and bicarbonate ions:

$$\ln\frac{[\mathrm{HCO_3}]_\mathrm{e} - [\mathrm{HCO_3}]_\mathrm{L}}{[\mathrm{HCO_3}]_\mathrm{e} - [\mathrm{HCO_3}]_\mathrm{o}} = \ln\frac{[\mathrm{Ca}]_\mathrm{e} - [\mathrm{Ca}]_\mathrm{L}}{[\mathrm{Ca}]_\mathrm{e} - [\mathrm{Ca}]_\mathrm{o}} = -k \cdot \frac{6(1-\varepsilon)}{d_\mathrm{p}\phi} \cdot \frac{L}{u} \tag{5}$$

The equilibrium concentrations are given by [1]:

$$[\mathrm{CO_2}]_\mathrm{e} = \frac{K_2}{2K_1K_\mathrm{sp}} \times [\mathrm{HCO_3^-}]_\mathrm{e}^3 = [\mathrm{CO_2}]_\mathrm{o} - \frac{1}{2}[\mathrm{HCO_3^-}]_\mathrm{e} = [\mathrm{CO_2}]_\mathrm{o} - [\mathrm{Ca}]_\mathrm{e} \tag{6}$$

where, K_1 and K_2 are the first and second dissociation constants of carbonic acid respectively and K_sp is the solubility product of $\mathrm{CaCO_3}$.

The experimental by Yamauchi et al. [2] carried out at 40°C yielded a value of $6\,\mathrm{k}/\phi = 31.3 \times 10^{-3}$ mm/s for the kinetic coefficient, while the experimental by Hasson and Bendrihem [1] carried out at 30°C gave the value of $6\,\mathrm{k}/\phi = 25.0 \times 10^{-3}$ mm/s.

The kinetic coefficient is known to depend on the crystal habit of the specific calcite pellets, their inner porosity, and the impurities they contain [3]. The objectives of this research were to measure the kinetic coefficient of certain specific pellets, to extend the scope of available calcite dissolution data and to study the temperature effect.

2. Experimental

Dissolution experiments were conducted using two Perspex columns (1.8 m high and 98 mm internal diameter) connected in series. Each column was filled to a height of 94 cm with limestone pellets supplied by the Zmitut 81 Company, Israel. The limestone pellets consisted of over 96% $\mathrm{CaCO_3}$ and the average size of the pellets was 2.0 mm. A schematic description of the experimental system is given in Fig. 1.

The limestone dissolution path along the packed bed was followed by monitoring the composition of water extracted from 15 sampling points located along the length of the two columns. Each sample was analyzed to determine its pH, alkalinity, and calcium contents.

Four test series were conducted. The effect of the inlet $\mathrm{CO_2}$ was examined at the average water temperature of 22°C and a superficial flow velocity of 4.56 mm/s at three $\mathrm{CO_2}$ concentrations (3.4, 4.3, 6.8 mmol/L). Tests at low $\mathrm{CO_2}$ concentrations (0.25, 0.75, 1.40 mmol/L) were also undertaken at a velocity of 4.56 mm/s and a temperature of 30 °C in order to resolve issue of applicability of the model at low $\mathrm{CO_2}$ concentrations. The velocity effect was studied by performing dissolution runs at two additional velocities (0.275, 0.757 mm/s) at a constant inlet $\mathrm{CO_2}$ concentration of 4.3 mmol/L and a temperature of 22°C. The effect of temperature was investigated in experiments performed at 22, 30 and 40°C at a superficial flow velocity of 4.56 mm/s and an inlet $\mathrm{CO_2}$ concentration of 4.3 mmol/L.

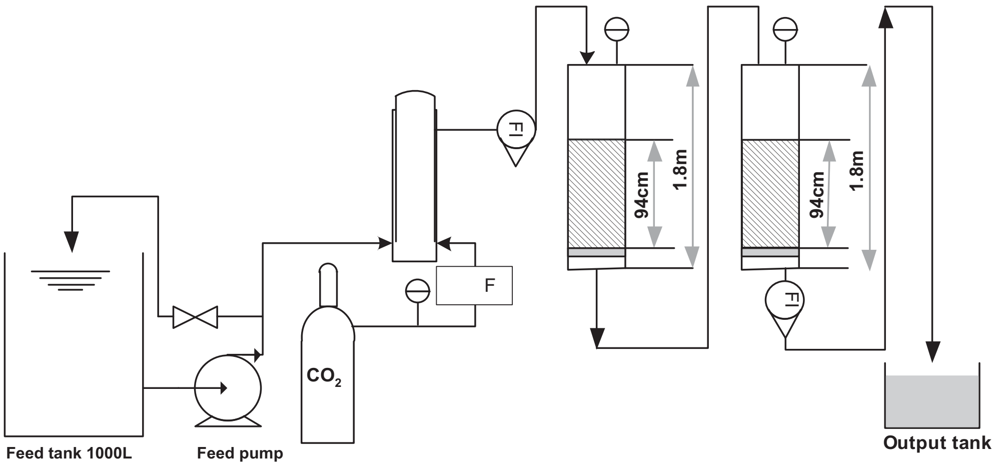

Fig. 1. Schematic diagram of the experimental system.

3. Results

3.1. Confirmation of the Yamauchi model

The Yamauchi model (Eq. 5) predicts a linear relationship for the plot of $\ln\frac{[X]_e-[X]_L}{[X]_e-[X]_0}$ vs. the bed height L, where X represents either $[HCO_3]$ or [Ca] and the subscripts 0, L, and e stand for inlet, bed height and equilibrium concentrations respectively. The slope of the line yields the value of the kinetic coefficient $6\,k/\phi$.

The data of all runs were found to conform very well with the Yamauchi et al. model thus strongly reaffirming its validity and dispelling the erroneous comments made in a recent review paper [4]. The driving force in all mass transfer processes is a concentration difference between bulk and equilibrium conditions. There is no reason whatsoever for the claim made in the above review that this fundamental postulate embodied in the Yamauchi model does not hold for calcite dissolution.

The agreement of the experimental data with those of the model is illustrated in Fig. 2. The profiles of both the bicarbonate and calcium ions given by Eq. 5 are seen to fall on identical straight lines passing through the origin with a correlation coefficient R^2 exceeding 0.99.

The excellent fit between the experimental dissolution profile and that of the Yamauchi et al. model is further illustrated in Fig. 3 which compares experimental alkalinity data with calculated values.

3.2. Correlation of the limestone dissolution rate coefficients

The velocity effect runs conducted at 22°C and a constant inlet CO_2 concentration of 4.3 mmol/L gave almost similar values of $6\,k/\phi = (6.95 \pm 0.15) \times 10^{-3}$, $(7.13 \pm 0.18) \times 10^{-3}$ and $(7.31 \pm 0.12) \times 10^{-3}$ mm/s at the three tested velocities (2.75, 4.56, 7.57 mm/s respectively).

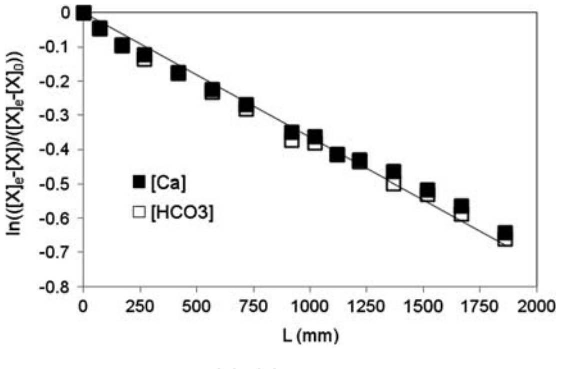

Fig. 2. Linear plot of $\ln\frac{[X]_e-[X]_L}{[X]_e-[X]_0}$ vs. bed height L conforming to that of the Yamauchi model.

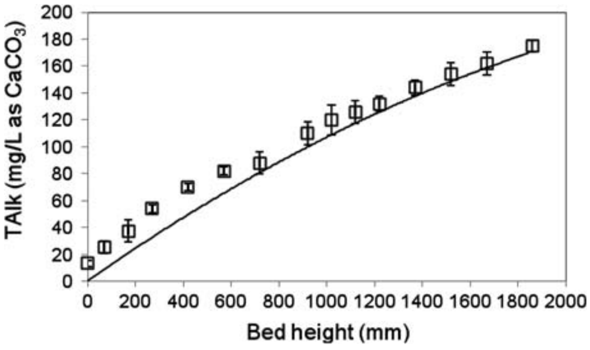

Fig. 3. Comparison of measured alkalinities (squares) with predicted values (line); $[CO_2]_o = 6.8$ mmol/L, u = 4.6 mm/s, $6\,k/\phi = 7.1 \times 10^{-3}$ mm/s.

The inlet CO_2 effect runs conducted at the concentrations of 3.4, 4.3, 6.8 mmol/L and a temperature of 22 ℃ gave an essentially identical value of the kinetic coefficient $(6\,k/\phi = (6.59 \pm 0.67) \times 10^{-3}$ mm/s). Close agreement of the kinetic coefficient over a wide range of inlet CO_2 concentrations and flow velocities renders further confidence on the validity of the model.

The effect of temperature on the rate coefficient was investigated at a superficial flow velocity of 4.56 mm/s and CO_2 inlet concentration of 4.3 mmol/L in runs conducted at temperatures of 20, 30 and 40℃. The data were analyzed according to the Arrhenius equation:

$$k = A \cdot e^{-\frac{E_a}{RT}} \tag{7}$$

where, k is the rate constant, A is the frequency factor, E_a is the activation energy, T is the absolute temperature and R is the universal gas constant (8.314 J/K mol). The equation predicts a linear relationship between $\ln(k)$ and $1/T$; the slope of the line (E_a/R) provides the value of the activation energy.

Fig. 4 displays a plot of $\ln(6\,k/\phi)$ vs. $1/T$. It is seen that the data fall on a straight line yielding an activation energy of 52 kJ/mol and a frequency factor of 10^7 mm/s. The value of the activation energy falls well within the range of 45–65 kJ/mol obtained in various studies of calcite dissolution [5–7]. The temperature dependence of the rate constant for the Zmitut 81 calcite pellets used in this study is therefore as follows:

$$\frac{6k}{\phi} = 1.06 \cdot 10^7 \cdot \exp-\left(\frac{52{,}000}{RT}\right)\ \text{mm/s} \tag{8}$$

Rather widely scattered kinetic coefficients were measured at a low CO_2 concentration range in a pre-

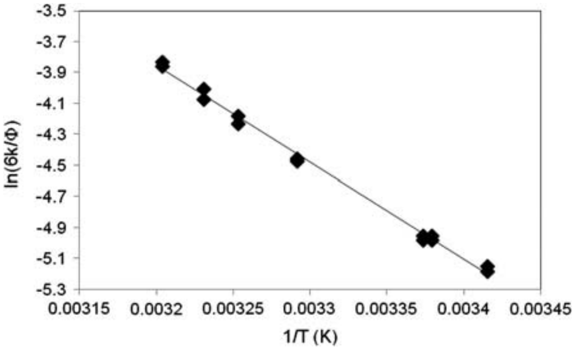

Fig. 4. Determination of the activation energy of limestone dissolution.

vious investigation [1]. The runs performed in this study at the low CO_2 concentrations of 0.25, 0.75 1.40 mol/L at a flow velocity of 4.56 mm/s and a temperature of 30 ℃ were far less scattered and gave the value of $6\,k/\phi = (12.0 \pm 0.16) \times 10^{-3}$ mm/s. This is in excellent agreement with the value of $6\,k/\phi = 11.5 \times 10^{-3}$ mm/s given by Eq. 8. It may therefore be concluded that the Yamauchi model is also valid for low CO_2 concentrations.

4. Hardening process optimization

The design of a hardening column has to meet certain water qualifications. Current Israeli regulations specify the following quality of hardened desalinated water: alkalinity >80 mg/L as $CaCO_3$; calcium between 80–120 mg/L as $CaCO_3$; $7.5 < pH < 8.3$ and Calcium Carbonate Precipitation Potential (CCPP) between 3 and 10 mg/L as $CaCO_3$.

The main operational parameters affecting the minimum cost design of a hardening column, based on specific limestone pellets are: the packed column height, the inlet CO_2 concentration and the blending ratio of hardened water with non-hardened desalinated water. As evident from the kinetics of dissolution (Eqs. (4) and (5)), a high inlet CO_2 concentration enables attainment of a desired calcium concentration in a shorter column. However, to meet the required alkalinity and pH conditions, the residual CO_2 must be neutralized with NaOH, as indicated in Fig. 5. When hardening only a fraction of the desalinated water and then blending it with untreated water, higher hardening levels are required calling for higher inlet CO_2 concentrations. The optimal design is obtained when the total cost, composed of the amortized cost of the hardening column and the cost of the chemicals CO_2 and NaOH, is at a minimum.

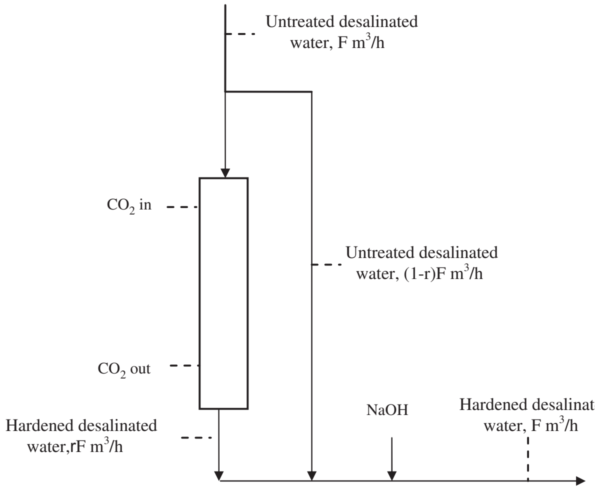

Fig. 5. Schematic flow sheet of desalinated water hardening system (*r* represents fractional flow of the treated water).

5. Conclusions

The extensive experimental data obtained in this study reaffirm a previous conclusion [1] that the Yamauchi et al. model [2] accurately describes the kinetics of dissolution of limestone pellets in a packed bed and can be confidently used for design purposes. The kinetic coefficient of $6\,k/\phi = 12 \times 10^{-3}$ mm/s measured at 30℃ in this study with Zmitut 81 pellets of 96% $CaCO_3$ purity is significantly lower than the kinetic coefficient of $6\,k/\phi = 25 \times 10^{-3}$ mm/s obtained at the same temperature in the study of the dissolution of "Akdolit hydrocarbonat pellets" [1] having a purity of 98% $CaCO_3$. This demonstrates the divergence in properties of various limestones and the need to verify the dissolution properties of the specific pellets used. Availability of reliable dissolution rate coefficients is essential for optimal hardening column design.

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