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STUDY ON SEAWATER SCRUBBING FOR SO₂ REMOVAL FROM SHIP'S POWER PLANT EXHAUST GAS

The mechanism of SO₂ 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 SO₂. 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 SO₂, the partial pressure of CO₂, tailwater temperature, pH and alkalinity of seawater. Experiment results indicated that the seawater desulfurization capacity increases with both increasing partial pressure of SO₂, pH and alkalinity and decreasing partial pressure of CO₂ 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 SO₂ removal efficiency are studied. It is observed a 97% removal efficiency, corresponding to meeting the SO_x limits in the SO_x 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 m³/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

- [SO₂(aq)] – SO₂ concentration in aqueous solution, kmol/m³
[CO₂(aq)] – CO₂ concentration in aqueous solution, kmol/m³
 P_{SO_2} – partial pressure of SO₂ in the gas phase, Pa
 P_{CO_2} – partial pressure of CO₂ in the gas phase, Pa
 H_{SO_2} – Henry's law constant for SO₂, 10⁻² mol/m³·Pa
 H_{CO_2} – Henry's law constant for CO₂, 10⁻² mol/m³·Pa
 K_1 – dissociation equilibrium constant of sulfurous acid, kmol/m³
 K_2 – dissociation equilibrium constant of bisulfite ion, kmol/m³
 K_3 – dissociation equilibrium constant of carbonic acid, kmol/m³

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- K_4 – dissociation equilibrium constant of bicarbonate ion, kmol/m³
 K_w – ionic product of water, kmol/m³
 C_s – desulfurization capacity of seawater, kmol/m³

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 SO₂, 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_x coming from the ship power plant is regulated by setting a maximum fuel sulfur content value of 3.5 wt. %. The SO_x limit applies to all ships. Besides this general regulation, tighter regulations must be fulfilled in some restricted areas, which is generally called SECA (SO_x 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_x 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 SO₂ performed better than distilled water, because of exploiting its inherent alkalinity.

Sun et al. [10] found that owing to the existence of complex CO₂-H₂O-HCO₃⁻-CO₃²⁻ 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 HCO₃⁻ and CO₃²⁻ ions, and the main alkalinity of sodium hydroxide solution are OH⁻ ions, whereas magnesium-base seawater contains the above said three alkalinity species. The effective diffusivities of OH⁻, HCO₃⁻ and CO₃²⁻ in water at 25 °C and infinite dilution are 5.27×10⁻⁹, 1.185×10⁻⁹ and 0.923×10⁻⁹ m²/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 SO₂ in solution. Actually, the solubility of SO₂ 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 SO₂ in seawater, where the effects of Pitzer interaction and activity coefficients on the solubility of SO₂ were be included in the calculations of equilibrium constants. The required minimum water supply rate was calculated according to the established solubility model of SO₂, so as to obtain the SO₂ 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 SO₂ removal by water scrubbing exhaust gas.

2. EXPERIMENTAL

The schematic of the experimental apparatus is shown in Fig. 1. Pure SO₂ and CO₂ were supplied with cylinders 1 and 4, respectively. The flow rates of SO₂ and CO₂ 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 SO₂ and CO₂ 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/m³, 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 SO₂ 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 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 3.4×10^6 1/s or more [14]).

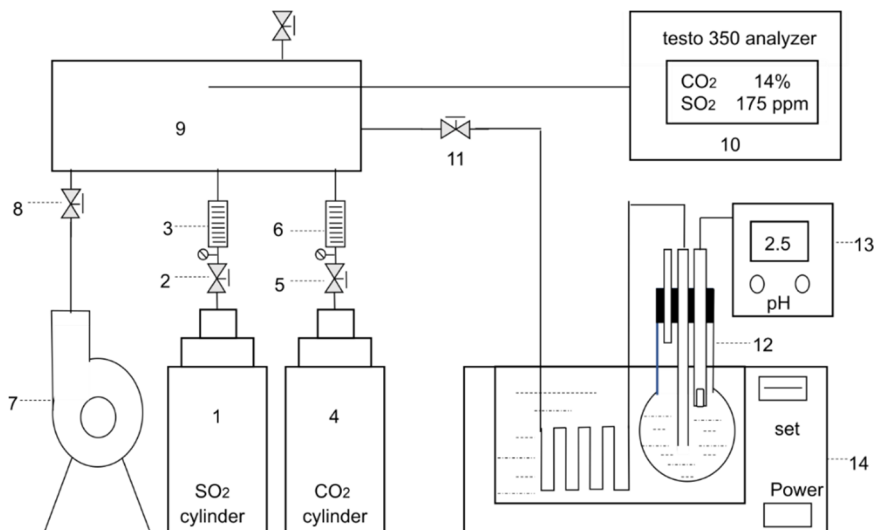


Fig. 1. Schematic of the experimental apparatus: 1 – SO_2 cylinder, 2, 5 – pressure reducing valve, 3, 6 – gas flow meters, 4 – CO_2 cylinder, 7 – air blower, 8, 11 – valve, 9 – mixing chamber, 10 – flue gas analyzer, 12 – reaction flask, 13 – pH meter, 14 – Electrical controlled constant temperature 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 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 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 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].

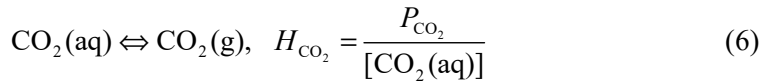
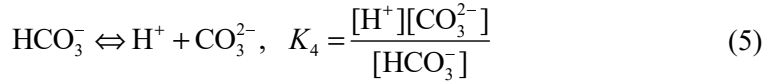
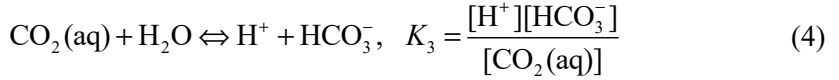
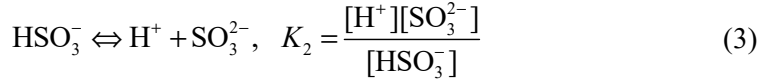
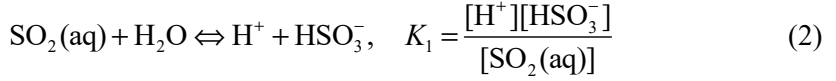
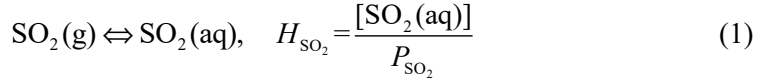


Table 1

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_{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_{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 CO₂ and SO₂ 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_{SO_2} and P_{CO_2} and are the partial pressures of SO₂ and CO₂ in the gas phase, respectively, H_{SO_2} , H_{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/m³, can be calculated according to the following equation.

$$C_s = [\text{SO}_2(\text{aq})] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] = \frac{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}{[\text{H}^+]^2} P_{\text{SO}_2} H_{\text{SO}_2}$$

$$= \frac{(10^{-\text{pH}})^2 + K_1 10^{-\text{pH}} + K_1K_2}{(10^{-\text{pH}})^2} P_{\text{SO}_2} H_{\text{SO}_2} \quad (14)$$

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 SO₂

As seen from Fig. 2, pH of tailwater decreases and C_s increases upon increasing partial pressure of SO₂, which can be explained by the equations of the reactions (1)–(3) being shifted to the right and more SO₂ absorbed and H⁺ 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 SO₂ partial pressure, which can be explained by the reaction between seawater and dissolved SO₂ producing HSO₃⁻ ions. In addition, the differences between the experimental and calculated values of pH and C_s are 0.3, 1.5 mol/m³, respectively, pointing that the influence salinity has been neglected. The salinity of seawater could improve the absorption of SO₂ in seawater [8, 9], while the coefficients, such as H_{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 .

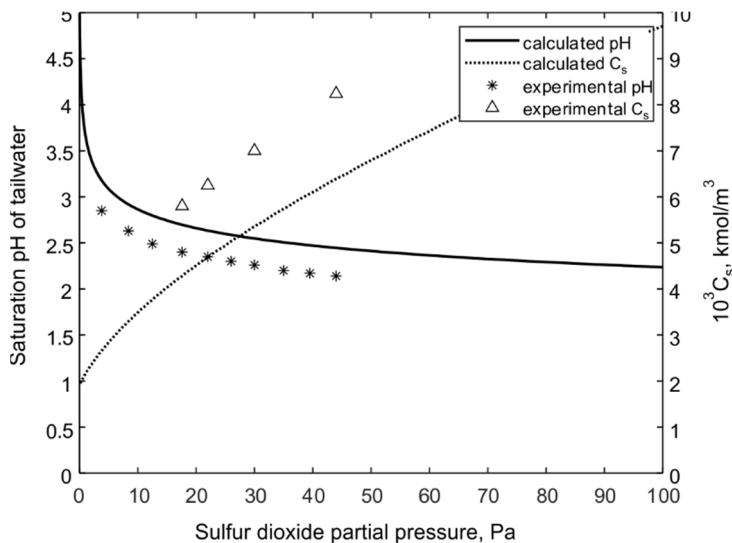


Fig. 2. Effect of the partial pressure of SO_2 on saturation pH of tailwater and desulfurization capacity of seawater

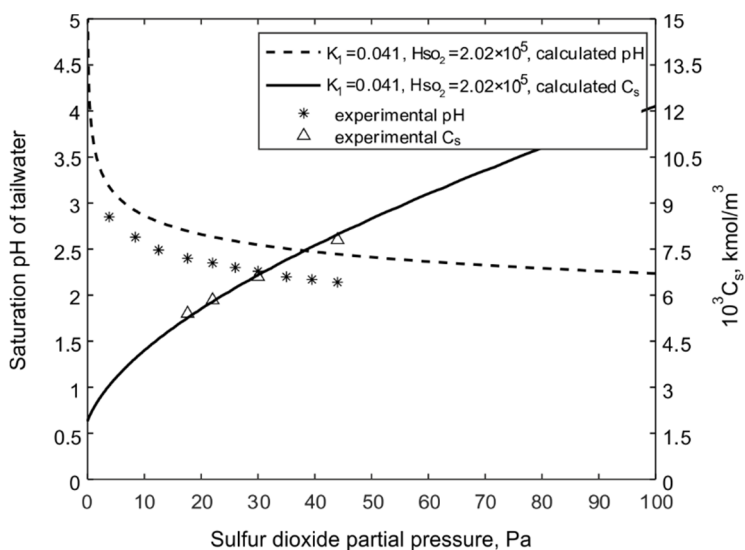


Fig. 3. Calculated and experimental saturation pH and C_s for increased values of H_{SO_2} and K_1 increase

The pH of tailwater is 2.28 and C_s 6.25 mol/m³ at 12 °C, under the partial pressure of 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/m³ [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/m³ 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 1.9649×10^{-7} mol/(m³·Pa), 0.0229 and 7.2868×10^{-8} kmol/m³, 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 2.02×10^{-7} mol/(m³·Pa) and 0.041 kmol/m³, 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 CO₂

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/m³, when P_{SO_2} is in the range of 18–44 Pa.

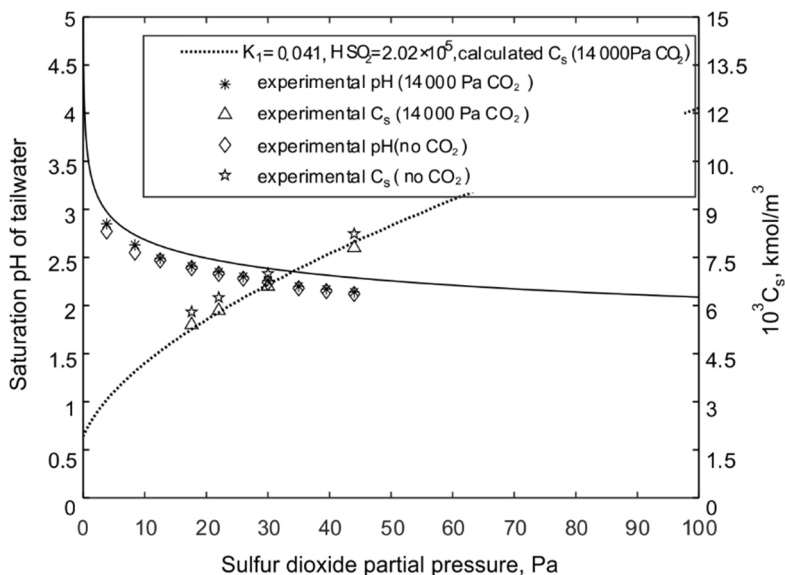


Fig. 4. Effect of the partial pressure of CO₂ on saturation pH of tailwater and desulfurization capacity of seawater

The experimental results show that the presence of CO₂ increases the saturation pH of tailwater, and decreases C_s . The presence of CO₂ can inhibit the absorption of SO₂ in seawater, but this inhibition effect is very small and becomes more and more weak with increasing partial pressure of SO₂. The reason is that H⁺ ions generated by the reaction

between the dissolved CO_2 and seawater inhibit the absorption of SO_2 , but the quantity of H^+ generated from the above reaction is too little due to smaller solubility of CO_2 , which results in weaker inhibition. The values of H_{CO_2} , K_3 and K_4 are far less than those of H_{SO_2} , K_1 , and K_2 in the same condition (Table 1). In addition, the binary interaction between dissolved SO_2 and CO_2 may decrease the numerical values of H_{SO_2} , K_1 and K_2 , which also has a little effect on the inhibition.

HCO_3^- and CO_3^{2-} mainly contribute to seawater alkalinity, and can be fully utilized to participate in the absorption of SO_2 in seawater, when no CO_2 is present in the flue gas. But, when there are large amounts of CO_2 , a small residue of HCO_3^- and CO_3^{2-} will exist in the tailwater, so although the seawater alkalinity stays the same, the actual alkalinity participating in the absorption of SO_2 is reduced, thereby C_s decreases. The experimental difference of 0.4 mol/m^3 does not change with increasing SO_2 partial pressure, which indicates the effect of CO_2 on the C_s may be related to the size of the partial pressure of CO_2 . The presence of SO_2 in flue gas has a negative impact on typical CO_2 capture processes utilizing aqueous amines [23]. It was found that the presence of CO_2 slightly reduces the SO_2 absorption rate [24]. Thus the influence on gas absorption between SO_2 and 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 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_{SO_2} , K_1 , and K_2 decrease rapidly with increasing temperature. Thus, concentrations of S(IV) and H^+ in tailwater decrease rapidly with the increasing temperature of the tailwater.

H_{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_{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_{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 $40 \text{ }^\circ\text{C}$.

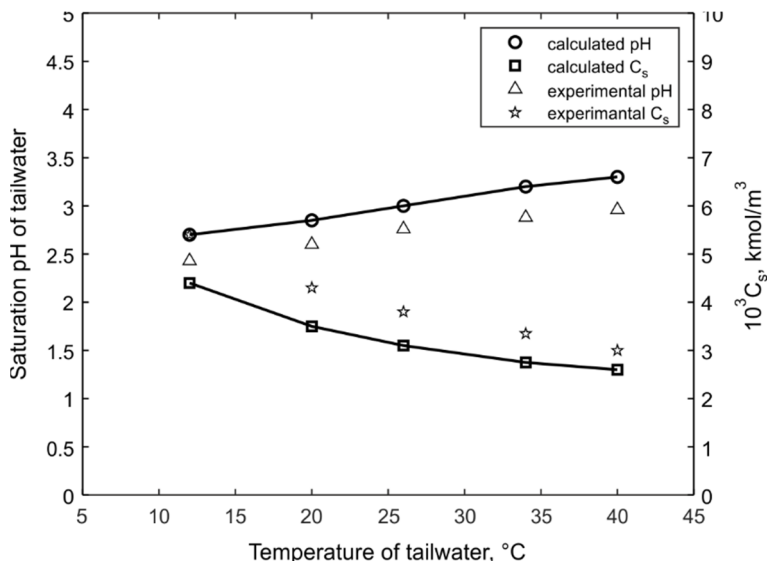


Fig. 5. Effect of temperature of tailwater on saturation pH of tailwater and desulfurization capacity of seawater

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 SO₂ 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⁻ ions can neutralize part of H⁺ ions in solution, which shifts the reaction (2) to the right. Thus, [H⁺] 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 SO₂. Shiva et al. [11] concluded that the pH of seawater (8–9.5) has no impact on SO₂ removal efficiency. These results are consistent with the finding of this paper.

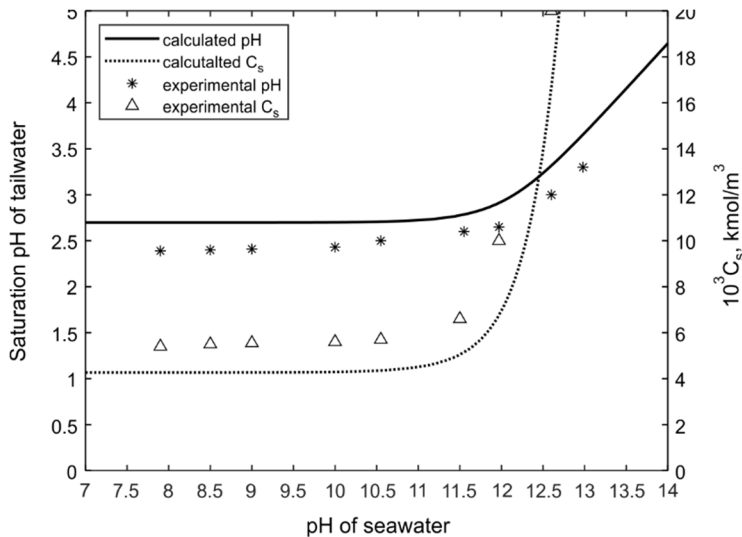


Fig. 6. Effect of pH of seawater on saturation pH of tailwater and desulfurization capacity of seawater

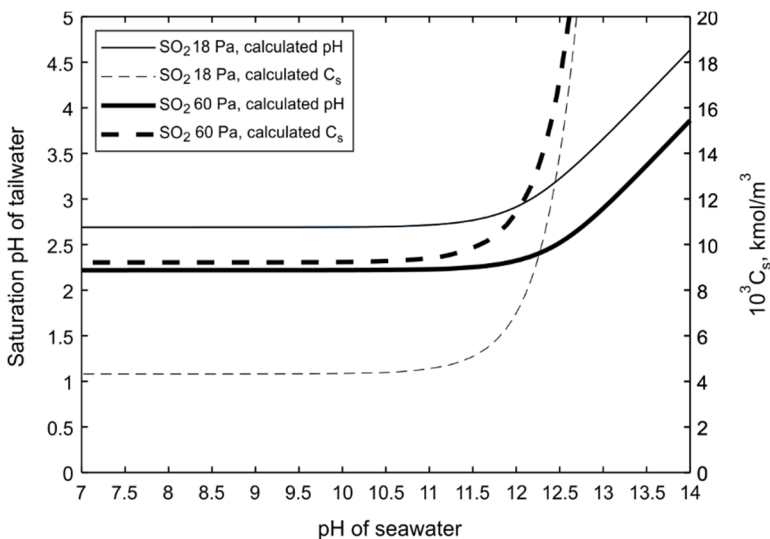


Fig. 7. Effect of pH of seawater on absorption at various dioxide sulfur pressures

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.

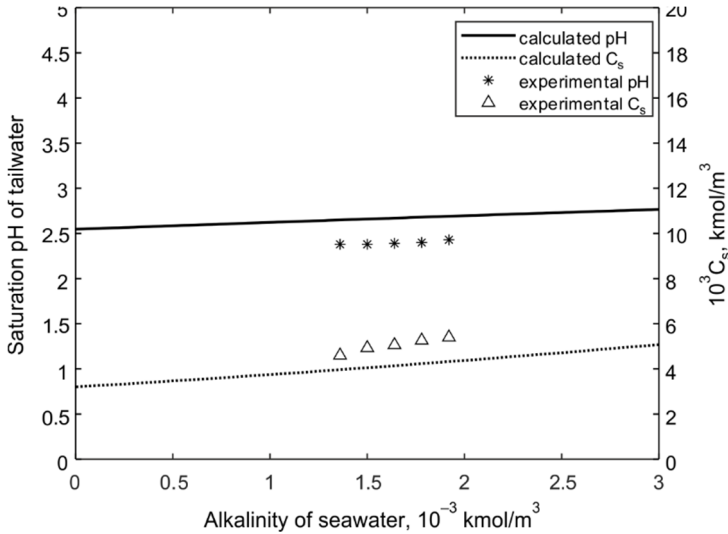


Fig. 8. Effect of alkalinity of seawater on saturation pH of tailwater and desulfurization capacity of seawater

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 ³	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 mol/m^3 , while C_s increases by 0.8 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_{SO_2} , K_1 , and K_2 to increase.

The alkalinity of seawater with 3.5% salinity is 1.92 mol/m^3 , and C_s is 5.4 mol/m^3 at the SO_2 partial pressure of 18 Pa and temperature of 12 °C. The alkalinity of seawater reflects its chemical absorption capability. So the difference value of 3.48 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_{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 SO_2 . The effect of alkalinity on the C_s is independent of the temperature and SO_2 partial pressure. So the C_s difference value minus seawater alkalinity is equal to the effect of salinity on C_s .

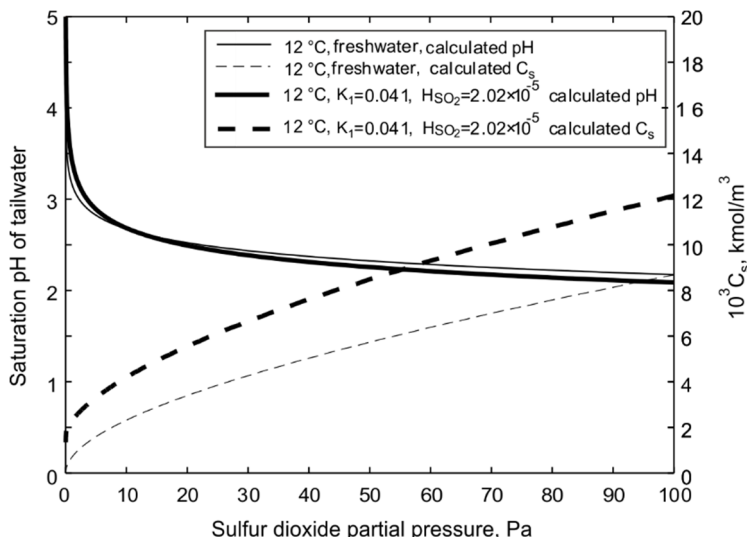


Fig. 9. Saturation pH and C_s of freshwater and seawater with 35‰ salinity at 12 °C

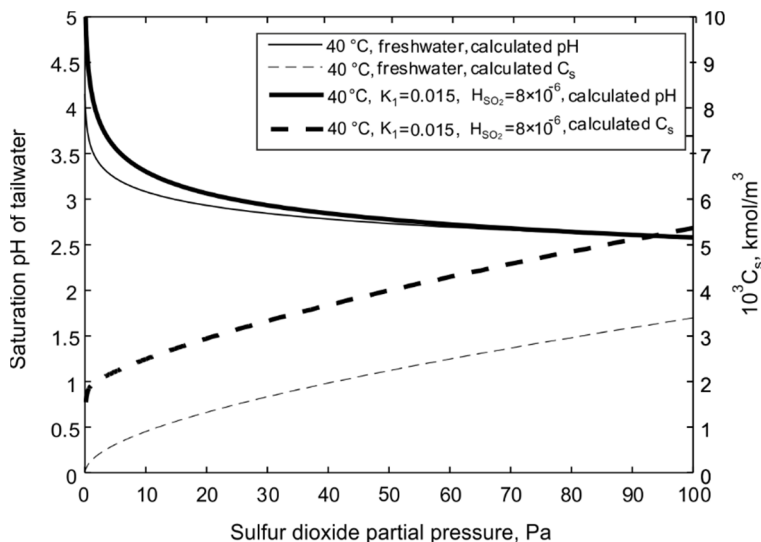


Fig. 10. Saturation pH and C_s with 35‰ salinity at the temperature of 40 °C

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 SO₂ 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 SO₂ can be seawater or freshwater. In the following paragraph, different scenarios will be investigated. The first scenario is 97% SO₂ removal by water scrubbing, i.e., corresponding to fuel sulfur content changing from 3.5 to 0.1 wt. %. The other scenario is 96% SO₂ 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 SO₂ emission

Absorbent	Fuel sulfur [wt. %]	$P_{\text{SO}_2 \text{ in}}$ [Pa]	C_s [mol/m ³]	C_s [g/m ³]	$P_{\text{SO}_2 \text{ out}}$ [Pa]	ΔP_{SO_2} [Pa]	SO ₂ red [g/kWh]	Absorbent amount [m ³ /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 SO₂ entering the scrubber and the amount of SO₂ dissolved in tailwater leaving the scrubber, have been applied.

Based on the fuel sulfur content and SFOC (g/kWh), the total specific amount of SO₂ (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 SO₂ entering and leaving the scrubber, respectively. The difference between them is the amount of SO₂ to be reduced. According to the standard data of two-stroke engines, the specific amount of SO₂ entering the scrubber can be converted to the partial pressure of SO₂ (Pa) [25], then the amount of SO₂ 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 SO₂ with the calculated C_s .

The required water supply rate ranges from 0.0348 to 0.0683 m³/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 SO₂ partial pressure, CO₂ partial pressure, temperature, pH and alkalinity of seawater, has been developed. The results indicate that such parameters as SO₂ partial pressure, seawater alkalinity, and temperature have a great influence on the seawater desulfurization capability, and the effect of CO₂ on the desulfurization capability may be related to the CO₂ partial pressure. An SO₂ 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 m³/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.

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