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The influence of CO_2 injection on the carbonate chemistry and scaling in multiple-effect distillers

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ABSTRACT

The injection of carbon dioxide (CO_2) into natural waters and aqueous solutions is used in several industrial applications. If pure water is saturated with 1600 ppm CO_2, its pH would reach a value of 4.0. In this work, the influence of CO_2 injection on the carbonate chemistry and scaling in multiple-effect distillers is studied. The approach is applied to a reference 5-stage multiple-effect distiller as a case with a distillate production of 380 t/h at a top brine temperature of 64°C. The pH of the feed seawater can be reduced of a factor of 2.15 when 150 ppm CO_2 is injected. CO_3^{2-} is considered limiting to scale formation because Ca^{2+} in seawater is much higher and is not limiting to $CaCO_3$ precipitation except under at unusual circumstances. Increasing the concentration of CO_2 in the feed water would lead to a decrease in the saturation ratios. The Langelier Saturation Index (LSI) values of calcite changed from 1.3 when zero amount is injected to reach a value of –0.81 when 150-ppm are injected. The calcite-based Ryznar Stability Index (RSI) values in the volume elements of the first stage in the reference distiller vary from ~7.1 (i.e. little scale) to ~4.8 (i.e. heavy scale).

Keywords: CO_2 injection; Carbonate system; Scale formation; Corrosion; Multiple-effect distillers

1. Introduction

Seawater is an aqueous mixed electrolyte. It attains its chemical composition through a variety of chemical reactions and physicochemical processes. Among these are: acid–base reactions, gas absorption and desorption processes, precipitation and dissolution of solids and adsorption processes at interfaces. The pH of seawater is usually in the range from 7.7 to 8.3 in surface waters. The pH is buffered by a set of reactions that take place between carbon dioxide (CO_2) and water [1].

The injection of CO_2 into natural waters and aqueous solutions has been used in several industrial applications; such as increasing the solubility of $BaCO_3$, the recovery of Na_2CO_3, Frasch process of sulphur mining (see Ellis et al. [2] for review) and recarbonation of the distillate [3–7]. CO_2 can be made available, depending on the local circumstances, from outside suppliers, in-plant production by combustion processes and reuse of the released gas in multi-stage flash (MSF) distillers and multiple-effect distillers (MED). The specific total CO_2 release in the MSF once-through distiller at a top brine temperature of 100°C is 3 times higher than the CO_2 release in the MED at 64°C [7]. The injection of CO_2 was suggested to retard scale formation in seawater desalination processes [2,8,9]. CO_2 reduces pH levels quickly, not stored as an acid solution non-corrosive when stored as a gas, requires less equipment and monitoring costs, requires no handling costs and can be utilized via a completely automated system

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[10]. If pure water is saturated with 1600 ppm carbon dioxide, its pH would reach a value of 4.0.

Alkaline scale triggered by the thermal decomposition of the HCO_3^- ions [2,8]. This, in turns, is related to solution pH. The proposed techniques to prevent scale formation can be summarised as follows [8,11]:

- The acidification of the feed seawater by sulphuric acid injection (pH ~4.0). At this pH value, all HCO_3^- and CO_3^{2-} are transformed to CO_2. At standard seawater alkalinity (TA = 2.3 mmol/kg) the required amount of acid is about 120 gram per ton seawater (g/t). Thus the release rate of CO_2 will be about 100 g/t [10]. It has been shown [12,13] that the release rates of CO_2 in the first stage in the reference ME distiller without seawater acidification is around 18 g/t.
- The use of anti-scale additives such as polyphosphates and polycarbonic acids. The inhibition action of polyphosphates decreases rapidly since they are hydrolysed at higher temperature (i.e. 90°C) and form calcium phosphate which is difficult to dissolve. Polycarbonic acids can be used at temperatures of up to 150°C. The development of new types of polymeric material additives and its dosing amounts is a very interesting and promising research topic.
- A combination of both acidification and additives.
- Mechanical cleaning (using sponge balls).
- Acid cleaning (pH ~2.0).

Multiple-effect (ME) distillation was the first process used to desalt a significant amount of seawater. This process takes place in a series of effects (stages) and uses the principle of reducing the ambient pressure in the various stages in order of their arrangement. This causes the feed water to boil in a series of stages without supplying additional heat. Vapor generated in the first stage gives up heat to the second stage for evaporation and is condensed inside the tubes. This continues for several stages. The seawater is either sprayed, or otherwise distributed onto the surface of horizontal tubes in a thin film to promote rapid boiling and evaporation. The condensate from the boiler steam is recycled to the boiler for reuse. The larger the number of stages, the less heat that is required as heat sources.

Al-Rawajfeh et al. [1,12,13] have modeled the CO_2 release rates in a reference 5-stages ME distiller. Recently, Al-Rawajfeh [14] has developed the same model to simulate the simultaneous desorption of CO_2 with the deposition of $CaCO_3$ and investigate their mutual effect. At a temperature of 30°C, a pH of 8.1, a salinity of 42 g/kg and a total alkalinity of 2.75×10^{-3} mol/kg, seawater contains 118 mg/kg HCO_3^- ions, 24 mg/kg CO_3^{2-} ions and 0.41 mg/kg CO_2. In the final condenser no CO_2 is released. The variations of the concentrations and the pH are due to the variation of the dissociation constants with increasing temperature. The pH decreases from 8.1 in seawater to 7.9 at the outlet of the final condenser.

The amount of $CaCO_3$ decreases from 127.3 g/t feed water in the first stage to 100.1 g/t in the last stage. This corresponds to average alkaline scale thickness of 165 to 130 μm and fouling resistance of 0.31–0.25 m^{2}K/kW [14].

For any given brine the input data required are:

- temperature
- amount of CO_2 injection
- total pressure
- salinity
- Ca^{2+} concentration

The program forces one to choose two values of the following: HCO_3^-, CO_3^{2-}, CO_2, TA, TC, and pH and then it calculates the remaining variables and $CaCO_3$ scale if any.

In the present study, the influence of CO_2 injection on the carbonate chemistry and scaling in multiple-effect distillers is studied.

2. The carbonate system in seawater

The carbonate system is a weak acid-base system which exists in seawater as dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate ions and complexes of these ions. Addition of an acid or a base to an aqueous solution of carbonate species changes the pH and the concentrations of all the species that constitute the system. A distinguishing feature of the carbonate system is that the gas phase forms an integral part of it. For a system initially in equilibrium, any change in the partial pressure of CO_2 in the gas phase induces a state of non-equilibrium between gas and aqueous phases. This causes, with time, an exchange of CO_2 between the phases resulting in a shift in pH and the species concentrations until equilibrium between the phases is re-established. A further feature is the relative insolubility of many carbonate minerals; the precipitation and dissolution of these minerals have a significant effect on the system's behaviour. As a consequence of these two features, it is often necessary to consider all three phases, aqueous, gas and solid, in order to describe the response of the system to external influences [15].

The reactions occurring in the carbonate system are illustrated in Fig. 1. The values between brackets represent the pH values at which the step proceeds or predominates at TC = 10^{-2} mol/kg, T_{SW} = 30°C and S_{SW} = 35 g/kg [14–16].

Carbon dioxide in seawater is governed by the following equilibria:

$$CO_2(g) \leftrightarrow CO_2(aq) \tag{1}$$

Subsequently, the dissolved gas combines with water to form carbonic acid H_2CO_3:

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \tag{2}$$

The carbonic acid dissociates to form bicarbonate HCO_3^- and carbonate CO_3^{2-}:

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \tag{3}$$

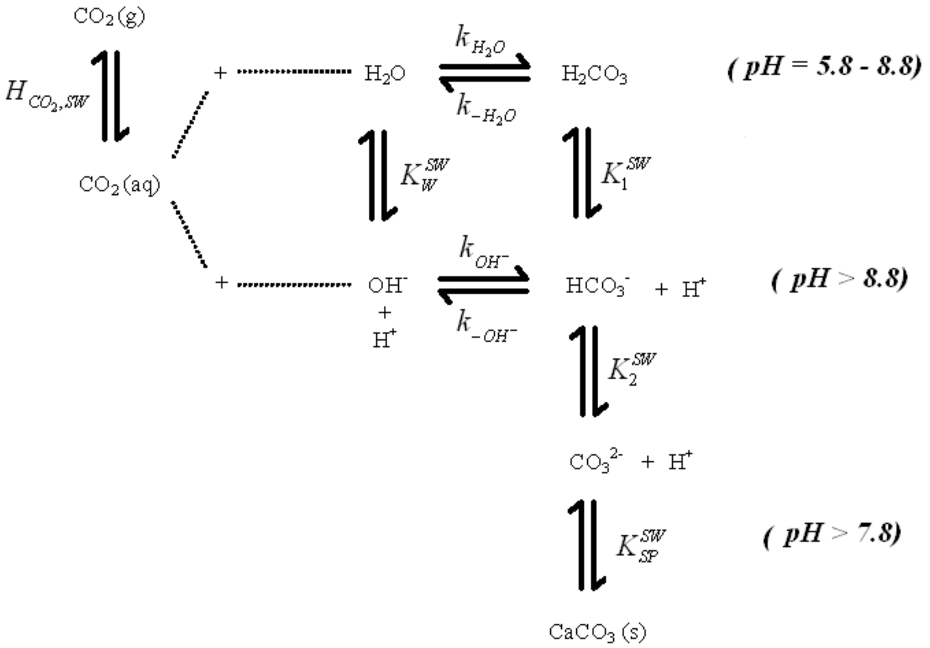

Fig. 1. Reactions in the carbonate system. Values between brackets are the pH values at which the step predominates at TC = 10^{-2} mol/kg, T_{SW} = 30°C and S_{SW} = 35 g/kg.

$$\mathrm{HCO_3^-} \leftrightarrow \mathrm{CO_3^{2-}} + \mathrm{H^+} \tag{4}$$

The water itself dissociates to form H^+ and OH^- ions:

$$\mathrm{H_2O} \leftrightarrow \mathrm{H^+} + \mathrm{OH^-} \tag{5}$$

The carbonate system in seawater is characterised by the interaction of major cations (Na^+, Mg^{2+}, Ca^{2+} and K^+) and major anions (Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}). These interactions can be described in terms of ion association formalism and, more recently, in terms of a specific interaction theory [17,18]. Insoluble calcium carbonate and magnesium hydroxide are being formed:

$$\mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \leftrightarrow \mathrm{CaCO_3}(s) \tag{6}$$

$$\mathrm{Mg^{2+}} + 2\mathrm{OH^-} \leftrightarrow \mathrm{Mg(OH)_2}(s) \tag{7}$$

When a certain total carbon dioxide content (TC) is dissolved in seawater, it is important to know which fraction thereof is present as CO_2, which as HCO_3^- ions and which as CO_3^{2-} ions. The distribution of the species depends on the pH value, the temperature and the ionic strength. The ratios of individual species in the carbonate system can be given by:

$$\%\alpha_{\mathrm{CO_2}} = \frac{[\mathrm{H^+}]^2}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]\cdot K_1^{\mathrm{SW}} + K_1^{\mathrm{SW}} K_2^{\mathrm{SW}}} \times 100 \tag{8}$$

$$\%\alpha_{\mathrm{HCO_3}} = \frac{[\mathrm{H^+}]\cdot K_1^{\mathrm{SW}}}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]\cdot K_1^{\mathrm{SW}} + K_1^{\mathrm{SW}} K_2^{\mathrm{SW}}} \times 100 \tag{9}$$

$$\%\alpha_{\mathrm{CO_3^{2-}}} = \frac{K_1^{\mathrm{SW}} K_2^{\mathrm{SW}}}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]\cdot K_1^{\mathrm{SW}} + K_1^{\mathrm{SW}} K_2^{\mathrm{SW}}} \times 100 \tag{10}$$

Fig. 2 represents a speciation diagram of CO_2, HCO_3^- and CO_3^{2-} as a function of pH at constant temperature and salinity (T = 30°C and S = 35 g/kg). At constant pH, the mole fraction of CO_2 decreases with increasing temperature, while the ratio of CO_3^{2-} rises. With increasing temperature the mole fraction of HCO_3^- rises at pH < 7. At higher pH values the mole fraction of HCO_3^- decreases.

At T = 30°C and S = 35 g/kg more than 87% of the total carbon dioxide content is dissolved as CO_2 at pH values lower than 5. With increasing pH value the mole fraction of CO_2 decreases, while the HCO_3^- concentration increases and reaches a maximum of 94.5% at pH = 7.4. A further increase of pH causes a decrease of HCO_3^- and an increase of CO_3^{2-}. At pH values higher than 10, more than 92% of the total carbon dioxide is present as CO_3^{2-}.

To remove the variations in total alkalinity (TA) and total carbon dioxide (TC) due to changes in salinity due to mixing, evaporation or dilution, normalized values NTA and NTC are used. NTA and NTC can be defined as follows [19]:

$$\mathrm{NTA} = \mathrm{TA}\cdot\frac{35}{S} \tag{11}$$

$$\mathrm{NTC} = \mathrm{TC}\cdot\frac{35}{S} \tag{12}$$

The carbonate system in the Arabian Sea was studied over an annual cycle by Millero et al. [19]. The surface

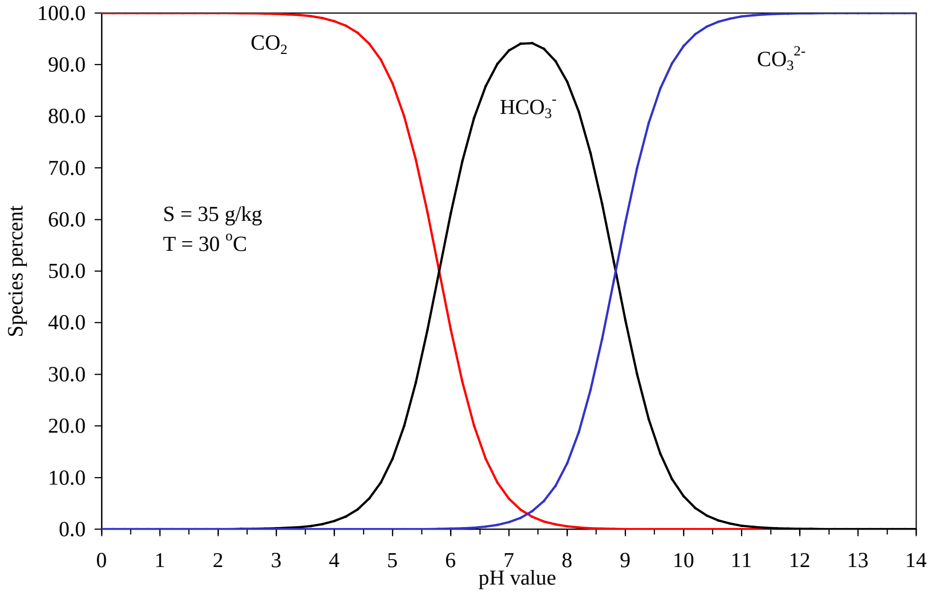

Fig. 2. Speciation diagram of CO_2, HCO_3^- and CO_3^{2-} as a function of pH value at $T = 30°C$ and $S = 35$ g/kg [1].

measurements (0–30 m) of pH, NTA and NTC were quite uniform through the year (pH = 8.1±0.05, NTA = 2290 ± 5 μmol/kg and NTC = 1950±20 μmol/kg). Consequently, changes in the normalized TA and TC can be attributed to the production and oxidation of plants material and formation and precipitation of $CaCO_3$.

3. Results and discussions

3.1. The influence on CO_2 release and the carbonate system

Fig. 3 shows the effect of CO_2 injection on the pH of the feed seawater (i.e. pH = 8.15). The calculated values are compared to the measured values of Ellis et al. [2] and showed a very good agreement. The correlation factor was $R^2 = 0.99$. The reduction of the pH is strongly affected by the amount of CO_2 injected in part per million (ppm). The pH of the seawater feed can be reduced by 2.15 units when 150 ppm CO_2 is injected.

Fig. 4 shows the specific CO_2 release (i.e. related to the feed water flow rate entering that stage) in the volume elements of the first stage in the reference distiller. Fig. 4 compares the changes in the specific CO_2 release with the volume elements at 45-ppm CO_2 injection with the case of no CO_2 injection. The first stage has been chosen because it has the highest temperature. The highest release rates are found to occur at the first volume elements because the amount of injected CO_2 is stripped easily due to the pressure drop in the stage. The specific CO_2 release decrease strongly in the preheating volume elements and after that the release rates begin to change slightly

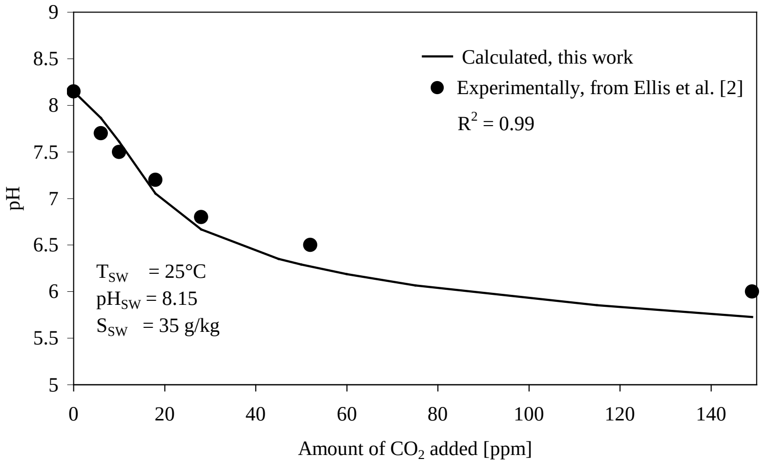

Fig. 3. Effect of the injected amounts of CO_2 on the pH of the seawater feed (i.e. $pH_{SW} = 8.15$).

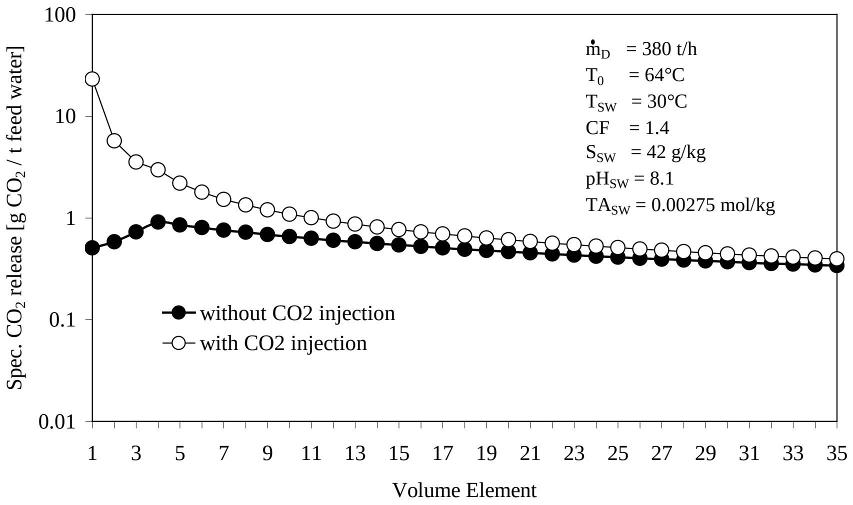

Fig. 4. Comparison of specific CO_2 release between 45-ppm CO_2 injection and the case of without injection in the volume elements in the reference ME distiller.

in the evaporation volume elements. The differences in release rates between the two cases become very small. This is attributed to the decrease in the driving force with releasing CO_2.

Fig. 5 shows the effect of the injection of 45 ppm CO_2 on the carbonate system in the reference ME distiller. The concentrations of the HCO_3^-, CO_2 and CO_3^{2-} show similar behaviour but higher changes to their behaviour without CO_2 injection. The concentration of HCO_3^-, CO_2 are higher while the concentration of CO_3^{2-} is lower. $[CO_3^{2-}]$ is considered limiting to scale formation because $[Ca^{2+}]$ in seawater is much higher than $[CO_3^{2-}]$ and is not limiting to $CaCO_3$ precipitation except under at unusual circumstances.

Fig. 6 shows the effect of CO_2 release on the pH value in the individual stages of the reference distiller with and without CO_2 injection. It should be noticed that the pH values are so low (solid symbols), because they refer to values calculated at the actual evaporation temperatures. CO_2 release shifts the pH to higher values. If the brine at the outlet is cooled down to the original seawater temperature of 30°C, the pH values will be higher. The release of CO_2 as a result of the thermal decomposition of HCO_3^- makes the pH of the solution to increase from 0.3 to 0.6 units higher that the pH of the seawater feed. Fig. 6 shows the effect of CO_2 injection on the pH values at two different amount of CO_2. The injection of CO_2 lowers the pH in the stages 0.4 units when 45 ppm CO_2 is injected.

3.2. The influence on scale formation

Waters with high calcium and bicarbonate, high pH, low carbon dioxide partial pressure, high salinity, and high temperatures favor the formation of $CaCO_3$ scale. The measurement of pH value may be the most questionable parameter in a brine analysis and one of the most

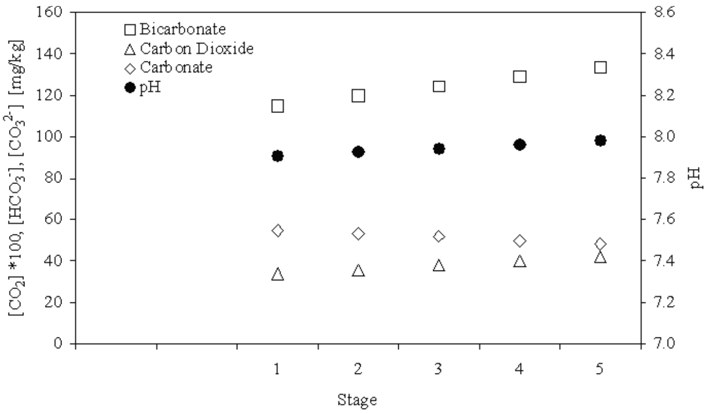

Fig. 5. Effect of the injection of 45 ppm CO_2 on the carbonate system in the reference ME distiller.

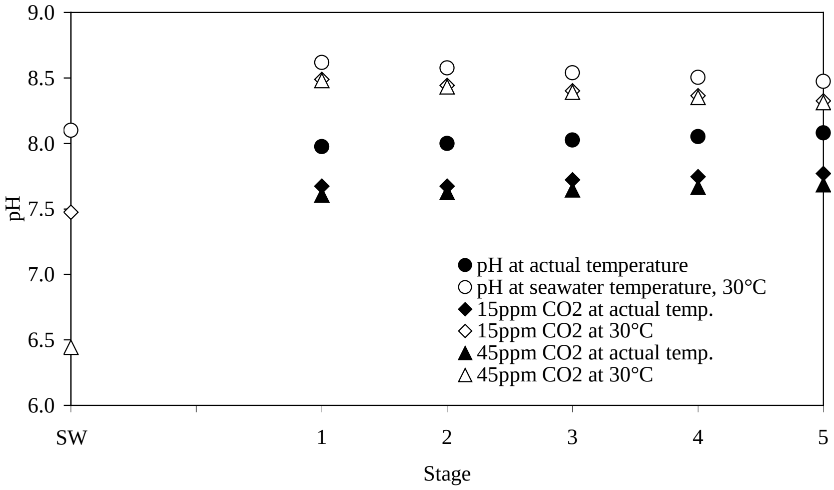

Fig. 6. Effect of 15 and 45 ppm CO_2 on the pH in the individual stages in the reference distiller.

critical in determining the saturation index or amount of $CaCO_3$ that will precipitate. Even slight change in pH can cause significant change in $CaCO_3$ precipitation. The introduction of some low-pH scale inhibitors tends to inhibit the formation $CaCO_3$ of simply on the basis of pH change.

There are two general categories of $CaCO_3$ saturation indices: the first determines whether water has tendency to precipitate $CaCO_3$ (i.e. supersaturated) or to dissolve it (under-saturated) and the second estimates the quantity of the precipitated or dissolved amount of $CaCO_3$. Rossum and Merill [20] presented several models and indices to evaluate water stability depending on $CaCO_3$ chemistry, among of them the Langelier Saturation Index (LSI) [21] and Ryznar Stability Index (RSI) [22]. The LSI and RSI can be calculated from the difference between the actual pH and the saturation pH (pH_S) of calcium carbonate as follows:

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH}_S \tag{13}$$

$$\mathrm{RSI} = 2\mathrm{pH}_S - \mathrm{pH} \tag{14}$$

The pH value of calcium carbonate saturation is defined as

$$\mathrm{pH}_S = \mathrm{pK}_2^{SW} - \mathrm{pK}_{SP}^{SW} + \mathrm{pTA} + \mathrm{p}\left[\mathrm{Ca}^{2+}\right] \tag{15}$$

where K_2^{SW} is the second dissociation constant of carbonic acid, K_{SP}^{SW} is the solubility product of calcium carbonate, TA is the total alkalinity and $[Ca^{2+}]$ is the concentration of calcium ions. The p-function designates the negative logarithm of that variable.

An evaluation of the LSI and RSI is given in Al-Rawajfeh et al. [16].

Increasing the concentration of CO_2 in the brines would lead to a decrease in the saturation ratios, and this would have serious implications for scale formation. Injection of CO_2 affects saturation indices. The LSI values of calcite changed from 1.3 when zero amount is injected to reach a value of –0.81 when 150-ppm are injected. When 45-ppm CO_2 are injected, the LSI stays positive but its values are lower than the original case. It varies from ~0.2 to 1.5 (using K_{SP}^{SW} of calcite) and ~0.1 to 1.4 (using K_{SP}^{SW} of aragonite) the inlet to the outlet of the brine.

The calcite-based RSI values in the volume elements of the first stage in the reference distiller are shown in Fig. 7. It varies from ~7.1 (i.e. little scale) to ~4.8 (i.e. heavy scale). The pH of the brine decreases with adding CO_2, this causes LSI to decrease and RSI to increase, i.e. scale tendency decreases.

$CaCO_3$ precipitation is higher in the preheating volume elements and then becomes less and less in the evaporation volume elements [14]. Because of $CaCO_3$ precipitation in a certain volume element, scaling species of the solution entering the next volume element become lower. CO_2 release rate decreases, because the difference between the concentration of CO_2 in the bulk and at the phase interface, release driving force, decreases. This can be attributed to the increase in salinity with evaporation which causes the solubility of CO_2 to drop. The flow rate and hence the Reynolds number decrease due to evaporation, thus mass transfer coefficient decreases.

The wetting rate decreases with increasing the evaporation. According to Glade et. al. [23], the quantity of scale strongly increases with decreasing wetting rate. The enhanced scaling tendency at low wetting rates might be attributed to the variation of the film thickness. The film thickness significantly decreases with decreasing wetting rate. High local solution concentrations, exceeding the average brine concentration, are assumed to form by fluid elements having either the smallest thickness or residing for a longer period of time in the film.

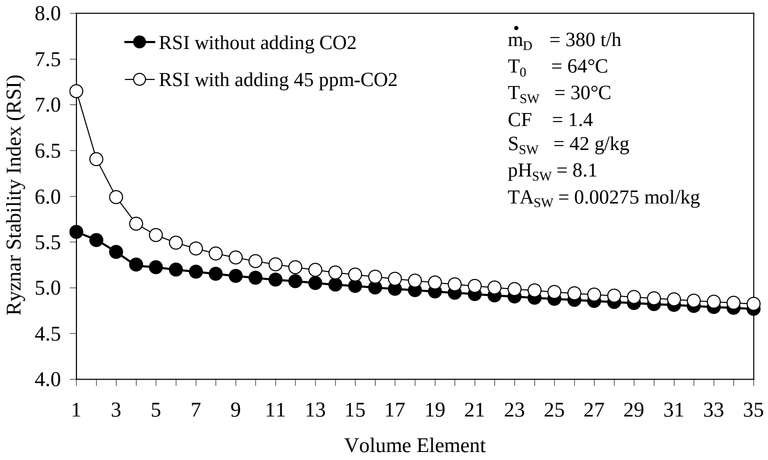

Fig. 7. Effect of the adding 45-ppm CO_2 on Ryznar Stability Index (RSI) of calcite.

4. Conclusion

The influence of CO_2 injection on the carbonate chemistry and scaling in multiple-effect distillers was studied. The reduction of the pH was strongly dependent on the amount of CO_2 injected; the pH of the feed seawater was reduced 2.15 units when 150 ppm CO_2 was injected. The concentrations of HCO_3^- and CO_2 slightly increased while the concentration of CO_3^{2-} slightly decreased. When 45 ppm CO_2 injected, the concentrations of the HCO_3^-, CO_2 and CO_3^{2-} showed higher changes relative to their behavior without injection. Injection of CO_2 in the feed water leads to a decrease in the saturation ratios. The pH of the brine decreases with adding CO_2, this causes LSI to decrease and RSI to increase, i.e. scale tendency decreases.

Acknowledgement

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