

# Modeling of CO<sub>2</sub> release and the carbonate system in multiple-effect distillers

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## Abstract

The release of CO<sub>2</sub> in multiple-effect distillers has scarcely been investigated and little has been published about it. There is no approach available to reliably predict the release rates in individual stages and the effects of influencing parameters. Until now the dimensioning of the design venting rates has been based mainly on experience and very sparse experimental data. The present work was aimed at gaining an in-depth understanding of the physical and chemical processes involved in CO<sub>2</sub> release and the carbonate system in multiple-effect distillers.

A model has been developed that describes the CO<sub>2</sub> release and the carbonate system in multiple-effect distillers. Included is the flow path of brine through the final condenser and the evaporator stages. The desorption of CO<sub>2</sub> was described as a problem of coupled mass transfer with chemical reaction. The mass transfer coefficient and the phase interface area were studied for the fluid dynamics of falling water films on horizontal tubes.

*Keywords:* CO<sub>2</sub> release; Carbonate system; MED; Mass transfer; Reaction kinetics; Modeling

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## 1. Introduction

The release of non-condensable (NC) gases from the brine and the leakage of air are of great importance for the design, operation, and costs of desalination distillers. NC gases accumulate in condensing zones and reduce the heat transfer for condensation [1–8]. Since even small amounts of NC gases have a significant adverse effect on the

condensation heat transfer rate, it is extremely important to eliminate the NC gases from the system through proper venting and to design the condensers in such a way that the effects of the NC gases are minimized [3,4,9,10]. Oxygen and carbon dioxide can be the source of serious vapor side corrosion problems [9–13]. The corrosion leads to tube leakages and plant outages and reduces the lifetime of distillers [10,13]. NC gas accumulation can lead to disturbances and

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instabilities in distiller operation. NC gas blanketing of the heat transfer surface in individual condensers can result in heat transfer blockage to the point of periodic or total failure of individual stages. Furthermore, NC gas accumulation in multi-stage flash (MSF) distillers can lead to pressure losses for interstage brine transfer causing high brine levels and periodic brine level surging accompanied by high conductivities in the distillate [14]. The removal of the NC gases by venting is linked with an extraction of vapor which means an energy loss for preheating or multiple reuse in multiple-effect distillers. The energy consumption of the venting system for extracting the NC gases needs to be taken into account. It is usually not considered in the performance ratio of a distiller, although, in cases of steam ejectors, steam of higher exergy than the main heat input is required. The release of  $\text{CO}_2$  from the evaporating brine in seawater distillers considerably influences the concentrations of  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$  and  $\text{OH}^-$  ions in the carbonate system of the brine and, thus, plays an important role in alkaline scale formation [15,16].

An underestimation of the NC gas release and, thus, too small venting rates lead to an accumulation of the NC gases with the described adverse effects on the heat transfer, operation, and material lifetime. An overestimation of the NC gas release and, thus, too high venting rates result in unnecessary vapor losses with the vent and a higher energy consumption of the venting system. Thus, a better understanding of the NC gas release is required for an optimization of the venting system. It would also be useful for the diagnosis of the distiller performance, troubleshooting, and maintenance. Reliable information about  $\text{CO}_2$  release is a prerequisite for simulating the scaling process and predicting scale formation.

Gases which are molecularly dissolved and do not chemically react in seawater, namely nitrogen, oxygen, and argon, can be removed almost completely in a deaerator. However, only part of the carbon dioxide can be removed by simple deaeration.

For the removal of  $\text{CO}_2$ , the addition of a strong acid to the feed water and a decarbonator, i.e. an atmospheric deaerator, are required. The acid lowers the pH value of the feed water and causes the conversion of the bicarbonate and carbonate ions to dissolved molecular  $\text{CO}_2$  which is then released almost completely in the decarbonator.

Multiple-effect (ME) distillers are commonly designed for low temperature operation with top brine temperatures below  $70^\circ\text{C}$ . Usually the feed water is not deaerated in a separate deaerator and additives are used for scale control.  $\text{O}_2$ ,  $\text{N}_2$ , Ar, and  $\text{CO}_2$  are liberated during the evaporation process.

Due to previous ignorance of the NC gas problem and its complexity, the predictive simulation of NC gas release in desalination distillers, particularly of  $\text{CO}_2$  release, has been scarcely investigated and given little attention in the desalination literature. Thus, considerable uncertainty exists in predicting the  $\text{CO}_2$  release rates in the individual stages of desalination distillers [17,18].

There are only very few investigations into NC gases in ME distillers [1,14,19]. They are mainly concerned with the effects of NC gases on heat transfer, energy consumption, and distiller operation, but less with the release process itself. Thus, the  $\text{CO}_2$  release process in ME distillers is poorly understood and there is no approach available to reliably predict the release rates in individual stages and the effects of influencing parameters.

A model has been developed for the prediction of  $\text{CO}_2$  release rates in the individual stages of ME distillers with horizontal tubes. In addition to the release rates the model allows for calculation of the  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$ ,  $\text{H}^+$ , and  $\text{OH}^-$  concentrations in the brine. Included is the flow path of seawater through the final condenser and the evaporator stages. The desorption of  $\text{CO}_2$  was described as a problem of mass transfer coupled with chemical reaction. A computer program was written for simulating the  $\text{CO}_2$  release and the

carbonate system. In previous papers [20,21] mass transfer and chemical reaction kinetics involved in the CO<sub>2</sub> release process and first simulation results of the computer program were described. This paper presents the main principles of the model for the description of the CO<sub>2</sub> release and the carbonate system in multiple-effect distillers.

## 2. Current state of knowledge of CO<sub>2</sub> release in desalination distillers

The first investigations into CO<sub>2</sub> release in desalination distillers relied on simple reaction models and sparse experimental data. Only chemical reactions in the brine were considered [22,23]. Mass transfer processes were completely neglected.

CO<sub>2</sub> release and alkaline scale formation, which is linked to the CO<sub>2</sub> release through chemical reactions, were investigated experimentally. Shams El Din and Mohammed [24] studied the chemistry of alkaline scale formation in industrial MSF distillers by extracting and analyzing brine samples from the water boxes and flash chambers. Moore et al. [25] carried out corresponding investigations into CO<sub>2</sub> release. Shams El Din and Mohammed [26,27] as well as Al-Sulami and Hodgkiess [28] performed laboratory studies on the mechanism and rates of chemical reactions in aqueous bicarbonate solutions with respect to alkaline scale formation.

Lukin and Kalashnik [29] and later Seifert [30] developed the first physical models that allowed the calculation of the CO<sub>2</sub> release rates in individual MSF distiller stages. The models are based on the assumption that mass transfer phenomena in the brine rather than the reaction kinetics control the desorption process. Chemical reaction kinetics were scarcely investigated.

Rigorous electrolyte thermodynamics were applied to the simulation of MSF distillers by Watzdorf and Marquardt [31]. The brine is

considered as a multi-component electrolyte system of varying complexity. Scale formation and CO<sub>2</sub> release are predicted assuming equilibrium conditions. The proper description of the electrolyte system and the equilibrium state in a thermodynamic model are considered to serve as a limiting case or as a prerequisite of any rate-based model.

Glade [32–34] found that the above mentioned investigations are not consistent with the classical theory of desorption with chemical reaction. The various possibilities of coupling reaction kinetics with mass transfer in the brine have not been investigated. Furthermore, the reaction kinetics involved in the release process of CO<sub>2</sub>, e.g. reaction mechanisms and rate constants of the rate-determining steps in the mechanisms, have not been described adequately in desalination literature. Glade [32–34] developed a model for the prediction of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> release rates in the individual stages of MSF distillers. In addition to the release rates the model allows for calculation of the HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, CO<sub>2</sub>, H<sup>+</sup> and OH<sup>-</sup> concentrations in the carbonate system of the brine. Included is the flow path of brine through the condensers, the brine heater and the flash chambers. In recycle distillers the deaerator is also considered. While the release of N<sub>2</sub> and O<sub>2</sub> is treated as a problem of mass transfer (physical desorption), the theory of mass transfer coupled with chemical reaction kinetics (chemical desorption) is applied to the problem of CO<sub>2</sub> release in MSF distillers.

As described above, the problem of CO<sub>2</sub> release has mainly been investigated in MSF distillers.

## 3. Description of the multiple-effect distillation process

A variety of multiple-effect process configurations has been installed. A common process configuration is shown in Fig. 1. For modeling the CO<sub>2</sub> release process, this configuration was chosen as a reference.

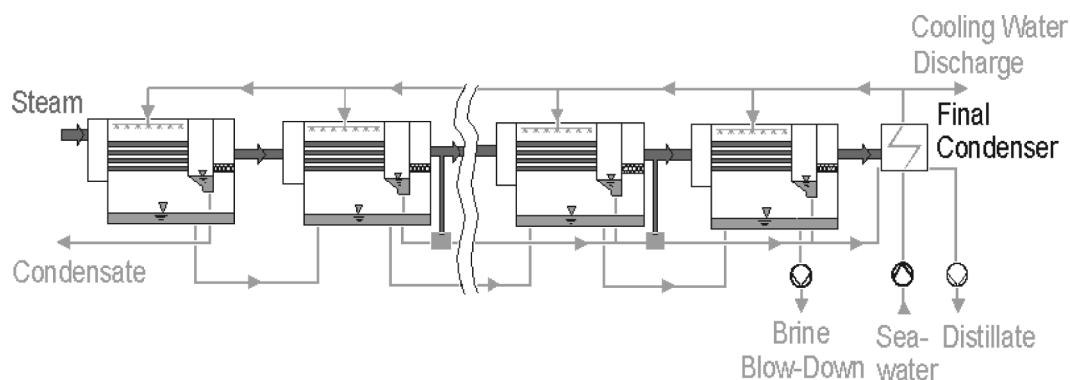


Fig. 1. Process configuration of the reference multiple-effect distiller.

ME distillers utilize horizontal tube falling film evaporators in a serial arrangement to produce through repetitive steps of evaporation and condensation, each at lower temperature and pressure, a multiple quantity of distillate from a given quantity of low grade input steam. Steam from the steam turbines of a power plant or a boiler is introduced into the tubes of the first cell. Simultaneously feed water is sprayed or otherwise distributed onto the tube bundle. The feed water flows in thin films down each bank of tubes. The steam condenses inside the tubes.

The condensate is often pumped back to the boiler for reuse. The enthalpy of condensation allows the feed water to be preheated to the boiling point on the upper tube rows and then part of it to be evaporated on the lower tube rows. The vapor produced is then fed inside the tubes of the second cell where it is condensed, thus evaporating part of the feed water of this cell on the outside of the tube bundle. This process is repeated from cell to cell. The vapor produced in the last cell is condensed in a separate heat exchanger called final condenser, which is cooled by the incoming seawater, thus preheating the feed water. The water condensed in each cell goes to the next cell, where some of it flashes at the lower pressure, and finally to the condenser. The distillate is then extracted by means of the distillate pump. The part of the

brine that has not been evaporated is often fed to the brine pool of the next cell, where some of it flashes at the lower pressure, and is finally discharged from the last cell by the brine blow-down pump. The vacuum in the evaporator is maintained by an ejector system which extracts the non-condensable gases present in the vapor phase.

Where higher pressure steam is available, the plant can be supplied with a thermal vapor compression (TVC) unit in order to increase the thermal efficiency. The vapor produced in the last cell is partially recompressed in a steam ejector which is fed by high pressure steam. This vapor mixture is used to heat the first cell.

#### 4. Description of the carbonate system in seawater

To understand and to describe the desorption process of  $\text{CO}_2$  in multiple-effect distillers, a detailed knowledge of the thermodynamics and the kinetics of the carbonate system in seawater is required.

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. Characteristic for seawater is its high salinity. 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  $\text{CO}_2$  and water.

Atmospheric gases dissolve in seawater and are distributed to all depths by mixing processes and currents. The most abundant gases in atmosphere and in seawater are nitrogen, oxygen, carbon dioxide, and argon.

The gases dissolved in seawater can be divided into two types: the first type is molecularly dissolved and does not react chemically such as  $\text{N}_2$ ,  $\text{O}_2$ , and Ar, while the other type chemically reacts in seawater such as  $\text{CO}_2$ .

The carbonate system is a weak acid–base system which exists in seawater as dissolved carbon dioxide, carbonic acid, bicarbonate, and carbonate ions. Basically, the system is derived from the dissolution of carbon dioxide gas and carbonate minerals into the water. Addition of an acid or a base to an aqueous solution of carbonate species gives rise to changes in pH and changes in 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  $\text{CO}_2$  in the gas phase induces a state of non-equilibrium between gas and aqueous phases. This causes, with time, an exchange of  $\text{CO}_2$  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 behavior. 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 [35].

#### 4.1. Chemical reactions in the carbonate system

Fig. 2 schematically shows the physical and chemical equilibria in the carbonate system.

$\text{CO}_2$  participates in a number of reactions when it comes into contact with aqueous solutions. One of these is the dissolution of the gaseous  $\text{CO}_2$ :



Hydration and dehydration of  $\text{CO}_2$  in aqueous bicarbonate–carbonate solutions occur by the following reaction mechanisms in parallel [36–39]:

Reaction mechanism I (acidic mechanism):

Step 1:

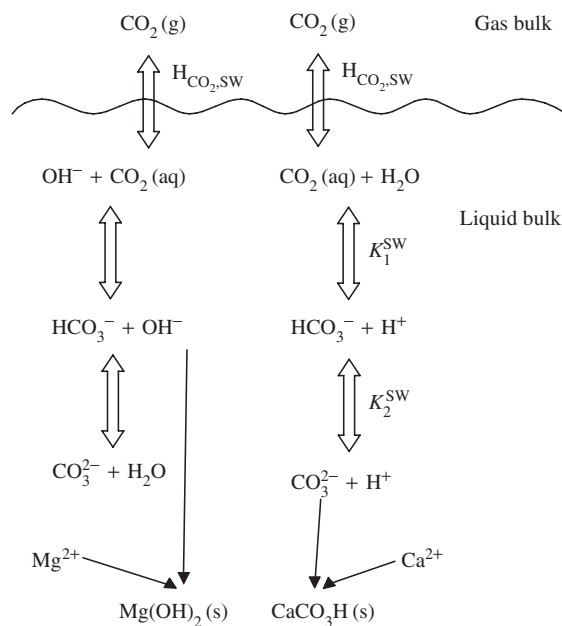
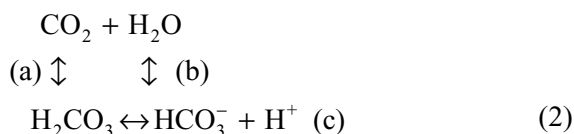
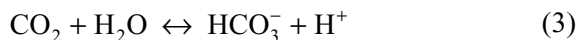


Fig. 2. A schematic representation of the carbonate system.

By combining the reaction rate constants, the reactions (2a), (2b), and (2c) can be summarized to the simplified scheme [39]:



Step 2:

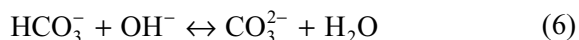


Reaction mechanism II (alkaline mechanism):

Step 1:



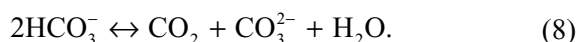
Step 2:



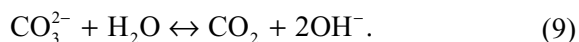
The water itself dissociates to form  $\text{H}^+$  and  $\text{OH}^-$  ions:



The overall reaction which occurs when  $\text{CO}_2$  is desorbed from an aqueous bicarbonate–carbonate solution is



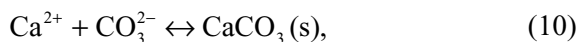
When a substantial amount of  $\text{OH}^-$  ions is present, the alkaline mechanism predominates and reaction (6) is completely shifted to the right. Thus the overall reaction, which is assumed to occur when  $\text{CO}_2$  is released from a strong alkaline aqueous solution, can be expressed as follows:



The carbonate system in seawater is characterized by the interaction of major cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$ ) and major

anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ). These interactions can be described in terms of an ion association formalism and, more recently, in terms of a specific interaction theory [39,40].

Additionally insoluble calcium carbonate and magnesium hydroxide can be formed:



#### 4.2. Solubility of $\text{CO}_2$ in seawater

Since the partial pressure and the concentration of  $\text{CO}_2$  dissolved in seawater are sufficiently small, the solubility can be described using Henry's law:

$$C_{\text{CO}_2} = H_{\text{CO}_2,\text{sw}} p_{\text{CO}_2} \quad (12)$$

where  $C_{\text{CO}_2}$  is the concentration of the dissolved  $\text{CO}_2$ ,  $p_{\text{CO}_2}$  is the partial pressure of  $\text{CO}_2$  and  $H_{\text{CO}_2,\text{sw}}$  is the Henry's law coefficient of  $\text{CO}_2$  in seawater.

Henry's law describes only the physical equilibrium between the phases and may only be applied to the fraction of the gas that is molecularly dissolved and not chemically bound [38,41,42]. Henry's law coefficient depends on the type of the gas and the solvent, the temperature, the total pressure and in the case of salt solutions it also depends on the ionic strength of the solution. The ionic strength  $I$  of a solution is defined as

$$I = \frac{1}{2} \sum_i z_i^2 m_i \quad (13)$$

where  $z_i$  is the charge of the ion  $i$  and  $m_i$  is the molality of the ion.

Millero [43] proposed a correlation between the ionic strength and the salinity of seawater:

$$I = \frac{19.92S}{1000 - 1.005S} \quad (14)$$

with  $S$  in g/kg and  $I$  in mol/kg. The ionic strength of standard seawater with  $S = 35$  g/kg is 0.72 mol/kg.

For small and moderate pressures  $p < 5$  bar, the pressure dependence of Henry’s law coefficient can be neglected [44]. The influence of the other gases is negligible provided that their concentrations are small.

The solubility of a gas is actually lowered in presence of salts in the solution. This effect is called “salting out”. Danckwerts [38] relates Henry’s law coefficient in the salt solution to that in water at the same temperature on the basis of a method originally proposed by Sechenov [45] by means of the expression

$$\log \left( \frac{H_{G,W}}{H_{G,SW}} \right) = hI \tag{15}$$

where  $I$  is the ionic strength and  $h$  is the summation of ion specific parameters of the positive ions ( $h_+$ ), negative ions ( $h_-$ ) and the gas specific parameter ( $h_G$ ):

$$h = h_+ + h_- + h_G \tag{16}$$

Ion and gas specific parameters were experimentally determined for various ions and gases [46]. It is assumed that the temperature dependence of  $h$  is confined to the change in  $h_G$ . The ion specific parameters are considered to be independent of temperature.

Henry’s law coefficient of  $CO_2$  in the brine can be determined by means of Eq. (15) using the correlation for Henry’s law coefficient in pure water given by Plummer and Busenberg [47] which is valid up to 334°C:

$$\begin{aligned} \log H_{CO_2,W} = & 108.3865 + 0.01985076 \cdot T \\ & - \frac{6919.53}{T} - 40.45154 \cdot \log T \\ & + \frac{669365}{T^2} \end{aligned} \tag{17}$$

with  $H_{CO_2,W}$  in mol/(kg atm) and  $T$  in K.

Because the main constituent of seawater is NaCl (73% of the ionic strength of seawater), the ion specific parameters of  $Na^+$  and  $Cl^-$  are the only considered parameters. The values given by Danckwerts [38] are  $h_+ = 0.091$  L/mol and  $h_- = 0.021$  L/mol. The  $CO_2$  specific parameters  $h_G$  between 0 and 50°C given by Danckwerts [38] were correlated with temperature by Glade [33] as follows:

$$h_G = -5 \times 10^{-3} - 5.3 \times 10^{-4} \vartheta \tag{18}$$

where  $h_G$  is in L/mol and  $\vartheta$  is in °C.

#### 4.3. pH scales and chemical equilibrium constants in seawater

In high salinity solutions, pH measurements by means of glass–calomel electrode systems standardized against low salinity aqueous NBS buffers do not give a reliable measure of  $H^+$  activity, i.e.

$$pH = -\log a_{H^+} \tag{19}$$

principally due to residual liquid junction effects.

For high salinity waters, various pH scales have been defined that are based on the comparison with buffers of similar ionic strength. For seawater, it was proposed [39,48–50] to use a pH scale that is based on the total concentration of  $H^+$  ions:

$$[H^+]^{SW} = [H^+]^{free} + [HSO_4^-] + [HF] \tag{20}$$

The pH value which is based on the seawater scale is defined as

$$pH^{SW} = -\log \frac{[H^+]^{SW}}{[ ]^0} \tag{21}$$

with  $[ ]^0 = 1$  mol/kg seawater.

The activity of  $H^+$  and the total concentration of  $H^+$  in seawater can be correlated by

$$a_{\text{H}^+} = \gamma_{\text{H}^+}^{\text{sw}} \frac{[\text{H}^+]^{\text{sw}}}{[\text{I}]^0} \quad (22)$$

where  $\gamma_{\text{H}^+}^{\text{sw}}$  is the apparent activity coefficient of the total  $\text{H}^+$  concentration in seawater.

In seawater at 25°C with a salinity of 35 g/kg, the difference between  $\text{pH}^{\text{sw}}$  and  $\text{pH}$  is about  $\Delta\text{pH} = 0.2$ . The  $\text{pH}$  of seawater has a clear influence on  $\text{CO}_2$  release. Hence, the  $\text{pH}$  scale employed becomes important.

The concentrations of the carbonic acid species can be determined using equilibrium constants. The definition of the equilibrium constants depends on the  $\text{pH}$  scale. In this work the  $\text{pH}^{\text{sw}}$  scale is used.

The equilibrium constant of the hydration reaction  $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$  is

$$K_{\text{H}_2\text{CO}_3}^{\text{sw}} = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]} \quad (23)$$

The value of  $K_{\text{H}_2\text{CO}_3}^{\text{sw}}$  is about  $10^{-3}$ , i.e. only about 0.1% of carbon dioxide is present as  $\text{H}_2\text{CO}_3$ . Since the concentration of non-dissociated  $\text{H}_2\text{CO}_3$  is very small and difficult to measure, one does not differentiate between  $\text{CO}_2(\text{aq})$  and  $\text{H}_2\text{CO}_3$  and the sum of their concentrations is used. Applying the law of mass action to the first dissociation of carbonic acid  $\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+$  yields

$$K_1^{\text{sw}} = \frac{[\text{H}^+]^{\text{sw}} [\text{HCO}_3^-]^{\text{sw}}}{[\text{CO}_2]} \quad (24)$$

where  $[\text{i}]^{\text{sw}}$  is the concentration of the component  $\text{i}$  that is free or involved in ion pairing and  $[\text{CO}_2]$  is the sum of the concentrations of  $\text{CO}_2$  and  $\text{H}_2\text{CO}_3$ .

The second dissociation constant of the reaction  $\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$  can be written as

$$K_2^{\text{sw}} = \frac{[\text{H}^+]^{\text{sw}} [\text{CO}_3^{2-}]^{\text{sw}}}{[\text{HCO}_3^-]^{\text{sw}}} \quad (25)$$

The stoichiometric equilibrium constant of water in seawater can be expressed as

$$K_w^{\text{sw}} = [\text{H}^+]^{\text{sw}} [\text{OH}^-]^{\text{sw}} \quad (26)$$

The stoichiometric dissociation constants  $K_1^{\text{sw}}$  and  $K_2^{\text{sw}}$  of carbonic acid in seawater were experimentally determined for temperatures up to 45°C and for salinities up to 50 g/kg [51–55]. The data are based on different  $\text{pH}$  scales.

In this work, correlations are used which were suggested by Millero [43] and are based on the experimental data of Goyet and Poisson [54] and Roy et al. [55]:

$$K_1^{\text{sw}} = 2.18867 - \frac{2275.036}{T} - 1.468591 \ln T + \left( -0.138681 - \frac{9.33291}{T} \right) S^{0.5} + 0.0726483 S - 0.00574938 S^{1.5}, \quad (27)$$

$$\ln K_2^{\text{sw}} = -0.84226 - \frac{3741.1288}{T} - 1.437139 \ln T + \left( -0.128417 - \frac{24.41239}{T} \right) S^{0.5} + 0.1195308 S - 0.00912840 S^{1.5}, \quad (28)$$

where  $K_1^{\text{sw}}$  and  $K_2^{\text{sw}}$  are on the basis mol/kg seawater,  $T$  is in K and  $S$  is in g/kg.

The equilibrium constant of water in seawater  $K_w^{\text{sw}}$  was measured for temperatures up to 35°C and salinities up to 44 g/kg [52,53,56]. Dickson and Riley [53] proposed the following correlation:

$$\log K_w^{\text{sw}} = - \left( \frac{3441}{T} + 2.241 - 0.09415 S^{0.5} \right) \quad (29)$$

where  $K_w^{\text{sw}}$  is on the basis mol/kg seawater,  $T$  is in K and  $S$  is in g/kg.

#### 4.4. Reaction rate constants

The reactions (2c), (4), and (6) can be considered as instantaneous and thus in equilibrium at all times, because they only involve a proton exchange [37,39,57]. The reactions (2a), (2b), and (5) between CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup>, however, are relatively slow, because they involve a rearrangement of the chemical structure in addition to the proton exchange [37,39,57,58]. The linear CO<sub>2</sub> molecule must be rearranged into the trigonal HCO<sub>3</sub><sup>-</sup> ion. Thus, reactions (2a), (2b), and (5) are the rate-determining steps in the reaction mechanisms.

The rate constant of reaction (3) can be calculated from the data of Pinsent et al. [59] which were recorrealted by Glade [33]:

$$\log k_{H_2O} = 3.71 - \frac{472808}{T^2} \quad (30)$$

with  $k_{H_2O}$  in 1/s and  $T$  in K.

The rate constant of reaction (5) can be calculated from Astarita et al. [58] for temperatures between 0 and 110°C and ionic strengths up to 7.75 mol/kg:

$$\log k_{OH^-} = 13.635 - \frac{2895}{T} + 0.08I \quad (31)$$

with  $k_{OH^-}$  in L/(mol s) and  $T$  in K.

As described by the authors in [20], the alkaline mechanism with the rate-determining step (5) predominates in the pH range prevailing in ME distillers, particularly at high temperatures.

#### 4.5. Description of the carbonate system in chemical equilibrium

The carbonate system in seawater can be described by the following six quantities:

- (1) Concentration of dissolved CO<sub>2</sub>, [CO<sub>2</sub>]
- (2) Concentration of bicarbonate ions, [HCO<sub>3</sub><sup>-</sup>]
- (3) Concentration of carbonate ions, [CO<sub>3</sub><sup>2-</sup>]
- (4) pH value or concentration of H<sup>+</sup> ions, [H<sup>+</sup>], or concentration of OH<sup>-</sup> ions, [OH<sup>-</sup>]

- (5) Total carbon dioxide content TC

$$TC = [HCO_3^-] + [CO_3^{2-}] + [CO_2] + [H_2CO_3]. \quad (32)$$

The concentration of H<sub>2</sub>CO<sub>3</sub> is so small that it can be neglected in Eq. (32).

- (6) Total alkalinity TA

The concentration of all bases that can accept a proton when seawater is titrated to the pH end point of carbonic acid:

$$TA = [HCO_3^-] + 2 [CO_3^{2-}] + [OH^-] - [H^+]. \quad (33)$$

TA and TC are independent of temperature, pressure and ionic strength if expressed in concentration units mol/kg seawater. The total alkalinity remains constant with absorption or desorption of CO<sub>2</sub> [43,49,60].

Total alkalinity TA can be related to chlorinity Cl according to the following relation [40]

$$TA = 0.0001185 Cl \quad (34)$$

where chlorinity can be expressed as

$$Cl = \frac{S}{1.80655} \quad (35)$$

with TA in mol/kg, Cl in g/kg and  $S$  in g/kg.

In chemical equilibrium the carbonate system is completely characterized by two of these six quantities. The remaining four quantities can be calculated by applying the law of mass action with the dissociation constants of carbonic acid and water in seawater. Given the measurable total alkalinity and the pH value, the remaining quantities can be determined as follows:

$$[H^+] = 10^{-pH^{SW}}, \quad (36)$$

$$[HCO_3^-] = \frac{TA [H^+] + [H^+]^2 - K_w^{SW}}{[H^+] + 2K_2^{SW}}, \quad (37)$$

$$[CO_3^{2-}] = \frac{K_2^{SW} [HCO_3^-]}{[H^+]}, \quad (38)$$

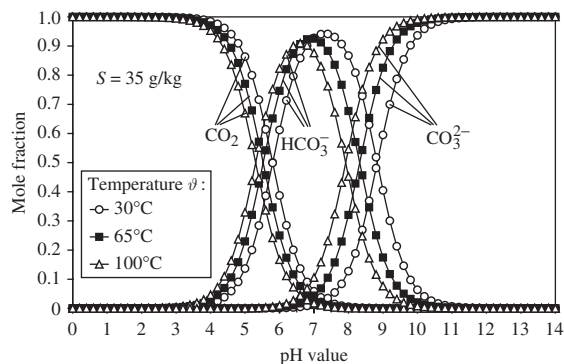


Fig. 3. Mole fractions of  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  as a function of pH value for different temperatures at  $S = 35 \text{ g/kg}$  [33].

$$[\text{CO}_2] = \frac{[\text{HCO}_3^-][\text{H}^+]}{K_1^{\text{SW}}}, \quad (39)$$

$$[\text{OH}^-] = \frac{K_w^{\text{SW}}}{[\text{H}^+]}, \quad (40)$$

and TC due to Eq. (32).

When a certain total carbon dioxide content TC is dissolved in seawater, it is important to know which fraction thereof is present as  $\text{CO}_2$ , which as  $\text{HCO}_3^-$  ions and which as  $\text{CO}_3^{2-}$  ions. The distribution of the species depends on the pH value, the temperature, and the ionic strength. The influence of temperature on the relative distribution of  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  at constant salinity is shown in Fig. 3. At constant pH, the mole fraction of  $\text{CO}_2$  decreases with increasing temperature, while the mole fraction of  $\text{CO}_3^{2-}$  rises. With increasing temperature the mole fraction of  $\text{HCO}_3^-$  rises at  $\text{pH} < 7$ . At higher pH values the mole fraction of  $\text{HCO}_3^-$  decreases.

## 5. Description of the $\text{CO}_2$ release model in multiple-effect distillers

The desorption of  $\text{CO}_2$  in ME distillers is a complex process involving chemical reaction kinetics, mass transfer processes as well as

phase equilibria at the brine/vapor interface. In the following, the main principles of the model for the description of the  $\text{CO}_2$  release and the carbonate system in ME distillers are presented.

### 5.1. The carbonate system in the final condenser

For the description of the carbonate system in the final condenser, the following assumptions are made:

- The seawater is in chemical equilibrium at the inlet of the final condenser.
- The pressure is high enough for the NC gases to remain dissolved in the brine. There is no gas release in the final condenser.
- The brine is well mixed in the final condenser.
- The influence of other reactions than those described in Chapter 4.1 is negligible.
- Calcium carbonate and magnesium hydroxide precipitate in negligible quantities.

In order to find out if the carbonate system in the final condenser is in chemical equilibrium, the average reaction time and the residence time can be compared.

The average reaction time of reaction (3) is given by

$$t_{\text{R,H}_2\text{O}} = \frac{1}{k_{\text{H}_2\text{O}} + k'_{\text{H}_2\text{O}}([\text{HCO}_3^-] + [\text{H}^+])}. \quad (41)$$

The rate constant of the backward reaction (3) can be written as

$$k'_{\text{H}_2\text{O}} = \frac{k_{\text{H}_2\text{O}}}{K_1^{\text{SW}}}. \quad (42)$$

The average reaction time of reaction (5) can be expressed as

$$t_{\text{R,OH}^-} = \frac{1}{k_{\text{OH}^-}([\text{CO}_2] + [\text{OH}^-]) + k'_{\text{OH}^-}}. \quad (43)$$

The rate constant of the backward reaction (5) is given by

$$k'_{OH^-} = \frac{k_{OH^-}}{K} = k_{OH^-} \cdot \frac{K_w^{SW}}{K_1^{SW}} \quad (44)$$

It was expected that for higher pH values the relaxation time of the reaction (3) would be in the order of the slower reaction. However, it was shown by Zeebe et al. [61] that the reaction (3) should be coupled with the dissociation reaction of water (reaction (7)). The time constant of the coupled system is about 500 times larger than the estimated relaxation time of the hydration of CO<sub>2</sub>. Simplified formulae for the relaxation times of the reactions (3) and (5) were suggested as follows [61]:

$$t_{R,H_2O} = \frac{1}{k_{H_2O} + k'_{H_2O} [H^+]}, \quad (45)$$

$$t_{R,OH^-} = \frac{1}{k_{OH^-} [OH^-] + k'_{OH^-}}. \quad (46)$$

Inserting Eq. (42) into Eq. (45) yields

$$t_{R,H_2O} = \frac{1}{k_{H_2O} \left( \frac{K_1^{SW} + [H^+]}{K_1^{SW}} \right)}. \quad (47)$$

Inserting Eq. (44) into Eq. (46) yields

$$t_{R,OH^-} = \frac{1}{k_{OH^-} \left( \frac{K_w^{SW}}{K_1^{SW}} + [OH^-] \right)}. \quad (48)$$

Assuming that the final condenser is a tube-and-shell heat exchanger, the residence time  $t_p$  of the brine inside the tubes can be expressed as

$$t_{p,FC} = \frac{n_{tubes} \frac{\pi}{4} d_i^2 L}{\dot{V}_b} \quad (49)$$

where  $n_{tubes}$  is the number of tubes,  $d_i$  is the inside diameter,  $L$  is the length of the tubes, and  $\dot{V}_b$  is the brine volume flow rate.

For typical tube bundle dimensions and volume flow rates, the residence time is between 2 and

14 s. For seawater with pH = 8.1 and  $S = 42$  g/kg and a final condenser outlet temperature of 43°C, the reaction times of reactions (3) and (5) are 10.3 and 1.2 s, respectively. Thus, the reaction time of the predominant reaction (5) is lower than the brine residence time. The reaction can be considered to be in chemical equilibrium.

Assuming that there is no gas release in the final condenser, and neither calcium carbonate nor magnesium hydroxide precipitate, the total alkalinity TA and the total carbon dioxide TC of the brine remain constant. If TA and TC are known, the equilibrium concentration of H<sup>+</sup> ions can be determined by solving the following equation:

$$\begin{aligned} [H^+]^3 + (TA + K_1^{SW}) [H^+]^2 + (TA K_1^{SW} \\ + K_1^{SW} K_2^{SW} + K_w^{SW} - TC K_1^{SW}) [H^+] \\ - \frac{K_1^{SW} K_2^{SW} K_w^{SW}}{[H^+]} + TA K_1^{SW} K_2^{SW} \\ - K_1^{SW} K_w^{SW} - 2TC K_1^{SW} K_2^{SW} = 0. \end{aligned} \quad (50)$$

The equilibrium concentrations of the species CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and OH<sup>-</sup> can be calculated due to Eqs. (37–40). Since the chemical equilibrium constants change with the temperature, the concentrations of the species CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and the pH value change, too.

### 5.2. The carbonate system in the effects

When the feed water enters the evaporator stages, the solubility of CO<sub>2</sub> suddenly decreases due to the pressure drop. CO<sub>2</sub> is released into the vapor space above the brine surface. The release of CO<sub>2</sub> disturbs the chemical equilibrium in the carbonate system. To restore it, new CO<sub>2</sub> is formed by chemical reactions and released again.

### 5.2.1. Balance equations for volume elements

For describing the carbonate system of the brine and the CO<sub>2</sub> release in the effects, the liquid film flowing over the horizontal tubes is divided into volume elements. The size of the volume elements was chosen due to the following requirements. On the one hand, the volume element must be big enough so that the residence time of the brine is higher than the reaction time and the reactions can occur in the volume element. On the other hand, the volume element must be so small that the amount of CO<sub>2</sub> released is lower than the amount of CO<sub>2</sub> that is molecularly dissolved in the volume element.

As in the final condenser, to find out if the carbonate system in the volume element is in chemical equilibrium, the average reaction time of the predominant reaction and the residence time can be compared. The average reaction time can be calculated due to Eq. (48). The residence time in the volume element can be calculated from the following expression:

$$t_{P, \text{Stage}} = \frac{V_{\text{film}} + V_{\text{jets}}}{\dot{V}_b} \quad (51)$$

where  $V_{\text{film}}$  is the volume of the water film on the tubes and  $V_{\text{jets}}$  is the volume of the water of the falling jets.

It was found that one volume element should contain three tubes plus the corresponding liquid jets. The quantities at the inlet of the volume element or inside the volume element are designated with the subscript “i” and the quantities at the outlet of the volume element or at the inlet of the next volume element are designated with the subscript “i+1”.

Precipitation of CaCO<sub>3</sub> and Mg(OH)<sub>2</sub> is assumed to occur at negligible rates. Total alkalinity TA and total carbon dioxide TC at the outlet of the volume element are calculated by means of mole balances. The total alkalinity TA does not change with CO<sub>2</sub> release, it is only influenced by the evaporation of water:

$$TA_{i+1} = \frac{TA_i \dot{m}_{b,i}}{\dot{m}_{b,i} - \dot{m}_{v,i}} \quad (52)$$

Total carbon dioxide (TC) is affected by both, the evaporation of water and by the release of CO<sub>2</sub>:

$$TC_{i+1} = \frac{TC_i \dot{m}_{b,i} - \dot{N}_{\text{CO}_2,i}}{\dot{m}_{b,i} - \dot{m}_{v,i}} \quad (53)$$

After determining the two quantities, total alkalinity and total carbon dioxide, the remaining quantities CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> as well as the pH can be calculated by applying the law of mass action due to Eqs. (36–40) and (50).

### 5.2.2. Mass transfer coupled with chemical reaction

Previously, the authors [20,32,33] described the fundamentals of mass transfer with chemical reaction in detail. In the following, the main principles and equations are summarized.

Since the difference between the partial pressure of CO<sub>2</sub> in equilibrium with the bulk liquid and the partial pressure at the phase interface, i.e. the degree of supersaturation, is small, CO<sub>2</sub> is released by quiescent desorption and not by bubble desorption. Thus, CO<sub>2</sub> is desorbed from the liquid free surface in a way analogous to gas absorption.

It is assumed that the liquid-side mass transfer controls the desorption process because the rate-determining reaction steps in the reaction mechanisms are relatively slow and the solubility of CO<sub>2</sub> in seawater is low. The mass transfer resistance in the gas phase is neglected.

Chemical desorption is a complex process involving chemical reaction kinetics, mass transfer processes, phase equilibria at the brine/vapor interface as well as fluid dynamics. Several useful predictions have been performed to describe the behavior of highly complicated absorption and desorption processes with chemical reactions

by using simplified models which simulate the situation well for practical purposes without introducing a large number of parameters. These are, among others, the film model, the penetration model and the surface renewal model. In many cases of mass transfer with chemical reaction, attempts have been made to identify the more reliable of the film model, the penetration model and the surface renewal model. For describing the rate of gas absorption or desorption in the presence of chemical reaction, only small differences exist between the models once the same value for the purely physical mass transfer coefficient is assumed. In fact, the accuracy of available experimental data is often insufficient to discriminate between the three models which do not usually differ by more than a few percent. Significant differences appear only when the reactants have greatly different diffusion coefficients [37,38,62]. For these reasons the simple film model is applied to the problem of CO<sub>2</sub> release in multiple-effect distillers.

The forward reaction of the rate-determining step (5) in the alkaline reaction mechanism is second order. If the OH<sup>-</sup> ions are present in excess so that their concentrations in the boundary layer at the gas/liquid interface are not considerably changed by the reaction and can be assumed to remain constant, reaction (5) can be considered to be pseudo-first-order.

It was found that in bicarbonate-carbonate solutions the concentration of OH<sup>-</sup> ions in the boundary range can be considered to remain constant, if the following condition is fulfilled [38,63]:

$$\left(C_{\text{CO}_2,\text{B}} - C_{\text{CO}_2,\text{Ph}}^*\right) \left( \frac{1}{C_{\text{CO}_3^{2-},\text{B}} - C_{\text{HCO}_3^-,\text{B}}} \right) \times \left( \sqrt{1 + \frac{D_{\text{CO}_2} k_2 C_{\text{OH}^-,\text{B}}}{(k_L^0)^2}} - 1 \right) \ll 1 \quad (54)$$

The condition given by Eq. (54) is fulfilled under typical operating conditions of ME distillers. Thus, reaction (5) can be considered to be pseudo-first-order with the rate law:

$$\frac{dC_{\text{CO}_2}}{dt} = -k_1 C_{\text{CO}_2} \quad (55)$$

with the pseudo-first-order rate constant

$$k_1 = k_2 C_{\text{OH}^-} \quad (56)$$

where  $k_2$  is the second-order rate constant of the forward reaction (5) and  $C_{\text{OH}^-}$  is the concentration of the OH<sup>-</sup> ions.

The complex system of non-linear differential equations that describes the concentration fields of the components in the carbonate system at the gas/liquid phase interface could be reduced to a set of two linear differential equations by applying the film theory and considering only CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> species in reaction (5):

$$\begin{aligned} D_{\text{CO}_2} \frac{d^2 C_{\text{CO}_2}}{dx^2} &= k_1 C_{\text{CO}_2} - k_{-1} C_{\text{HCO}_3^-}, \\ D_{\text{HCO}_3^-} \frac{d^2 C_{\text{HCO}_3^-}}{dx^2} &= k_{-1} C_{\text{HCO}_3^-} - k_1 C_{\text{CO}_2}. \end{aligned} \quad (57)$$

The boundary condition at the gas/liquid interface at  $x = 0$  and at the other edge of the boundary layer at  $x = \delta_b$  are given by

$$\begin{aligned} x = 0: & \begin{cases} C_{\text{CO}_2} = C_{\text{CO}_2,\text{Ph}}^* \\ \frac{dC_{\text{HCO}_3^-}}{dx} = 0, \end{cases} \\ x = \delta_b: & \begin{cases} C_{\text{CO}_2} = C_{\text{CO}_2,\text{B}} \\ C_{\text{HCO}_3^-} = C_{\text{HCO}_3^-,\text{B}}. \end{cases} \end{aligned} \quad (58)$$

The solution of the differential equations for the CO<sub>2</sub> desorption rate is a very complex term [33,64]:

$$\dot{N}_{\text{CO}_2} = k_L^\circ A_{\text{Ph}} \frac{(1 + DK)(C_{\text{CO}_2, \text{B}} - C_{\text{CO}_2, \text{Ph}}^*) + DK \left[ 1 - \frac{1}{\cosh \left( Ha \sqrt{1 + \frac{1}{KD}} \right)} \right] \left( \frac{1}{K} C_{\text{HCO}_3^-, \text{B}} - C_{\text{CO}_2, \text{B}} \right)}{1 + DK \frac{\tanh \left( Ha \sqrt{1 + \frac{1}{KD}} \right)}{Ha \sqrt{1 + \frac{1}{KD}}}} \quad (59)$$

with the Hatta number.

$$Ha = \frac{\sqrt{k_1 D_{\text{CO}_2}}}{k_L^\circ}, \quad (60)$$

the equilibrium constant  $K$  of reaction (5) considered to be pseudo-first-order

$$K = \frac{K_1^{\text{SW}}}{K_w^{\text{SW}}} [\text{OH}^-]^{\text{eq}}, \quad (61)$$

and the ratio of the diffusion coefficients of  $\text{HCO}_3^-$  and  $\text{CO}_2$  in the brine

$$D = \frac{D_{\text{HCO}_3^-}}{D_{\text{CO}_2}}. \quad (62)$$

Danckwerts and Sharma [63] indicated that for technical purposes it can be assumed that the diffusion coefficients of different gases and ions in aqueous solutions, except for  $\text{H}^+$  and  $\text{OH}^-$  ions which have higher diffusion coefficients, can be considered to have similar values. Thus, in the present work it is assumed that  $D_{\text{HCO}_3^-} \approx D_{\text{CO}_2}$ .

### 5.2.3. The phase interface area

The phase interface area for  $\text{CO}_2$  release consists of three parts: the surface area of the brine being distributed onto the first tube row, the surface area of the brine flowing over the tubes and the surface area of the concentrated brine collected at the bottom of the evaporator. The following

analysis puts the main focus on the surface area of the brine flowing over the tubes.

For modeling the phase interface area, the different patterns of liquid flow between adjacent tubes in a bank of horizontal tubes were studied. The flow rate and the tube spacing in ME distillers are in the range that mainly liquid columns can be expected to occur between the tubes. The phase interface area is the sum of the surface area of the liquid film on the tubes plus the surface area of the liquid between the tubes. The phase interface area can be expressed as

$$A_{\text{Ph}} = A_{\text{film}} + A_{\text{jets}} \quad (63)$$

where  $A_{\text{film}}$  is the surface area of the liquid film on a tube and  $A_{\text{jets}}$  is the surface area of the liquid jets between two adjacent tubes.

The thickness of the liquid film on the tubes, the diameter and the number of the liquid jets between the tubes mainly depend on the wetting rate of the tubes, the physical properties of the feed water as well as on the tube diameter, tube length, and spacing. A detailed description of the determination of the phase interface area was given by the authors in [20].

### 5.2.4. The mass transfer coefficient

Despite the importance of horizontal tube evaporators, information for predicting mass transfer coefficients is still limited, particularly for higher temperatures and evaporation conditions. A number

of experimental investigations have been performed to predict the mass transfer rates across falling films on horizontal tubes. Different test liquids, Reynolds number ranges, tube spacings and hence flow characteristics were examined. An overview of the investigations was given and different approaches for calculating the mass transfer coefficient were compared by the authors [20].

Owing to a lack of suitable correlations, the mass transfer was described using the empirical correlation proposed by Nosoko et al. [65]. Recently, Nosoko et al. [65] experimentally investigated falling water films on horizontal tubes in a vertical row and the associated gas absorption. They performed the experiments only for a narrow range of film temperatures between 18 and 23°C. For tube spacings between 10 and 15 mm and Reynolds numbers between  $40 < Re < 600$ , they proposed the following power law correlation:

$$Sh = 0.01144 Re^{0.86} Sc^{0.5} \quad (64)$$

with the Sherwood number

$$Sh = \frac{k_L^\circ \delta_f}{D_i} \quad (65)$$

where  $\delta_f$  is the thickness of the water film at 90° from the top of the horizontal tubes, and the Reynolds number

$$Re = \frac{4\Gamma}{\mu} \quad (66)$$

with the wetting rate

$$\Gamma = \frac{\dot{m}}{2L}, \quad (67)$$

and the Schmidt number

$$Sc = \frac{\nu}{D_i}. \quad (68)$$

### 5.2.5. The diffusion coefficient

The diffusion coefficient of  $CO_2$  in seawater  $D_{CO_2,SW}$  can be calculated approximately from

the diffusion coefficient in pure water by relating the viscosities:

$$D_{CO_2,SW} = \frac{\mu_W}{\mu_{SW}} D_{CO_2,W} \quad (69)$$

where  $D_{CO_2,W}$  is the diffusion coefficient of  $CO_2$  in water, and  $\mu_W$  and  $\mu_{SW}$  are the dynamic viscosities of water and seawater, respectively.

McLachlan and Danckwerts [66] proposed an empirical correlation for the diffusion coefficient of  $CO_2$  in pure water:

$$\log_{10} D_{CO_2,W} = -4.1764 + \frac{712.52}{T} - \left( \frac{2.5907}{T^2} \cdot 10^5 \right) \quad (70)$$

with  $D_{CO_2,SW}$  in  $cm^2/s$  and  $T$  in K.

The diffusion coefficient of  $CO_2$  in seawater was calculated to be between  $2.4 \times 10^{-9}$  and  $4.6 \times 10^{-9} m^2/s$  at temperatures between 40 and 70°C and salinities between 35 and 70 g/kg.

### 5.2.6. The physical equilibrium at the phase interface

For the determination of the  $CO_2$  concentration in the brine at the phase interface, the following assumptions are made:

- Physical equilibrium prevails at the phase boundary.
- The partial pressures and concentrations of the NC gases are sufficiently small, and Henry's law can be applied.
- The deviation of the thermal equation for the state of the NC gases and the water vapor from that for the ideal gas is negligible at the low pressures in ME distillers.
- The released gases are removed continuously with the ascending vapor so that no accumulation occurs in the gas phase over the brine.

According to Henry's law the  $CO_2$  concentration in the brine at the free liquid surface is

proportional to the CO<sub>2</sub> partial pressure in the gaseous phase over the liquid:

$$C_{\text{CO}_2,\text{Ph},i} = H_{\text{CO}_2,\text{SW}} \cdot p_{\text{CO}_2,i} \quad (71)$$

The CO<sub>2</sub> partial pressure in the gaseous phase over the free liquid surface in the volume element *i* is

$$p_{\text{CO}_2,i} = \frac{\dot{N}_{\text{CO}_2,i}}{\dot{N}_{\text{v},i}} p_{\text{v},i} \quad (72)$$

where  $\dot{N}_{\text{v},i}$  is the molar flow rate of the vapor in the volume element *i*.

The partial pressure of vapor over the free liquid surface results from Dalton's law as follows:

$$p_{\text{v},i} = p_{\text{tot}} - p_{\text{CO}_2,i} - p_{\text{N}_2,i} - p_{\text{O}_2,i} \quad (73)$$

By inserting Eq. (73) into Eq. (72), the partial pressure of CO<sub>2</sub> in the gas phase over the free liquid surface can be obtained as follows:

$$p_{\text{CO}_2,i} = \frac{\dot{N}_{\text{CO}_2,i} (p_{\text{tot}} - p_{\text{N}_2,i} - p_{\text{O}_2,i})}{\dot{N}_{\text{v},i} + \dot{N}_{\text{CO}_2,i}} \quad (74)$$

In this work, the feed water is considered to be degassed and the residual concentrations of N<sub>2</sub>, O<sub>2</sub> and Ar are negligible.

### 5.2.7. The desorption regime

Depending on the Hatta number *Ha* and the chemical equilibrium constant *K*, a number of asymptotic solutions of Eq. (59) can be found [37,38]. Applying the model to a reference ME distiller under typical operating conditions, the chemical equilibrium constant *K* in Eq. (61) was calculated to be between 80 and 250. Using Eq. (64) for the mass transfer coefficient, the Hatta number is calculated to be between 0.3 and 1, i.e. desorption takes place in the transition regime from slow to fast reaction. Mass transfer and chemical reactions simultaneously take place in the boundary layer at the phase

interface. The bulk of the brine is in chemical equilibrium. The chemical rate constant becomes more important and the mass transfer coefficient less important in the correlation for the CO<sub>2</sub> release rate. Eq. (59) approaches to

$$\dot{N}_{\text{CO}_2} = k_L^o A_{\text{Ph}} \frac{(1 + K) \left( C_{\text{CO}_2,\text{B}}^{\text{eq}} - C_{\text{CO}_2,\text{Ph}}^* \right)}{1 + K \frac{\tanh \left( Ha \sqrt{1 + \frac{1}{K}} \right)}{Ha \sqrt{1 + \frac{1}{K}}}} \quad (75)$$

Mass transfer is slightly enhanced by the reaction.

## 6. Conclusions

A model has been developed for the prediction of the CO<sub>2</sub> release and the description of the carbonate system in multiple-effect distillers. Included is the flow path of brine through the final condenser and the effects. The theory of desorption with chemical reaction is applied to the problem of CO<sub>2</sub> release in multiple-effect distillers. The main features of the proposed model are

- The carbonate system in seawater is described by the following six quantities: total alkalinity TA, total carbon dioxide TC, pH value, HCO<sub>3</sub><sup>-</sup> concentration, CO<sub>3</sub><sup>2-</sup> concentration and dissolved molecular CO<sub>2</sub> concentration. In chemical equilibrium the carbonate system is completely characterized by two of these six quantities. The remaining four quantities can be calculated by applying the law of mass action with the dissociation constants of carbonic acid and water in seawater. In order to focus on the effects of the CO<sub>2</sub> release and the process conditions, such as temperature and salinity, on the carbonate system, precipitation of CaCO<sub>3</sub> and Mg(OH)<sub>2</sub> is assumed to occur at negligible rates.
- Given the measurable total alkalinity TA and the pH of seawater, the concentrations of

$\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{CO}_2$  in seawater as well as the total carbon dioxide TC can be determined.

- In the final condenser, the brine is preheated under non-boiling conditions. The total pressure is high enough to keep  $\text{CO}_2$  in solution. It is proposed to compare the reaction time and the brine residence time in order to find out if the reactions are fast enough to assume that chemical equilibrium prevails in the carbonate system. The total alkalinity TA and the total carbon dioxide TC remain constant in the final condenser. The concentrations of  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  as well as the pH are determined by applying the law of mass action with the dissociation constants.
- For describing the carbonate system and the  $\text{CO}_2$  release in the evaporator stages, it is proposed to divide the brine film flowing over the horizontal tubes into volume elements. Total alkalinity TA and total carbon dioxide TC at the outlet of the volume elements are calculated by means of mole balances. The total alkalinity TA does not change with  $\text{CO}_2$  release, it is only influenced by the concentration of the brine due to water evaporation. Total carbon dioxide TC is affected by both, the brine concentration due to evaporation and by the release of  $\text{CO}_2$ . The remaining four quantities can be calculated by applying the law of mass action with the dissociation constants of carbonic acid and water in seawater.
- Detailed investigations into the reaction kinetics revealed that the hydration and dehydration of  $\text{CO}_2$  in aqueous bicarbonate–carbonate solutions occur by two reaction mechanisms in parallel. In the temperature and pH range assumed to prevail in the effects, the alkaline reaction mechanism with the steps  $\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-$  and  $\text{HCO}_3^- + \text{OH}^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$  predominates. The rates of the reaction steps differ notably. The reaction  $\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-$  is relatively slow and therefore it is the rate-determining step in the alkaline reaction mechanism.
- It is assumed that the liquid-side mass transfer controls the desorption process, because the rate-determining reaction steps in the reaction mechanisms are relatively slow and the solubility of  $\text{CO}_2$  in seawater is low. The mass transfer resistance in the gas phase is neglected.
- Since the difference between the partial pressure of  $\text{CO}_2$  in equilibrium with the bulk liquid and the partial pressure at the phase interface, i.e. the degree of supersaturation, is small,  $\text{CO}_2$  is released by quiescent desorption and not by bubble desorption.
- The complex system of nonlinear differential equations that describes the concentration fields of the components in the carbonate system at the gas/liquid phase interface could be reduced to a set of two linear differential equations and solved analytically.
- The phase equilibrium at the brine/vapor interface is described by applying Henry's law.
- Information for predicting mass transfer coefficients in water films flowing over horizontal tubes is still limited. Mass transfer is described by using an empirical correlation  $Sh = f(Re, Sc)$ .
- The interfacial area is described as the sum of the surface area of the liquid film on the tubes plus the surface area of the liquid between the tubes. For modeling the phase interface area, the different patterns of liquid flow between adjacent tubes in a bank of horizontal tubes were studied. The thickness of the water film on the tubes, the average diameter and the number of water jets between the tubes were determined, assuming that the flow rate and the tube spacing in ME distillers are in the range that mainly liquid columns can be expected to occur between the tubes.

A better knowledge of the chemical equilibrium constants of carbonic acid in seawater as well as the solubility of CO<sub>2</sub> at high temperatures and high salinities could contribute to an increase in the accuracy of the model. Moreover, further investigations into the mass transfer coefficient and the phase interface area could improve the model predictions.

### Nomenclature

$A_{\text{film}}$	surface area of the liquid film on the tube, m <sup>2</sup>	$K_2^{\text{SW}}$	second dissociation constant of carbonic acid in seawater on the basis mol/kg solution
$A_{\text{jets}}$	surface area of the water jets between adjacent tubes, m <sup>2</sup>	$K_{\text{sp}}$	solubility product constant on the basis mol/kg solution
$A_{\text{ph}}$	phase interface area, m <sup>2</sup>	$K_{\text{W}}^{\text{SW}}$	dissociation constant of water in seawater on the basis mol/kg solution
$C_i$	concentration of the component $i$ , mol/m <sup>3</sup>	$k_1$	first order rate constant of the forward reaction, 1/s
$D_i$	diffusion coefficient of the component $i$ , m <sup>2</sup> /s	$k_{-1}$	first order rate constant of the backward reaction, 1/s
$d_i$	inside diameter, m	$k_2$	second order rate constant, m <sup>3</sup> /(mol s)
$Ha$	Hatta number	$k_{\text{L}}^{\circ}$	mass transfer coefficient in liquid phase without chemical reaction, m/s
$H_{ij}$	Henry's law coefficient of the gas $i$ in the solution $j$ , mol/(m <sup>3</sup> bar)	$L$	length of tubes
$h$	sum of the ion and gas specific parameters, kg/mol, L/mol	$m_i$	molality of the component $i$ , mol/kg solvent
$h_+$	ion specific parameter for cations, kg/mol, L/mol	$\dot{m}$	mass flow rate, kg/s
$h_-$	ion specific parameter for anions, kg/mol, L/mol	$\dot{m}_{\text{b}}$	brine mass flow rate, kg/s
$h_{\text{G}}$	gas specific parameter, kg/mol, L/mol	$\dot{m}_{\text{v}}$	vapor mass flow rate, kg/s
$I$	ionic strength, mol/kg	$\dot{N}_i$	molar desorption rate of the component $i$ , mol/s
$[i]$	concentration of the component $i$ , mol/kg solution	$\dot{n}_i$	molar desorption flux of the component $i$ , mol/(m <sup>2</sup> s)
$[i]^{\text{SW}}$	concentration of the component $i$ that is free and involved in ion-pairs in seawater, mol/kg solution	$n_{\text{tubes}}$	number of tubes
$K$	equilibrium constant of the pseudo-first-order reaction	$p_i$	partial pressure of the component $i$ , N/m <sup>2</sup> , bar
$K_1^{\text{SW}}$	first dissociation constant of carbonic acid in seawater on the basis mol/kg solution	pH	pH value
		$Re$	Reynolds number
		$S$	salinity, g/kg
		$Sc$	Schmidt number
		$Sh$	Sherwood number
		$T$	temperature, K
		TA	total alkalinity, mol/kg
		TC	total carbon dioxide content, mol/kg
		$t_{\text{p}}$	residence time, s
		$t_{\text{R}}$	average reaction time, s
		$V$	liquid volume, m <sup>3</sup>
		<i>Greeks</i>	
		$\delta_{\text{b}}$	thickness of the boundary layer in the liquid at the gas/liquid interface, m
		$\gamma$	activity coefficient

$\Gamma$	half mass flow rate per unit tube length, kg/(m s)
$\mu$	dynamic viscosity, kg/(m s)
$\nu$	kinematic viscosity, m <sup>2</sup> /s
$\vartheta$	temperature, °C

### Indices

B	bulk
CO <sub>2</sub>	carbon dioxide
eq	chemical equilibrium
G	gas
HCO <sub>3</sub> <sup>-</sup>	bicarbonate ion
H <sub>2</sub> O	water
i	component
L	liquid side
N <sub>2</sub>	nitrogen
O <sub>2</sub>	oxygen
OH <sup>-</sup>	hydroxide ion
Ph	phase interface
s	solid
SW	seawater
tot	total
v	vapor
W	water
*	physical equilibrium

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