

The potential of CO₂ stripping for pretreating brackish and wastewater desalination feeds

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Abstract

Many scaling species such as CaCO₃, Mg(OH)₂ and Ca₃(PO₄)₂ present in brackish and wastewater feeds can be removed by precipitation processes induced by raising the pH level of the raw water. These processes require dosage of alkaline chemicals such as NaOH, lime or magnesia. An interesting possibility for eliminating the need for chemical dosage exists in the case of feed waters having high carbonate contents. In this case, simple air bubbling enables stripping the acidic CO₂ component of the carbonate system, thus acting to raise the pH level of the solution without chemical addition. The present work analyzes parameters affecting the pH level induced by CO₂ removal from solution. Simulation results show that a high pH, exceeding 9, can be achieved with waters having a moderate carbonate level. Batch experiments were conducted to verify conclusions from the simulation study and to provide kinetic data relating the mass transfer coefficient with air sparging parameters. Continuous flow experiments showed that most of dissolved CO₂ can be successfully stripped out by ambient air at retention times below 2 h. Results of this study indicate a marked potential for beneficial application of a CO₂ stripping pretreatment process for brackish and wastewater feeds having a sufficient carbonate content.

Keywords: CO₂ stripping; Carbonate equilibria; pH increase; Hardness removal; CaCO₃ precipitation

1. Introduction

Many scaling species such as CaCO₃, Mg(OH)₂ and Ca₃(PO₄)₂ present in brackish and wastewater feeds can be removed by precipitation processes induced by raising the pH level of the raw water. These processes require

dosage of alkaline reagents such as NaOH, lime or magnesia.

Reduction in the use of chemicals is of general interest from both environmental and economic considerations. An interesting possibility for eliminating the dosage of alkaline reagents exists in the case of feed waters having relatively high carbonate contents. In this case, simple air bubbling enables stripping of the acidic CO₂

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component of the carbonate system, thus acting to raise the pH level of the solution without chemical addition.

The potential of the CO₂ air stripping technique has so far been considered in connection with wastewater treatment processes. Battistoni et al. [1] applied the CO₂ stripping process for phosphate removal from supernatant anaerobically digested sludge. The pH increase induced precipitation of the phosphate in the form of struvite (MgNH₄PO₄) and hydroxyapatite (Ca₅OH(PO₄)₃). Kim et al. [2] utilized CO₂ stripping in an anaerobic sludge blanket process of a papermaking wastewater. The pH increase served to eliminate the alkalinity produced by biological COD degradation through CaCO₃ precipitation. Lahav et al. [3] applied the CO₂ stripping process for controlling the pH in fish ponds. The stripping technique was used by Kawase et al. [4] for increasing the pH of acidified water effluent produced in the flue gas desulphurization process. Cohen and Kirchman [5] pointed out that due to the presence of CO₂ in ambient air, stripping a carbonate solution by air provides a somewhat lower maximum pH value than that obtained by using a pure gas such as N₂ or O₂.

The present paper summarizes results of a study aiming to characterize the effects of various parameters on the pH level that can be induced by air stripping of dissolved CO₂. Water compositions for which CO₂ stripping is more advantageous than conventional alkali addition treatment are analyzed. Parameters influencing the design of an air sparging system are evaluated. Results demonstrating efficient CaCO₃ precipitation by CO₂ stripping in a continuous flow crystallizer are presented.

2. Theoretical background

2.1. Effects generated by CO₂ release in carbonate-rich solutions

Carbon dioxide dissolved in water is first converted to carbonic acid which then dissociates

to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions according to the following equilibria:

$$K'_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (1)$$

$$K'_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (2)$$

where K'_1 and K'_2 are the first and second dissociation constants of carbonic acid and $[\text{CO}_2]$ is the concentration of dissolved carbon dioxide (which includes the minute concentration of the residual carbonic acid $[\text{H}_2\text{CO}_3]$).

The distribution of the carbonate species can be readily evaluated from measurements of the solution pH and the total alkalinity [6]. In the absence of phosphates, borates and silicates, the total alkalinity of the carbonate solution is given by:

$$T_{\text{Alk}} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- - \text{H}^+ \quad (3)$$

From Eqs. (1–3), concentrations of the carbon species are found to depend on solution pH and total alkalinity according to the following relations:

$$[\text{CO}_3^{2-}] = \left(T_{\text{Alk}} + [\text{H}^+] - \frac{K'_w}{[\text{H}^+]} \right) \frac{K'_2}{2K'_2 + [\text{H}^+]} \quad (4)$$

$$[\text{HCO}_3^-] = \left(T_{\text{Alk}} + [\text{H}^+] - \frac{K'_w}{[\text{H}^+]} \right) \frac{[\text{H}^+]}{2K'_2 + [\text{H}^+]} \quad (5)$$

$$[\text{CO}_2] = \left(T_{\text{Alk}} + [\text{H}^+] - \frac{K'_w}{[\text{H}^+]} \right) \times \frac{[\text{H}^+]^2}{2K'_1K'_2 + [\text{H}^+]K'_1} \quad (6)$$

where K'_w is the water dissociation and the dash (') denotes correction for ionic strength effects. The total carbon content, C_T , as a function of T_{Alk} and pH of the solution is therefore:

$$C_T = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{CO}_2$$

$$= \left(\frac{T_{\text{Alk}} + \text{H}^+ - \frac{K_w}{\text{H}^+}}{1 + 2 \frac{K_2}{\text{H}^+}} \right) \left(1 + \frac{K_2}{\text{H}^+} + \frac{\text{H}^+}{K_1} \right) \quad (7)$$

The effectiveness of CO_2 stripping for the generation of alkaline conditions and a high CaCO_3 precipitation potential is illustrated in Figs. 1 and 2. Fig. 1 shows the development of alkaline conditions by CO_2 desorption from a solution having the following initial composition: $\text{Ca}^{2+} = 112$ PPM, $T_{\text{Alk}} = 350$ PPM as CaCO_3 , $\text{pH} = 7$, ionic strength = 0.036 mol/L and LSI = 0.1. The initial total carbon of this solution is 8.29 mmol/L. It is seen in Fig. 1 that desorption of 2 mmol/L of CO_2 , which represents less than 25% of the initial C_T , increases the pH level from 6.9 to 9.0 thereby augmenting the CO_3^{2-} concentration by a factor as high as 100. The

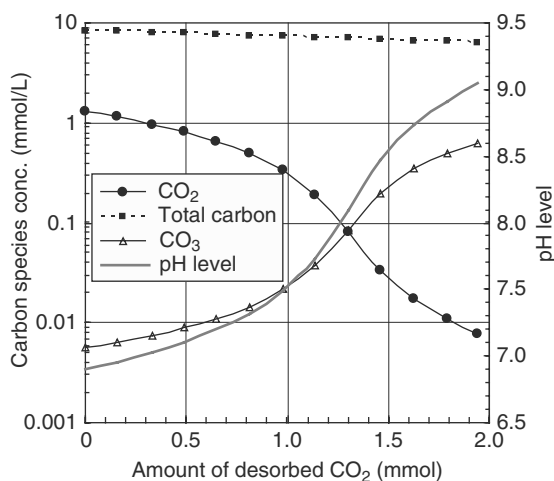


Fig. 1. Effect of CO_2 desorption on the pH and on the carbon species distribution ($T_{\text{Alk}} = 350$ PPM as CaCO_3).

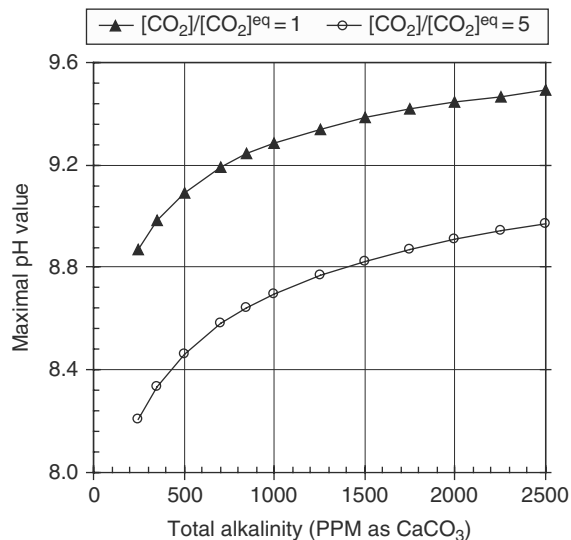


Fig. 2. Theoretical and actual pH levels that can be achieved by CO_2 desorption from solutions of different T_{Alk} .

end effect is an increase of the supersaturation level by the same factor (from LSI = 0.1 to LSI = 2.1).

The maximum pH level that can be achieved by air stripping of a carbonate solution is restricted by the CO_2 content of ambient air. This limiting condition is given by the equilibrium solubility of CO_2 corresponding to its partial pressure in air. Fig. 2 shows limiting values of the pH for solutions having total alkalinities in the range of 250–2500 PPM as CaCO_3 . Two cases are considered: the theoretical case of equilibrium between the solution and the ambient air $[\text{CO}_2]_{\text{residual}}/[\text{CO}_2]^{\text{eq}} = 1$) and the more realistic case of partial CO_2 desorption ($[\text{CO}_2]_{\text{residual}}/[\text{CO}_2]^{\text{eq}} = 5$). Equilibrium desorption of the dissolved CO_2 to the ambient air would induce pH levels higher than 9 for solutions having a total alkalinity exceeding 400 PPM (as CaCO_3). Partial desorption of CO_2 can induce pH values higher than 9 only for solutions having a total alkalinity exceeding 2500 PPM (as CaCO_3). Clearly, the residual CO_2 content,

which is dictated by the efficiency of the air sparging process, is a crucial design variable. Parameters affecting the desorption efficiency were therefore investigated.

2.2. Comparison of CaCO_3 precipitation by alkali addition with precipitation by CO_2 stripping

The overall CaCO_3 precipitation reaction is given by



In an alkali dosage process in which it is desired to maintain a certain precipitation pH level, NaOH will be consumed in two reaction steps — CO_3^{2-} formation and neutralization of CO_2 formed in the precipitation reaction:

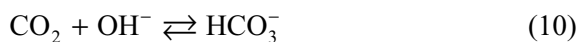
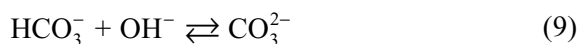


Fig. 3 shows the amount of NaOH required in the absence of CaCO_3 precipitation in order

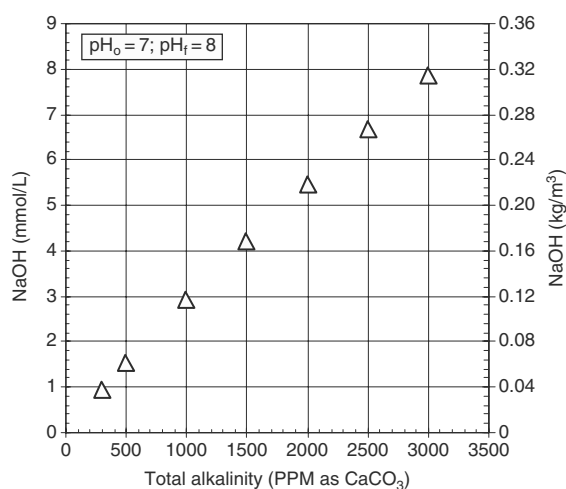


Fig. 3. NaOH consumed in increasing the pH level from 7 to 8 for solutions having different T_{Alk} .

to raise the pH level from 7 to 8 of solutions having different alkalinities. Since the buffer capacity of a carbonate solution increases with the total alkalinity level, the alkali consumption grows significantly with the increase in solution alkalinity. In raising the pH by the CO_2 stripping process, order of magnitude calculations show that the increase of T_{Alk} from 300 to 3000 (PPM as CaCO_3) augments the air consumption by a few percent only.

Fig. 4 shows the amount of NaOH consumed when the pH increase is accompanied by CaCO_3 precipitation for various initial total alkalinities and for the same initial and final pH values of 7 and 8 respectively. The concentrations ratio of initial total alkalinity to initial Ca^{2+} (in equivalent units) was held constant at 1.25. The alkali supplied to the solution served to increase the pH level and to maintain a constant LSI precipitation potential. It is seen that neutralization of the CO_2 released in the CaCO_3 precipitation reaction increased the NaOH consumption by a factor as high as 3.5. The CO_2 stripping process has the advantage that the CO_2 produced by the precipitation reaction is stripped by the aeration

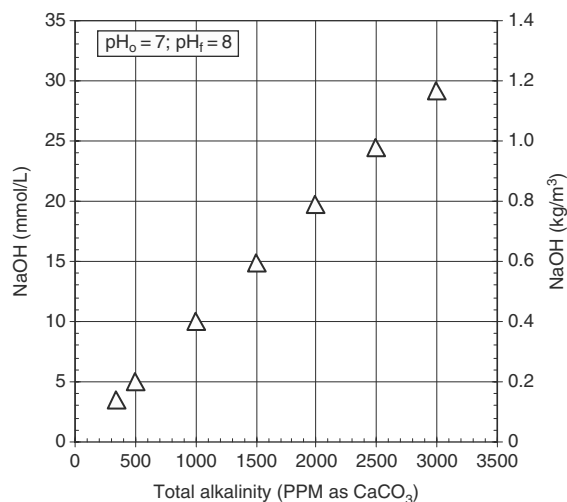


Fig. 4. NaOH consumed in increasing the pH level from 7 to 8 in the presence of CaCO_3 precipitation.

process. Calculations show that though the air consumption is also increased by a factor of 3.5, it is almost unaffected by the total alkalinity level of the solution.

3. Experimental

3.1. Characterization of the air stripping operation

The air flow rate and the corresponding power consumption of the air used for the CO₂ stripping operation depend on mass transfer aspects which are related to two sets of parameters:

- Geometrical details of the sparging system (impeller agitation speed, sparger geometry, etc.).
- Solution composition parameters (pH, total alkalinity, etc.).

Mass transfer characterization of the air stripping operation was based on the following considerations. The CO₂ stripping process does not alter the value of the total alkalinity. Loss of acidity induced by CO₂ desorption raises the pH and reduces the concentrations of the CO₂ and of C_T. Since a change in the pH alters the distribution of the carbon species, R_{CO₂}, the specific rate of CO₂ desorption [mol/s m³], is given by the change in total carbon content C_T and not by the change in the CO₂ concentration:

$$R_{\text{CO}_2} = \frac{N_{\text{CO}_2}}{V_L} = -\frac{dC_T}{dt} \quad (11)$$

where N_{CO_2} is the CO₂ desorption rate [mol/s] and V_L is the total solution volume.

The kinetics of CO₂ desorption can be characterized by the following overall mass transfer equation based on the liquid phase driving force:

$$R_{\text{CO}_2} = -\frac{dC_T}{dt} = K_L a \left([\text{CO}_2]_{\text{bulk}} - [\text{CO}_2]^{\text{eq}} \right) \quad (12)$$

where K_L is the overall mass transfer coefficient [m/s], a is the interfacial area of the air bubbles

per unit solution volume ($a = A_G/V_L$) [1/m], $[\text{CO}_2]_{\text{bulk}}$ is the bulk CO₂ concentration and $[\text{CO}_2]^{\text{eq}}$ is the concentration of CO₂ at equilibrium with the gaseous phase. Since evaluation of the interfacial area of the bubbles is difficult, it is customary to define the mass transfer in the system by the magnitude of an overall volumetric mass transfer coefficient $K = K_L a$ [1/s] which combines the intrinsic mass transfer coefficient with the interphase mass transfer area.

Values of K were determined by measuring the pH of the aerated solution versus time. Using Eqs. (4–7), the pH data were converted to plots of $-dC_T/dt$ vs. dissolved CO₂ concentration. The slope of the linear curve obtained provided the value of the volumetric mass transfer coefficient K (see Fig. 8).

The effectiveness of the CO₂ stripping process in a given aeration apparatus can be assessed from the magnitude of K achieved in the system. Major parameters affecting the magnitude of K are the air flow rate and the solution agitation speed.

3.2. Effects of agitation speed and air flow rate on the volumetric mass transfer coefficient

Magnitudes of the volumetric mass transfer coefficient were determined from batch experiments conducted in a 21 L vessel schematically shown in Fig. 5. To simplify calculations and to avoid CaCO₃ precipitation, the experimental solution contained only dissolved NaHCO₃. In all experiments the initial pH of the solution was adjusted to 6.9 by CO₂ bubbling. The solution was then subjected to aeration for a period of 20 min and the increase of the pH level with time was recorded. The solution composition and experimental conditions are summarized in Table 1.

Fig. 6 shows the results of the pH increase with time at different aeration rates for a constant agitation speed of 500 RPM. Fig. 7 shows the results of the pH increase with time for different

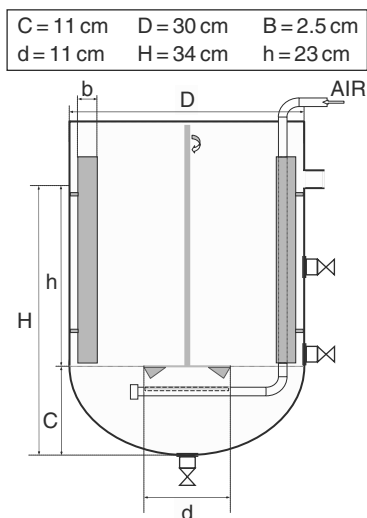


Fig. 5. Aeration vessel.

agitation speeds at a constant aeration rate of 15 LPM. The injection air was essentially at atmospheric pressure and room temperature. Fig. 8 shows the rate of C_T depletion from solution as a function of the momentary CO_2 concentration for various aeration rates at a constant agitation speed of 500 RPM. It is seen that the data fall on substantially linear plots.

Mass transfer coefficients represented by the slopes of such lines are plotted in Fig. 9, which shows the effect of the aeration rate on K at different agitation speeds. It is evident that agitation speed is the major design parameter. At relatively low agitation speeds, increase of the aeration rate has little effect, probably due to the limiting condition of a “flooding velocity”. High agitation speeds presumably act to delay the flooding phenomenon and hence enable the increase of K with the increase in aeration rate.

Table 1

Conditions in the batch aeration experiments

Na^+	1132 PPM	Ionic strength	0.052 M
T_{Alk} (as $CaCO_3$)	2460 PPM	Temperature	33.5°C
Aeration rate	6 – 25 LPM	Agitation	250–500 RPM
Initial pH = 6.9			

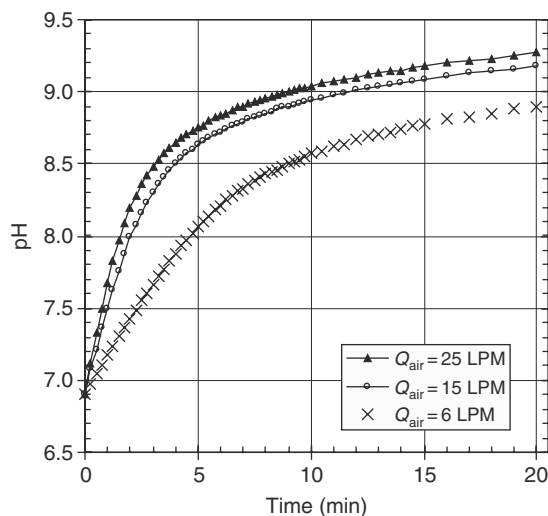


Fig. 6. Increase of the pH of the solution at different aeration rates for the agitation speed of 500 RPM.

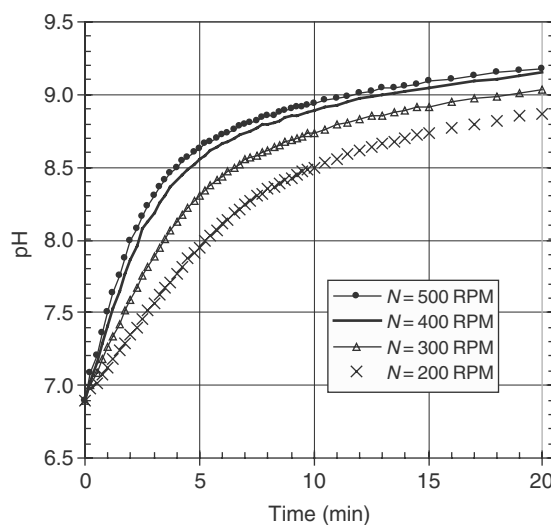


Fig. 7. Increase of the pH of the solution at different agitation speed at the aeration rate of 15 LPM.

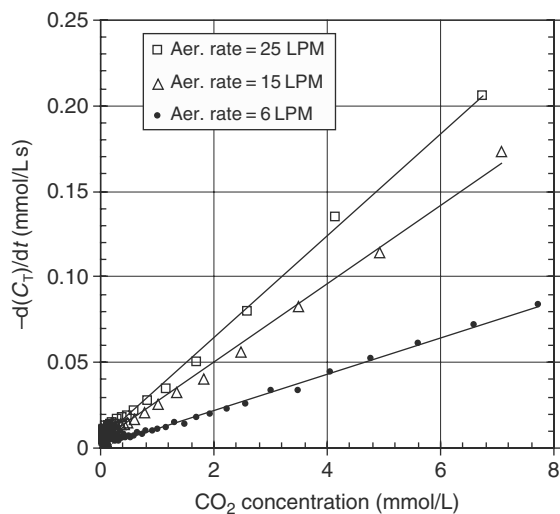


Fig. 8. Rate of CO₂ desorption vs. momentary CO₂ concentration at the agitation speed of 500 RPM.

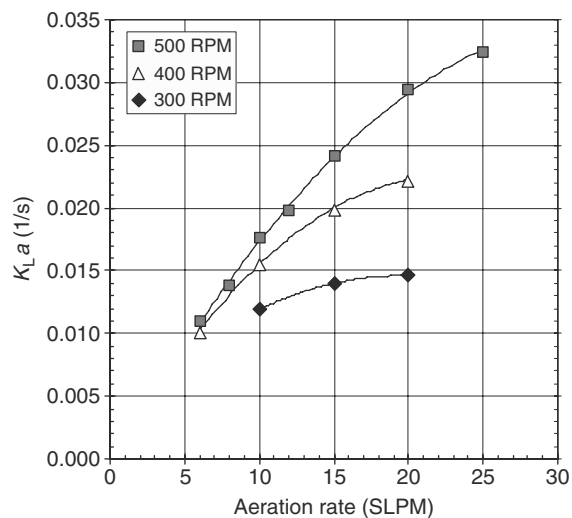


Fig. 9. Dependence of the mass transfer coefficient on the aeration rate at different agitation speeds.

3.3. CaCO₃ precipitation by CO₂ stripping

The effectiveness of the CO₂ stripping process in CaCO₃ precipitation is illustrated by the results obtained in the continuous flow experimental system shown in Fig. 10. Feed solution

was stored in a 180 L feed tank. A desired initial pH level was adjusted in the intermediate vessel. Precipitation of CaCO₃ occurred in the 21 L MSMMPR crystallizer shown in Fig. 5.

The feed used in the experiments (Table 2) consisted of a solution held at supersaturation

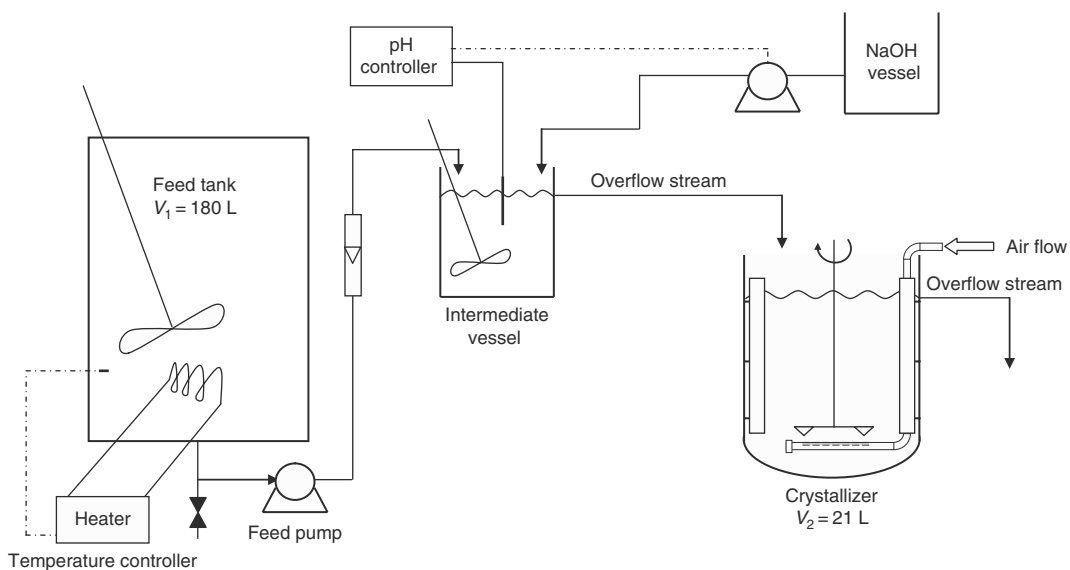


Fig. 10. Continuous flow precipitation system.

Table 2
Conditions in the continuous flow precipitation experiments

Ion	Concentration, PPM	Parameter	Range
Ca ²⁺	680	Temperature	33.3°C
Na ⁺	2708	Residence time	2 h
T _{Alk} (as CaCO ₃)	2450	Aeration rate	6–25 SLPM
Cl ⁻	5300	Agitation	500 RPM
Anti-scalant (Permatreat 191)	25	Initial pH	7.5

with respect to CaCO₃ by the presence of an anti-scalant; it simulated the typical composition of a concentrate emanating from a brackish water desalination plant. The agitation speed was set to the optimal value of 500 RPM suggested by the batch experiments. The pH and Ca²⁺ and T_{Alk} concentrations were periodically measured during an experimental run. Each experiment lasted for a period corresponding to at least 5 retention times so as to ensure that the final measurements represented steady state conditions.

Fig. 11 shows typical results for the depletion of Ca²⁺ ions resulting from CaCO₃ precipitation

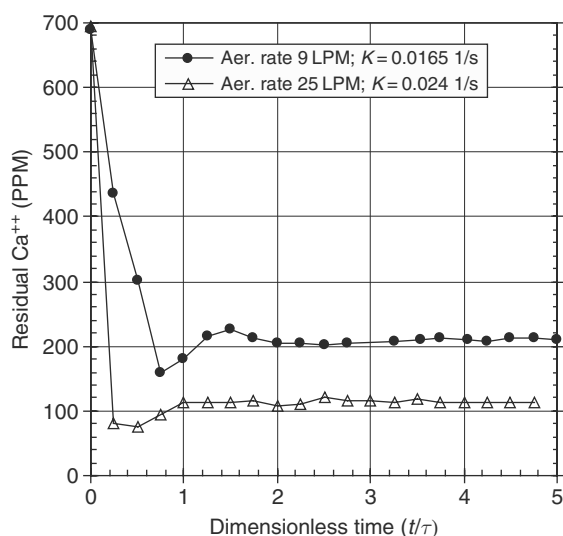


Fig. 11. Decay of the residual Ca²⁺ concentration in the crystallizer with time for different aeration rates at agitation speed of 500 RPM.

as a function of the dimensionless time, t/τ for two different aeration rates. It is seen that steady state conditions were achieved in crystallizer after a period corresponding to two residence times.

The effectiveness of CaCO₃ precipitation by CO₂ stripping depends on the parameters affecting the volumetric mass transfer coefficient. Fig. 12 shows the enhancement of the precipitation reaction conversion observed at increasing levels of the volumetric mass transfer coefficient which was induced by augmenting either the air flow rate or the agitation speed. Fig. 13

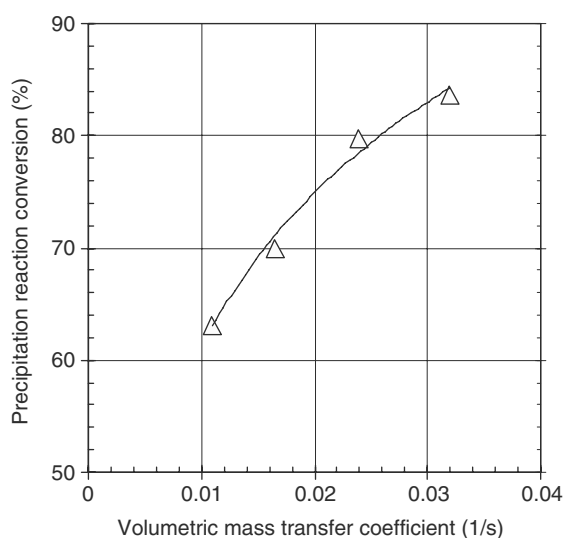


Fig. 12. Enhancement of the CaCO₃ precipitation reaction by increase of the mass transfer coefficients ($\tau = 2$ h).

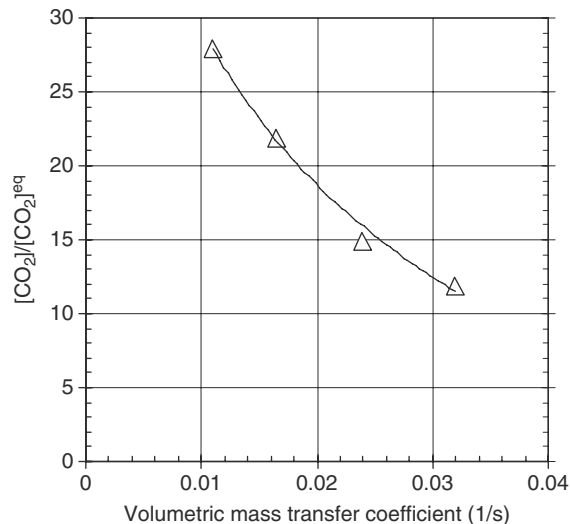


Fig. 13. Reduction of the residual $[\text{CO}_2]/[\text{CO}_2]^{\text{eq}}$ ratio by increase of the mass transfer coefficients ($\tau = 2$ h).

shows that solution CO_2 concentration approaches the equilibrium air CO_2 value as the volumetric CO_2 mass transfer is increased.

4. Concluding remarks

The theoretical and experimental results presented in this study illustrate the marked potential of the CO_2 stripping process for replacing alkali dosage in precipitation processes induced by pH increase. The inherent advantages of reduced chemical consumption and environmental benefits justify further development of the CO_2 stripping technique for desalination applications.

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