

YIPING MA<sup>1</sup>, LEPING XU<sup>1</sup>, PENGHAO SU<sup>2</sup>, DAOLUN FENG<sup>2</sup>, KAILIANG YANG<sup>2</sup>

## STUDY ON SEAWATER SCRUBBING FOR SO<sub>2</sub> REMOVAL FROM SHIP'S POWER PLANT EXHAUST GAS

The mechanism of SO<sub>2</sub> absorption in seawater is investigated, and the experiment was carried out accordingly. Emphasis is on applications of seawater scrubbing of ship's power plant exhaust gas containing SO<sub>2</sub>. The formulated model is used to predict the influence of various parameters on both pH of tailwater and seawater desulfurization capability, e.g., the partial pressure of SO<sub>2</sub>, the partial pressure of CO<sub>2</sub>, tailwater temperature, pH and alkalinity of seawater. Experiment results indicated that the seawater desulfurization capacity increases with both increasing partial pressure of SO<sub>2</sub>, pH and alkalinity and decreasing partial pressure of CO<sub>2</sub> and temperature. The study shows the desulfurization capacity of seawater with 3.5% salinity is approximately twice that of freshwater. Different scenarios in which the required absorbent supply rate for a given SO<sub>2</sub> removal efficiency are studied. It is observed a 97% removal efficiency, corresponding to meeting the SO<sub>x</sub> limits in the SO<sub>x</sub> emission control areas (SECA) while operating on a heavy fuel oil containing sulfur 3.5 wt. %, requires a minimum water supply rate of 0.0407–0.0683 m<sup>3</sup>/kWh, depending mainly on the water composition in terms of alkalinity and salinity. Such data are important in assessing the operation cost of the water scrubbing system.

### SYMBOLS

- [SO<sub>2</sub>(aq)] – SO<sub>2</sub> concentration in aqueous solution, kmol/m<sup>3</sup>  
[CO<sub>2</sub>(aq)] – CO<sub>2</sub> concentration in aqueous solution, kmol/m<sup>3</sup>  
 $P_{\text{SO}_2}$  – partial pressure of SO<sub>2</sub> in the gas phase, Pa  
 $P_{\text{CO}_2}$  – partial pressure of CO<sub>2</sub> in the gas phase, Pa  
 $H_{\text{SO}_2}$  – Henry's law constant for SO<sub>2</sub>, 10<sup>-2</sup> mol/m<sup>3</sup>·Pa  
 $H_{\text{CO}_2}$  – Henry's law constant for CO<sub>2</sub>, 10<sup>-2</sup> mol/m<sup>3</sup>·Pa  
 $K_1$  – dissociation equilibrium constant of sulfurous acid, kmol/m<sup>3</sup>  
 $K_2$  – dissociation equilibrium constant of bisulfite ion, kmol/m<sup>3</sup>  
 $K_3$  – dissociation equilibrium constant of carbonic acid, kmol/m<sup>3</sup>

---

<sup>1</sup>Merchant Marine College, Shanghai Maritime University, Shanghai 201306, China, corresponding author Y. Ma, e-mail address: ypma@shmtu.edu.cn

<sup>2</sup>College of Ocean Science and Engineering, Shanghai Maritime University, Shanghai 201306, China.

- $K_4$  – dissociation equilibrium constant of bicarbonate ion, kmol/m<sup>3</sup>  
 $K_w$  – ionic product of water, kmol/m<sup>3</sup>  
 $C_s$  – desulfurization capacity of seawater, kmol/m<sup>3</sup>

## 1. INTRODUCTION

Heavy fuel oil (HFO) containing high sulfur is usually used to power large marine diesel engines. During combustion, sulfur is oxidized mainly to SO<sub>2</sub>, which influence human health and the environment, causing asthma and other breathing difficulties to human and producing acid rain affecting the growth of flora and fauna as well as water-life [1].

According to *Regulations for the Prevention of Air Pollution from Ships, IMO Annex VI of MARPOL 73/78* [2], SO<sub>x</sub> coming from the ship power plant is regulated by setting a maximum fuel sulfur content value of 3.5 wt. %. The SO<sub>x</sub> limit applies to all ships. Besides this general regulation, tighter regulations must be fulfilled in some restricted areas, which is generally called SECA (SO<sub>x</sub> emission control areas) and includes the Baltic Sea, The North Sea, and the English Channel, etc. In SECA, at least one of the following two conditions shall be fulfilled:

- The fuel sulfur content shall not exceed 0.1 wt. %.
- The installation of an exhaust gas cleaning system is required to reduce the total emission of sulfur oxides to 0.4 g/kWh or less.

Jiang et al. [3] found that the price spread between marine gas oil and heavy fuel oil is a determining factor in making this choice. Marine gas oil tends to have higher net present values than scrubbers when the price spread of fuel is less than 231 €/tonne. Ma et al. [4] concluded that a scrubber system using current heavy fuel oils has the potential to reduce SO<sub>x</sub> emissions with lower well-to-wake energy consumption and greenhouse gas emissions than switching to production of low sulfur fuels at the refinery [4]. An extensive survey of the available scrubbers provided by the Ship Operation Cooperation Program (SOCP) revealed that scrubbing technologies were generally categorized as either wet or dry systems [5]. Compared with dry desulfurization, wet scrubbing is a promising technology applied to ship because of its higher desulfurization efficiency and has at least three variants including open-loop, closed-loop and hybrid systems [6].

An open-loop system can be used on the high sea, where the inherent alkalinity of seawater is used as absorbent, and no additives are needed. The closed-loop system using sodium hydroxide or other alkaline substances as absorbent can be used in any sea area, especially in the wharves and estuaries. The hybrid system means switching to an open-loop system or closed-loop system at an open sea or sensitive sea.

Seawater is obtained conveniently for maritime vessels. Therefore, many theoretical and experimental studies have already been performed on seawater scrubbing for marine exhaust gas desulfurization [7–11]. Caiazzo et al. [7] indicated that seawater scrubbing SO<sub>2</sub> performed better than distilled water, because of exploiting its inherent alkalinity.

Sun et al. [10] found that owing to the existence of complex CO<sub>2</sub>-H<sub>2</sub>O-HCO<sub>3</sub><sup>-</sup>-CO<sub>3</sub><sup>2-</sup> equilibrium system, the mass transfer coefficient of seawater was about twice as large as that of aqueous NaOH solution with pH of 8.35. Furthermore, Tang et al. [6, 12] pointed out that magnesium-base seawater scrubbing flue gas has more satisfactory desulfurization efficiency. In addition, absorption of sulfur dioxide with sodium hydroxide solutions was also studied [13].

The main contribution to seawater alkalinity are HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> ions, and the main alkalinity of sodium hydroxide solution are OH<sup>-</sup> ions, whereas magnesium-base seawater contains the above said three alkalinity species. The effective diffusivities of OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> in water at 25 °C and infinite dilution are 5.27×10<sup>-9</sup>, 1.185×10<sup>-9</sup> and 0.923×10<sup>-9</sup> m<sup>2</sup>/s, respectively [14], and their differences are very small. So, according to the definition of enhancement factor [15], it has little relation with the alkaline substance category but is closely related to the total quantity of alkaline substance. Pitzer interaction model [16, 17], or activity coefficients [9] is taken into account in calculating the solubility of SO<sub>2</sub> in solution. Actually, the solubility of SO<sub>2</sub> in seawater and other parameters including thermodynamic and dissociation equilibrium constants, etc., all greatly depend on salinity [8, 9, 18].

Based on the above mentioned three alkalinity substances, the authors of this paper intended to set up the solubility model of SO<sub>2</sub> in seawater, where the effects of Pitzer interaction and activity coefficients on the solubility of SO<sub>2</sub> were be included in the calculations of equilibrium constants. The required minimum water supply rate was calculated according to the established solubility model of SO<sub>2</sub>, so as to obtain the SO<sub>2</sub> cleaning efficiency comparable to that of switching from HFO to MGO with 0.1 wt. % sulfur content. Such information is important in assessing the operation costs of SO<sub>2</sub> removal by water scrubbing exhaust gas.

## 2. EXPERIMENTAL

The schematic of the experimental apparatus is shown in Fig. 1. Pure SO<sub>2</sub> and CO<sub>2</sub> were supplied with cylinders 1 and 4, respectively. The flow rates of SO<sub>2</sub> and CO<sub>2</sub> were adjusted by valves 2 and 5 and monitored by rotor flow meters 3 and 6, respectively. Air was pumped into the mixing chamber 9 by an air blower 7. The simulated flue gas was obtained in the mixing chamber 9. The concentration of SO<sub>2</sub> and CO<sub>2</sub> was measured using a Testo-350 Gas Analyzer 10. Seawater solution was made of distilled water and sea salt, and the salinity, pH, and alkalinity were 3.5 wt. %, 7.98 and 1.92 mol/m<sup>3</sup>, respectively. The determination of alkalinity in seawater solution was conducted using potentiometric titration [19] (a turbulent ball tower, which is by nature a 2-meter high tower with its inner diameter of 285 mm, will scrub SO<sub>2</sub> from flue gas in next experiment, where a large quantity of seawater is needed. In order to verify the research results

of this paper in the next experiment, this and the next experiment used the same seawater solutions made of sea salt and water). The absorption of  $\text{SO}_2$  was carried out in reaction flask 12, which was heated to and kept certain temperature in bath box 14 (the reactions existed in the flask here and the real scrubber on board are the same, and the water–gas interactions can be treated as instantaneous reactions with the rate constant of  $3.4 \times 10^6$  1/s or more [14]).

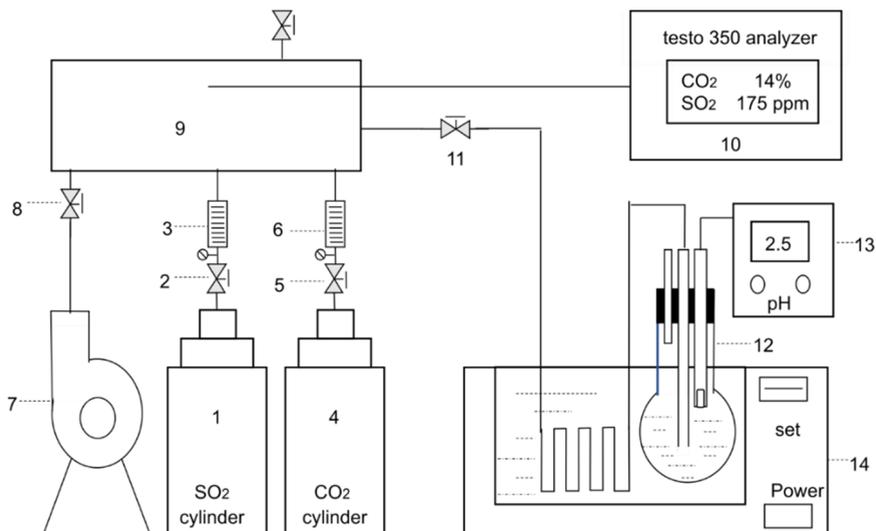


Fig. 1. Schematic of the experimental apparatus: 1 –  $\text{SO}_2$  cylinder, 2, 5 – pressure reducing valve, 3, 6 – gas flow meters, 4 –  $\text{CO}_2$  cylinder, 7 – air blower, 8, 11 – valve, 9 – mixing chamber, 10 – flue gas analyzer, 12 – reaction flask, 13 – pH meter, 14 – Electrical controlled constant temperature bath box

The real scrubber is high enough and the liquid–gas ratio is very small, the seawater solution at the bottom of the scrubber is saturated in absorbing  $\text{SO}_2$ . Hence, the reaction flask here is the equivalent of a high enough scrubber used in some specific conditions). pH and temperature of seawater were detected using a Mettler Toledo-Delta 320 pH meter. The quantity of  $\text{SO}_2$  absorbed in seawater was measured using the iodine titration method [20].

### 3. MODEL

When the reading of pH meter came to constant, seawater changed into the saturated solution for  $\text{SO}_2$ . The reaction expressions of dissolution equilibrium and ionization equilibrium are given by formulas (1)–(7) [21], and equilibrium coefficients are given in Table 1 [14].

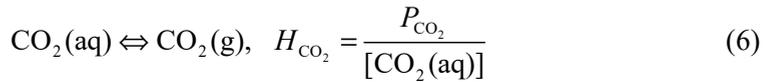
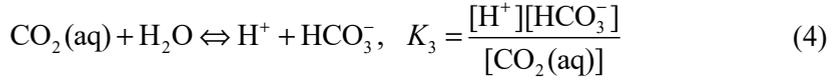
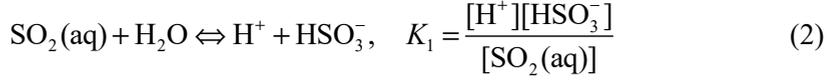
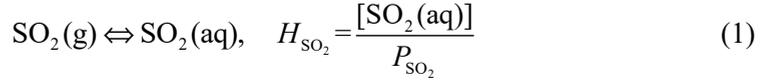


Table 1

Correlation coefficients for constants in the seawater desulfurization process [14]

Constant	A	B	C	D	E	F	G	H
$\ln(1/H) = A/T + B\ln T + CT + DH$								
$H_{\text{SO}_2}$	-5578.8	-8.76152	0	68.418				
$\ln K_i = A/T + B\ln T + CT + DK$								
$K_1$	26404.29	160.3981	-0.275224	-924.6255				
$K_2$	-5421.93	-4.6899	-0.0498769	43.3136				
$K_w$	-13445.9	-22.4773	0	140.932				
$\ln H = 100A/T + B\ln(T/100) + CT/100 + D + S[E - F(T/100) + G(T/100)^2]$								
$H_{\text{CO}_2}$	93.4517	23.3585	0	-60.2409	0.023517	0.023656	0.0047036	
$\ln K = A/T + B\ln T + CT + D + ES^{0.5} + FS + GS^{1.5} + HS^2 + \ln(1 - 0.001005S)$ , S is salinity								
$K_3$	$A = -14554.21$	$B = -45.0575$	$E = -228.4 + 9714.4/T + 34.5 \cdot \ln T$		$F = 54.2 - 2310.5/T - 8.2 \ln T$			
	$C = 0$	$D = 290.9097$	$G = -3.97 + 170.2/T + 0.6 \ln(T)$		$H = -0.0026$			
$K_4$	$A = -11843.79$	$B = -33.7485$	$E = -167.7 + 6551.4/T + 25.9 \ln(T)$		$F = 39.8 - 1566.1/T - 6.2 \ln(T)$			
	$C = 0$	$D = 207.6548$	$G = -2.9 + 116.3/T + 0.46 \ln(T)$		$H = -0.006$			

The parameters with subscripts 0 stand for initial values, and those without subscript stand for final values. Provided that the total concentration of cations and anions that do not react before the absorption of CO<sub>2</sub> and SO<sub>2</sub> is  $\sum[\text{cation}^{n+}]_0$  and  $\sum[\text{anion}^{m-}]_0$ , the neutrality condition is:

$$\sum n[\text{Cation}^{n+}]_0 + [\text{H}^+]_0 = \sum m[\text{Anion}^{m-}]_0 + [\text{OH}^-]_0 + [\text{HCO}_3^-]_0 + 2[\text{CO}_3^{2-}]_0 \quad (8)$$

Seawater solution is also neutral after the absorption of gases, and the neutrality condition takes the form:

$$\begin{aligned} \sum n[\text{Cation}^{n+}]_0 + [\text{H}^+] = \sum m[\text{Anion}^{m-}]_0 + [\text{OH}^-] \\ + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] \end{aligned} \quad (9)$$

Combining equation (9) and equation (10), we obtain:

$$\begin{aligned} [\text{OH}^-]_0 + [\text{HCO}_3^-]_0 + 2[\text{CO}_3^{2-}]_0 - [\text{H}^+]_0 = [\text{OH}^-] + [\text{HCO}_3^-] \\ + 2[\text{CO}_3^{2-}] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] - [\text{H}^+] \end{aligned} \quad (10)$$

According to Henry's law and dissociation equilibrium, equation (11) can be deduced by combining equilibrium equations (1)–(7) and (10).

$$\begin{aligned} [\text{H}^+]^3 + \left( [\text{HCO}_3^-]_0 + 2[\text{CO}_3^{2-}]_0 + \frac{K_w}{[\text{H}^+]_0} - [\text{H}^+]_0 \right) [\text{H}^+]^2 - K_w[\text{H}^+] \\ = (K_3[\text{H}^+] + 2K_3K_4)P_{\text{CO}_2}H_{\text{CO}_2} + (K_1[\text{H}^+] + 2K_1K_2)P_{\text{SO}_2}H_{\text{SO}_2} \end{aligned} \quad (11)$$

Substituting:

$$[\text{H}^+] = 10^{-\text{pH}} \quad (12)$$

Assuming that the saturated solution is tailwater, its pH can be expressed as

$$\begin{aligned} (10^{-\text{pH}})^3 + \left( [\text{HCO}_3^-]_0 + 2[\text{CO}_3^{2-}]_0 + \frac{K_w}{10^{-\text{pH}_0}} - 10^{-\text{pH}_0} \right) (10^{-\text{pH}})^2 - K_w 10^{-\text{pH}} \\ = (K_3 10^{-\text{pH}} + 2K_3K_4)P_{\text{CO}_2}H_{\text{CO}_2} + (K_1 10^{-\text{pH}} + 2K_1K_2)P_{\text{SO}_2}H_{\text{SO}_2} \end{aligned} \quad (13)$$

$[\text{HCO}_3^-]_0 + 2[\text{CO}_3^{2-}]_0$  stand for the initial alkalinity of carbonates in seawater,  $K_w/10^{-\text{pH}_0} - 10^{-\text{pH}_0}$  are decided by the initial pH and temperature of seawater,  $P_{\text{SO}_2}$  and  $P_{\text{CO}_2}$  and are the partial pressures of SO<sub>2</sub> and CO<sub>2</sub> in the gas phase, respectively,  $H_{\text{SO}_2}$ ,  $H_{\text{CO}_2}$ ,  $K_w$ ,  $K_1$ – $K_4$  strongly depend on the temperature and salinity of tail seawater. Equation (13) shows that the pH of tailwater depends on the initial alkalinity and pH of seawater, and flue gas and on the temperature of tailwater.

The desulfurization capacity of seawater  $C_s$ , mol/m<sup>3</sup>, can be calculated according to the following equation.

$$\begin{aligned} C_s &= [\text{SO}_2(\text{aq})] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] = \frac{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}{[\text{H}^+]^2} P_{\text{SO}_2} H_{\text{SO}_2} \\ &= \frac{(10^{-\text{pH}})^2 + K_1 10^{-\text{pH}} + K_1K_2}{(10^{-\text{pH}})^2} P_{\text{SO}_2} H_{\text{SO}_2} \quad (14) \end{aligned}$$

If the initial parameters of flue gas and seawater are known, pH of tailwater and the desulfurization capacity of seawater can be calculated through equations (13) and (14), respectively.

## 4. RESULTS AND DISCUSSION

### 4.1. EFFECT OF PARTIAL PRESSURE OF SO<sub>2</sub>

As seen from Fig. 2, pH of tailwater decreases and  $C_s$  increases upon increasing partial pressure of SO<sub>2</sub>, which can be explained by the equations of the reactions (1)–(3) being shifted to the right and more SO<sub>2</sub> absorbed and H<sup>+</sup> produced consequently. It also shows that the pH decreases quickly to 2.5 or so, and then the decrease is slow but the increase of  $C_s$  is not linear with increasing SO<sub>2</sub> partial pressure, which can be explained by the reaction between seawater and dissolved SO<sub>2</sub> producing HSO<sub>3</sub><sup>-</sup> ions. In addition, the differences between the experimental and calculated values of pH and  $C_s$  are 0.3, 1.5 mol/m<sup>3</sup>, respectively, pointing that the influence salinity has been neglected. The salinity of seawater could improve the absorption of SO<sub>2</sub> in seawater [8, 9], while the coefficients, such as  $H_{\text{SO}_2}$ ,  $K_1$ , and  $K_2$  shown in Table 1 adopted by the theoretical calculations (equations (13) and (14)), do not take salinity of seawater into account. These coefficients increase with increasing salinity of seawater, so ignoring the influence of salinity during calculation will lead to larger pH and smaller  $C_s$ .

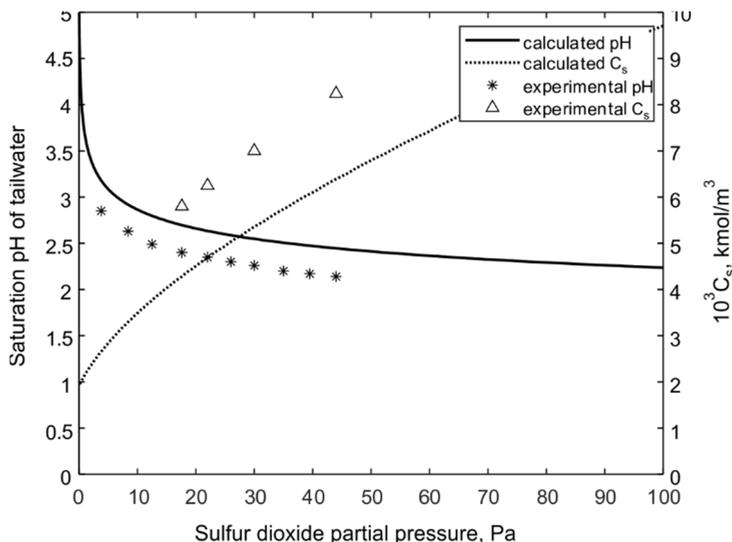


Fig. 2. Effect of the partial pressure of  $\text{SO}_2$  on saturation pH of tailwater and desulfurization capacity of seawater

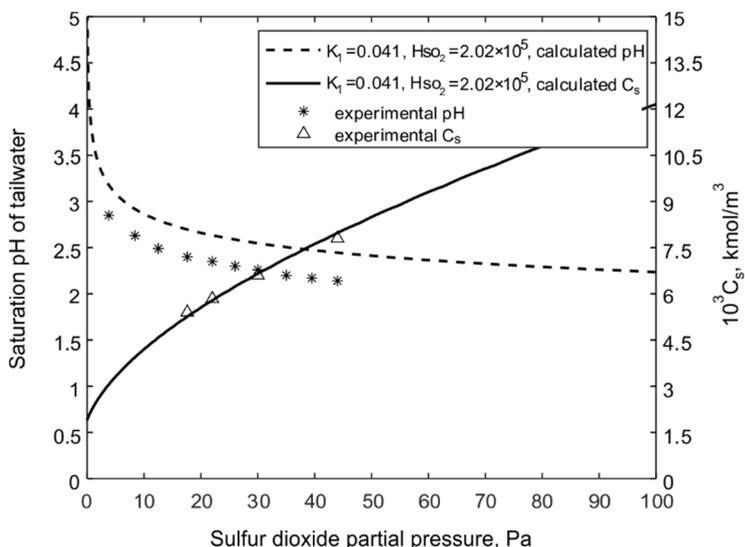


Fig. 3. Calculated and experimental saturation pH and  $C_s$  for increased values of  $H_{\text{SO}_2}$  and  $K_1$  increase

The pH of tailwater is 2.28 and  $C_s$  6.25 mol/m<sup>3</sup> at 12 °C, under the partial pressure of  $\text{SO}_2$  22 Pa, and salinity 35%. According to the experimental conditions, the  $C_s$  values calculated by other authors were 3.12 [8] and 9.9 mol/m<sup>3</sup> [22]. The differences in  $C_s$  are mainly derived from the difference of tailwater pH, e.g., the range of pH is 2.5–2.6 in [8].

The calculated  $C_s$  will increase by 1 mol/m<sup>3</sup> when pH decreases by 0.15, so a small change in pH leads to larger changes in  $C_s$  (Figs. 2 and 3).

$H_{SO_2}$ ,  $K_1$  and  $K_2$  at 12 °C are  $1.9649 \times 10^{-7}$  mol/(m<sup>3</sup>·Pa), 0.0229 and  $7.2868 \times 10^{-8}$  kmol/m<sup>3</sup>, respectively (Table 1). In addition, the mole fraction of  $SO_3^{2-}$  is almost 0, and that of  $HSO_3^-$  is the largest in solutions with pH of 2–4, so  $K_2$  can be ignored under low pH. The calculated values of pH and  $C_s$  are closest to experimental results, when  $H_{SO_2}$  and  $K_1$  increase to  $2.02 \times 10^{-7}$  mol/(m<sup>3</sup>·Pa) and 0.041 kmol/m<sup>3</sup>, respectively. The maximum errors of pH and  $C_s$  are 0.15 and 5%, respectively, after modification of the coefficients (Fig. 3).

#### 4.2. EFFECT OF PARTIAL PRESSURE OF CO<sub>2</sub>

The effect of  $P_{CO_2}$  on pH of tailwater and  $C_s$  is shown in Fig. 4. When the  $P_{SO_2}$  is 4 Pa, the difference in experimental pH is 0.1. But if  $P_{SO_2}$  increases to 44 Pa, then the difference in pH will decrease to 0.02. Concerning  $C_s$ , the difference values of experimental  $C_s$  are all about 0.4 mol/m<sup>3</sup>, when  $P_{SO_2}$  is in the range of 18–44 Pa.

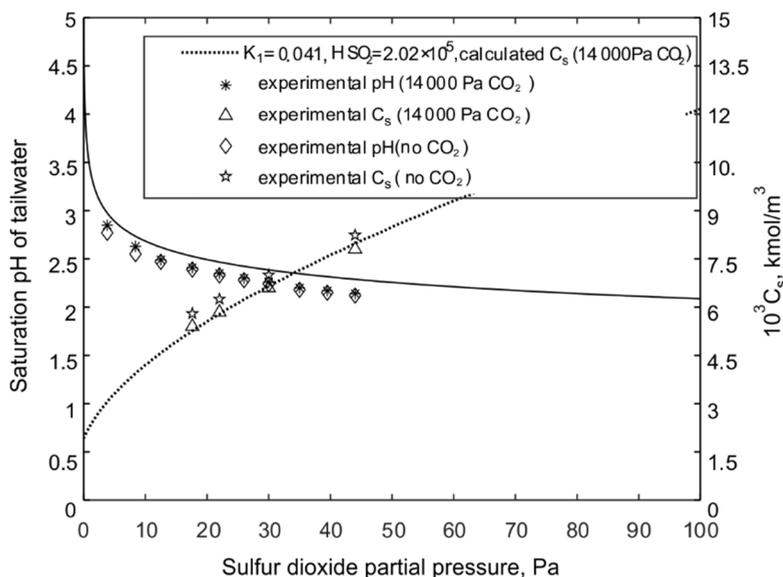


Fig. 4. Effect of the partial pressure of CO<sub>2</sub> on saturation pH of tailwater and desulfurization capacity of seawater

The experimental results show that the presence of CO<sub>2</sub> increases the saturation pH of tailwater, and decreases  $C_s$ . The presence of CO<sub>2</sub> can inhibit the absorption of SO<sub>2</sub> in seawater, but this inhibition effect is very small and becomes more and more weak with increasing partial pressure of SO<sub>2</sub>. The reason is that H<sup>+</sup> ions generated by the reaction

between the dissolved  $\text{CO}_2$  and seawater inhibit the absorption of  $\text{SO}_2$ , but the quantity of  $\text{H}^+$  generated from the above reaction is too little due to smaller solubility of  $\text{CO}_2$ , which results in weaker inhibition. The values of  $H_{\text{CO}_2}$ ,  $K_3$  and  $K_4$  are far less than those of  $H_{\text{SO}_2}$ ,  $K_1$ , and  $K_2$  in the same condition (Table 1). In addition, the binary interaction between dissolved  $\text{SO}_2$  and  $\text{CO}_2$  may decrease the numerical values of  $H_{\text{SO}_2}$ ,  $K_1$  and  $K_2$ , which also has a little effect on the inhibition.

$\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  mainly contribute to seawater alkalinity, and can be fully utilized to participate in the absorption of  $\text{SO}_2$  in seawater, when no  $\text{CO}_2$  is present in the flue gas. But, when there are large amounts of  $\text{CO}_2$ , a small residue of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  will exist in the tailwater, so although the seawater alkalinity stays the same, the actual alkalinity participating in the absorption of  $\text{SO}_2$  is reduced, thereby  $C_s$  decreases. The experimental difference of  $0.4 \text{ mol/m}^3$  does not change with increasing  $\text{SO}_2$  partial pressure, which indicates the effect of  $\text{CO}_2$  on the  $C_s$  may be related to the size of the partial pressure of  $\text{CO}_2$ . The presence of  $\text{SO}_2$  in flue gas has a negative impact on typical  $\text{CO}_2$  capture processes utilizing aqueous amines [23]. It was found that the presence of  $\text{CO}_2$  slightly reduces the  $\text{SO}_2$  absorption rate [24]. Thus the influence on gas absorption between  $\text{SO}_2$  and  $\text{CO}_2$  is mutual.

#### 4.3. EFFECT OF TEMPERATURE OF TAIL SEAWATER

The effect of temperature of tail seawater on pH of tailwater and  $C_s$  is shown in Fig. 5. It shows that the pH of tailwater increases sharply, and the  $C_s$  decreases rapidly with increasing temperature of tail seawater.

The absorption of  $\text{SO}_2$  in seawater is of physical and chemical nature. The physical absorption mainly depends on the temperature of the solution. Upon increasing tailwater temperature, the chemical absorption stays unchanged but the physical absorption decreases, which decreases  $C_s$ . The values of  $H_{\text{SO}_2}$ ,  $K_1$ , and  $K_2$  decrease rapidly with increasing temperature. Thus, concentrations of  $\text{S(IV)}$  and  $\text{H}^+$  in tailwater decrease rapidly with the increasing temperature of the tailwater.

$H_{\text{SO}_2}$  and  $K_1$  are  $7.763 \times 10^{-8} \text{ mol}/(\text{m}^3 \cdot \text{Pa})$  and  $0.0088 \text{ kmol}/\text{m}^3$ , respectively, at  $40 \text{ }^\circ\text{C}$  (Table 1). Figure 5 shows that difference still exists between the calculation and experimental values at this temperature. The values of pH and  $C_s$  are closest to experimental results when  $H_{\text{SO}_2}$  and  $K_1$  increase to  $8 \times 10^{-8} \text{ mol}/(\text{m}^3 \cdot \text{Pa})$ , and  $0.015 \text{ kmol}/\text{m}^3$ , respectively. The effect of temperature on the increase of  $H_{\text{SO}_2}$  and  $K_1$  for the seawater salinity 3.5% is shown in Table 2, where  $H_{\text{SO}_2 \text{ ad}}$  (the added value of the coefficient) is defined as  $(H_{\text{SO}_2 \text{ increased}} - H_{\text{SO}_2})/H_{\text{SO}_2}$ , e.g.,  $H_{\text{SO}_2 \text{ ad}}$  is equal to  $(8 \times 10^{-6} - 7.763 \times 10^{-6})/7.763 \times 10^{-6}$  at  $40 \text{ }^\circ\text{C}$ .

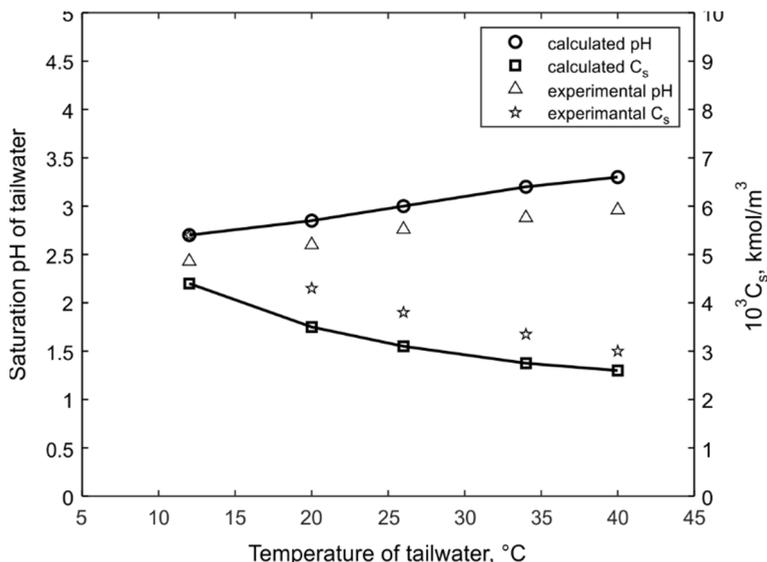


Fig. 5. Effect of temperature of tailwater on saturation pH of tailwater and desulfurization capacity of seawater

Table 2

Relation between added coefficients and temperature

The added value of the coefficient	Temperature [°C]		
	12	26	40
$H_{\text{SO}_2, \text{ad}}$	0.028	0.029	0.030
$K_{1, \text{ad}}$	0.79	0.75	0.70

#### 4.4. EFFECT OF pH OF SEAWATER

The effect of pH of seawater on pH of tailwater and  $C_s$  is shown in Fig. 6. Upon increasing pH of seawater, both the pH of tailwater and  $C_s$  increase, especially when the pH of seawater is higher than 11.5, the pH and  $C_s$  increase sharply. The chemical absorption of SO<sub>2</sub> in seawater depends on seawater alkalinity, which is mainly related to the total concentration of bicarbonate, carbonate, hydroxide ions and other minor constituents [9]. OH<sup>-</sup> ions can neutralize part of H<sup>+</sup> ions in solution, which shifts the reaction (2) to the right. Thus, [H<sup>+</sup>] decreases, and  $C_s$  increases. Figure 7 shows the effect of pH of seawater on the pH of tailwater and  $C_s$  show a similar trend at various partial pressures of SO<sub>2</sub>. Shiva et al. [11] concluded that the pH of seawater (8–9.5) has no impact on SO<sub>2</sub> removal efficiency. These results are consistent with the finding of this paper.

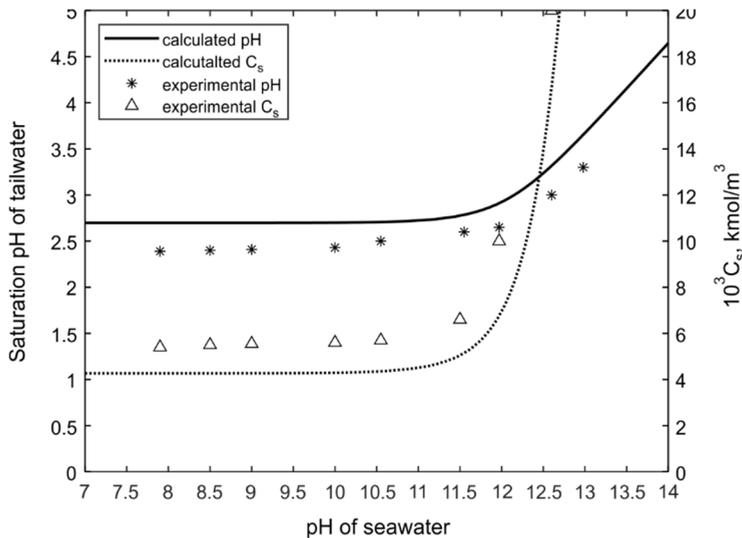


Fig. 6. Effect of pH of seawater on saturation pH of tailwater and desulfurization capacity of seawater

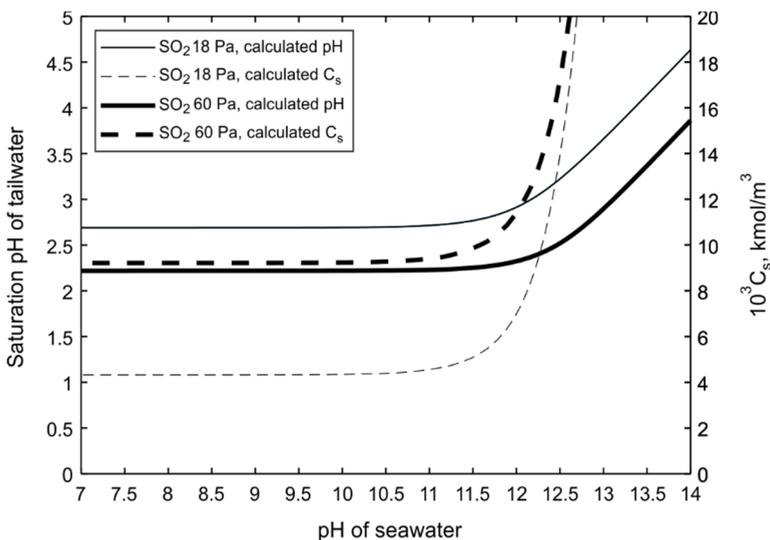


Fig. 7. Effect of pH of seawater on absorption at various dioxide sulfur pressures

#### 4.5. EFFECT OF ALKALINITY OF SEAWATER

The effect of seawater alkalinity on pH of tailwater and  $C_s$  is shown in Fig. 8 and Table 3.

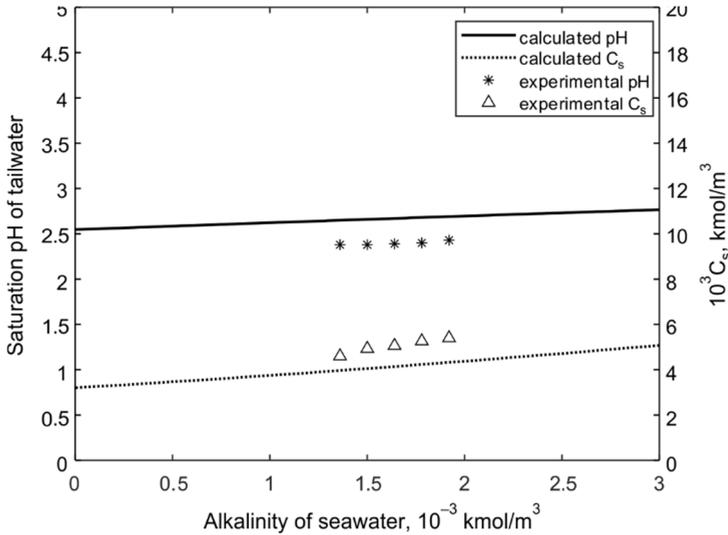


Fig. 8. Effect of alkalinity of seawater on saturation pH of tailwater and desulfurization capacity of seawater

Table 3

Properties of artificial seawater with different salinity

Salinity, wt. %	1.5	2.0	2.5	3.0	3.5
pH	7.9	7.97	8	8.05	7.98
Alkalinity, mol/m <sup>3</sup>	1.36	1.50	1.65	1.78	1.92

Figure 8 shows that both pH of tailwater and  $C_s$  increase slowly with increasing alkalinity of seawater. Increased alkalinity neutralizes part of  $H^+$  ions in solution, which makes reaction 2 shift to the right. When the seawater salinity increases from 1.5% to 3.5%, its alkalinity increases by  $0.56 \text{ mol/m}^3$ , while  $C_s$  increases by  $0.8 \text{ mol/m}^3$ , and is bigger than the increase of alkalinity. The reason is that, besides the increase of alkalinity, the increase of salinity also causes the values of  $H_{\text{SO}_2}$ ,  $K_1$ , and  $K_2$  to increase.

The alkalinity of seawater with 3.5% salinity is  $1.92 \text{ mol/m}^3$ , and  $C_s$  is  $5.4 \text{ mol/m}^3$  at the  $\text{SO}_2$  partial pressure of 18 Pa and temperature of  $12^\circ\text{C}$ . The alkalinity of seawater reflects its chemical absorption capability. So the difference value of  $3.48 \text{ mol/m}^3$  can be expressed as the physical absorption capability of seawater. The results of this experiment indicate that the potential physical absorption capability of seawater is great.

Salinity can enhance the values of  $H_{\text{SO}_2}$ ,  $K_1$ , and  $K_2$ , thus more  $H^+$  ions are generated with increasing salinity. However, due to the seawater alkalinity part of them may be neutralized. Thus, the effect of salinity on the pH of tailwater is opposite to that of alkalinity.

In terms of  $C_s$ , the difference value of  $C_s$  between freshwater and seawater depends strongly on alkalinity and salinity and increases with the increasing partial pressure of  $\text{SO}_2$ . The effect of alkalinity on the  $C_s$  is independent of the temperature and  $\text{SO}_2$  partial pressure. So the  $C_s$  difference value minus seawater alkalinity is equal to the effect of salinity on  $C_s$ .

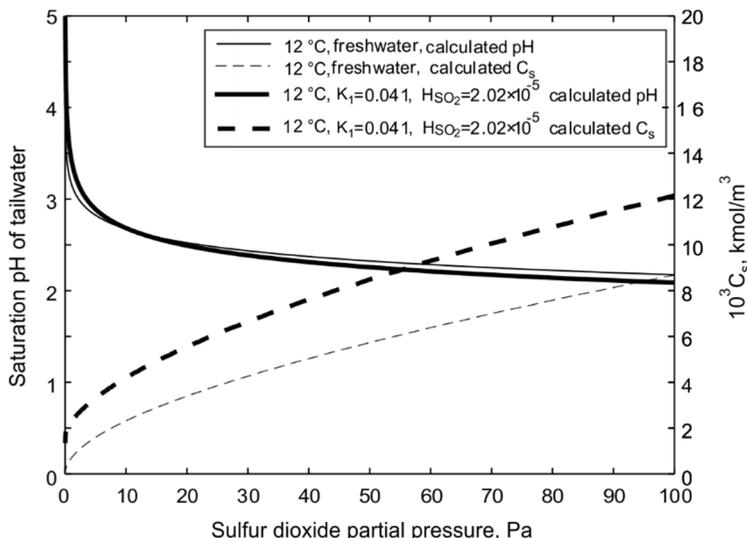


Fig. 9. Saturation pH and  $C_s$  of freshwater and seawater with 35‰ salinity at 12 °C

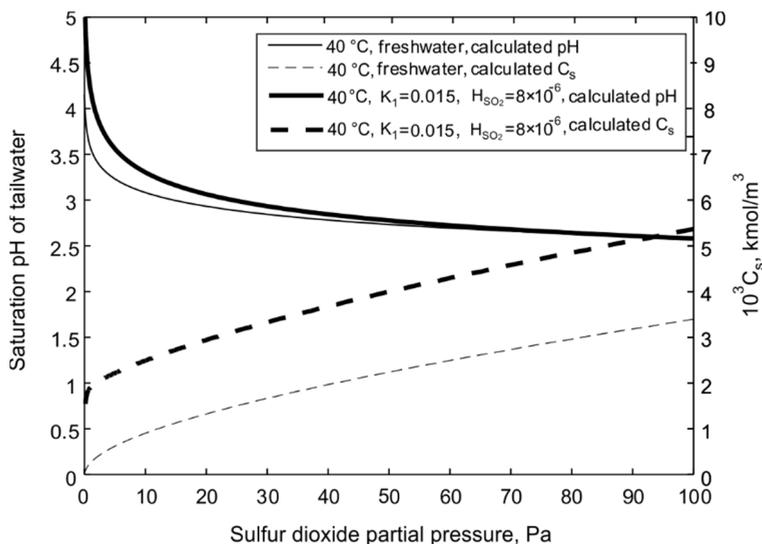


Fig. 10. Saturation pH and  $C_s$  with 35‰ salinity at the temperature of 40 °C

It can be seen in Fig. 9 and comparing with the Fig. 10, at the lower temperature alkalinity and salinity seem to be the two most significant factors in enhancing the SO<sub>2</sub> absorption, whereas at higher temperature alkalinity of seawater seems to be the only most significant factor due to a decrease of dissociation constant with increase of temperature.

## 5. CALCULATION OF THE WATER SUPPLY RATES

Since seawater salinity and alkalinity differ at various different parts of the sea, even almost freshwater occurs in a lot of river estuary, so the absorbent scrubbing for SO<sub>2</sub> can be seawater or freshwater. In the following paragraph, different scenarios will be investigated. The first scenario is 97% SO<sub>2</sub> removal by water scrubbing, i.e., corresponding to fuel sulfur content changing from 3.5 to 0.1 wt. %. The other scenario is 96% SO<sub>2</sub> removal corresponding to fuel sulfur content changing from 2.7% (global average fuel sulfur content) to 0.1 wt. %. The calculated results are given in Table 4.

Table 4

Calculated required absorbent supply rates for 97 and 96% reduction in SO<sub>2</sub> emission

Absorbent	Fuel sulfur [wt. %]	$P_{\text{SO}_2 \text{ in}}$ [Pa]	$C_s$ [mol/m <sup>3</sup> ]	$C_s$ [g/m <sup>3</sup> ]	$P_{\text{SO}_2 \text{ out}}$ [Pa]	$\Delta P_{\text{SO}_2}$ [Pa]	SO <sub>2</sub> red [g/kWh]	Absorbent amount [m <sup>3</sup> /kWh]
Seawater	3.5	70	4.7	150.4	2	68	6.12	0.0407
Seawater	2.7	54	4.2	134.4	2	52	4.68	0.0348
Freshwater	3.5	70	2.8	89.6	2	68	6.12	0.0683
Freshwater	2.7	54	2.4	76.8	2	52	4.68	0.0609

The following assumptions are put forward during calculations: the specific fuel oil consumption (SFOC) of diesel engines is 180 g/kWh and the tailwater temperature is ca. 40 °C. The exhaust gas pressure being close to ambient pressure, meeting gas–liquid equilibrium between the partial pressure of SO<sub>2</sub> entering the scrubber and the amount of SO<sub>2</sub> dissolved in tailwater leaving the scrubber, have been applied.

Based on the fuel sulfur content and SFOC (g/kWh), the total specific amount of SO<sub>2</sub> (g/kWh) can be observed both for the actual sulfur content and the limiting sulfur value of 0.1 wt. %, which are the amounts of SO<sub>2</sub> entering and leaving the scrubber, respectively. The difference between them is the amount of SO<sub>2</sub> to be reduced. According to the standard data of two-stroke engines, the specific amount of SO<sub>2</sub> entering the scrubber can be converted to the partial pressure of SO<sub>2</sub> (Pa) [25], then the amount of SO<sub>2</sub> dissolved in tailwater ( $C_s$ ) is calculated based on equations (13) and (14). The required water amount is acquired by dividing the removed specific amount of SO<sub>2</sub> with the calculated  $C_s$ .

The required water supply rate ranges from 0.0348 to 0.0683 m<sup>3</sup>/kWh (Table 4), which depends on the type of water (i.e., seawater or freshwater), the sulfur content in fuel and the required removal efficiency. The calculations clearly show that substantial water amounts are required. However, tailwater is forbidden to discharge to the sea directly for its lower pH and needed to increase its pH to 6.5 through dilution. The amount of seawater used in dilution is approximately 3 times that of seawater scrubbing exhaust gas. Nevertheless, the data listed in Table 4 are essential in assessing the operation cost of seawater scrubbing desulfurization.

## 6. CONCLUSION

A model for calculating the pH of tailwater and seawater desulfurization capacity in function of a variety of parameters such as SO<sub>2</sub> partial pressure, CO<sub>2</sub> partial pressure, temperature, pH and alkalinity of seawater, has been developed. The results indicate that such parameters as SO<sub>2</sub> partial pressure, seawater alkalinity, and temperature have a great influence on the seawater desulfurization capability, and the effect of CO<sub>2</sub> on the desulfurization capability may be related to the CO<sub>2</sub> partial pressure. An SO<sub>2</sub> emission reduction of 97%, corresponding to fuel sulfur content changing from 3.5 to 0.1 wt. % has been found to require approximately 0.0407–0.0683 m<sup>3</sup>/kWh of water, which depends on the alkalinity and salinity of scrubbing water. Such data are important in assessing the operation cost of a seawater scrubber system.

## REFERENCES

- [1] CULLINANE K., CULLINANE S., *Atmospheric emissions from shipping. The need for regulation and approaches to compliance*, Trans. Rev., 2013, 33, 377.
- [2] IMO. Annex VI of MARPOL 73/78, *Regulations for the prevention of air pollution from ships and NO<sub>x</sub> technical code*, International Maritime Organization, London 1998.
- [3] JIANG L., KRONBAK J., CHRISTENSEN L.P., *The costs and benefits of sulphur reduction measures. Sulphur scrubbers versus marine gas oil*, Trans. Res., 2014, 28, 19.
- [4] MA H.R., STEERNBERG K., RIERA-PALOU X., TAIT N., *Well-to-wake energy and greenhouse gas analysis of SO<sub>x</sub> abatement options for the marine industry*, Transp. Res. D-Transp. Environ., 2012, 17, 301.
- [5] Ship Operations Cooperative Program. *Exhaust gas cleaning system selection guide*, File No. 10047.01, US Department of Transportation, Ellicott City, MD, 2011.
- [6] TANG X., LI T., YU H., ZHU Y., *Prediction model for desulphurization efficiency of onboard magnesium-base seawater scrubber*, Ocean Eng., 2014, 76, 98.
- [7] CAIAZZO G., LANGELLA G., MICCIO F., SCALA F., *An experimental investigation on seawater SO<sub>2</sub> scrubbing for marine application*, Environ. Prog. Sustain. Energy, 2013, 36, 1179.
- [8] GHAZI A.E., HISHAM H.E., NAGLAA E.D., *Solubility of sulfur dioxide in seawater*, Ind. Eng. Chem. Res., 2001, 40, 1434.
- [9] ANDREASEN A., MAYER S., *Use of seawater scrubbing for SO<sub>2</sub> removal from marine engine exhaust gas*, Energy Fuels, 2007, 21, 3274.

- [10] SUN X., MENG F., YANG F., *Application of seawater to enhance  $SO_2$  removal from simulated flue gas through hollow fiber membrane contactor*, J. Membr. Sci., 2008, 312, 6.
- [11] DARAKE S., RAHIMI A., HATAMIPOUR M.S., HAMZELOU P.,  *$SO_2$  removal by seawater in a packed-bed tower. Experimental study and mathematical modeling*, Sep. Sci. Technol., 2014, 49, 988.
- [12] TANG X., LI T., HAO Y., WU X., ZHU Y., *Removal efficiency of magnesium-based seawater desulfurization for marine flue gas*, J. Basic Sci. Eng., 2012, 20, 1081.
- [13] SCHULTES M., *Absorption of sulphur dioxide with sodium hydroxide solution in packed columns*, Chem. Eng. Technol., 1998, 21, 201.
- [14] EBRAHIMI S., PICIOREANU C., KLEEREBEZEM R., HEIJNEN J., LOOSDRECHT M.V., *Rate-based modeling of  $SO_2$  absorption into aqueous  $NaHCO_3/Na_2CO_3$  solutions accompanied by the desorption of  $CO_2$* , Chem. Eng. Sci., 2003, 58, 3589.
- [15] BIARD P.F., COUVERT A., *Overview of mass transfer enhancement factor determination for acidic and basic compounds absorption in water*, Chem. Eng. J., 2013, 222, 444.
- [16] MILLERO F.J., HERSHEY J.P., GEORGE J., ZHANG J.Z., *The solubility of  $SO_2$  and the dissociation of  $H_2SO_3$  in NaCl solutions*, J. Atmos. Chem., 1989, 8, 377.
- [17] COX C., PASEL C., LUCKASA M., BATHEN D., *Absorption of  $SO_2$  in different electrolyte solutions, seawater and brine*, Fluid Phase Equil., 2015, 402, 89.
- [18] DOUABUL A., RILEY J., *Solubility of sulfur dioxide in distilled water and decarbonated seawater*, Chem. Eng., 1979, 24, 274.
- [19] ISO 22719:2008. *Water quality. Determination of total alkalinity in seawater using high precision potentiometric titration*, 30 June 2011.
- [20] China State Environmental Protection Administration. *Determination of sulphur dioxide from exhausted gas of stationary source. Iodine titration method*, 7 December 2000.
- [21] XIA J., RUMPF B., MAURER G., *Solubility of sulfur dioxide in aqueous solutions of acetic acid, sodium acetate, and ammonium acetate in the temperature range from 313 to 393 K at pressures up to 3.3 MPa. Experimental results and comparison with correlations/predictions*, Ind. Eng. Chem. Res., 1999, 38, 1149.
- [22] JUAN R.S., ALVAREZ M., DIAZ M.C., MARRERO M.C., *Absorption equilibria of dilute  $SO_2$  in seawater*, Chem. Eng., 2004, 49, 1710.
- [23] BEYAD Y., PUXTY G., WEI S., YANG N., XU D., MAEDER M., *An  $SO_2$  tolerant process for  $CO_2$  capture*, Int. J. Green. Gas Con., 2014, 31, 205.
- [24] LIU Y., LIU D., WALL T., *Reporting of well stirred scrubber results. Scrubbing of  $SO_2$  and  $CO_2$  by caustic solutions at atmospheric pressure*, The University of Newcastle, NSW, Australia, February 2012.
- [25] ERAN S., *Handbook of Air Pollution from Internal Combustion Engines. Pollutant Formation and Control*, Academic Press, New York 1998.