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EXPERIMENTAL INVESTIGATION OF SEAWATER SCRUBBING OF SO₂ IN TURBULENT CONTACT ABSORBERS AND SPRAY ABSORBERS

The SO_x emissions of the marine engine are regulated by international maritime conventions. In this paper, the effect of various parameters, including SO₂ partial pressure, liquid to gas ratio (L/G), alkalinity and pH, was investigated by seawater scrubbing experiment in a turbulent contact absorber (TCA) and a spray absorber (SA) on a laboratory scale. The experimental data showed that the desulfurization efficiency of TCA was mainly dependent on the value of L/G and irrelevant to the changing way of L/G; the appropriate L/G of TCA was 2.3 dm³/m³ and pH of effluent water was 2.4–2.8 at the L/G of 1.1–2.8 dm³/m³. Comparatively, the desulfurization efficiency of increasing liquid flow rate was better than that of decreasing gas flow rate in the SA experiment. At the gas velocity of 1.58 m/s and L/G of 2.3 dm³/m³, the desulfurization efficiencies and drop pressures of TCA and SA were 75.9% and 42.4%, 690 and 260 Pa, respectively. The results indicate that TCA chosen as an absorber is likely to be a competitive desulfurization technique for controlling marine diesel emission.

1. INTRODUCTION

According to *Regulations for the Prevention of Air Pollution from Ships, IMO Annex VI of MARPOL 73/78*, SO_x contained in the flue gas of marine engine is regulated by setting a maximum fuel sulfur content value of 3.5 wt. %. Besides this general regulation, tighter regulations must be fulfilled in some restricted areas, which are generally called SECA (SO_x emission control areas). In SECA, at least one of the following two conditions shall be fulfilled: (1) the fuel sulfur content shall not exceed 0.1 wt. %, (2) the installation of an exhaust gas cleaning system is required to reduce the total emissions of sulfur oxides to 0.4 g/(kW·h) or less.

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Ma et al. conclude that a scrubber system using current heavy fuel oil 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 [1]. An extensive survey of the available scrubber provided by the Ship Operation Cooperation Program (SOCP) reveals that scrubbing technologies are generally categorized as either dry or wet system [2]. Osaka et al. studied the removal of SO_2 from the diesel exhaust gas with desulfurization efficiency of 80%, in which DeSO_x filter of manganese oxide was used to capture SO_2 [3]. Compared with dry desulfurization, wet scrubbing is a promising technology because of higher desulfurization efficiency and faster reaction rate. Oikawa et al. point out that, compared to the conventional wet limestone system, the seawater desulfurization system offers many advantages in terms of process, design, operation and cost-effectiveness [4]. Compared to lowering the fuel sulfur content, seawater scrubbing of the exhaust gas is economically superior. Seawater with inherent alkalinity is obtained conveniently for maritime vessels. Therefore, many theoretical and experimental studies have already been performed on seawater scrubbing for marine exhaust gas desulfurization [5, 6].

At present, packed columns [7] or spray absorbers (SAs) [6, 8] are usually used for scrubbing of SO_2 from marine engine gas. Liu et al. built a mathematical model, mainly focusing on action and mass transfer characteristic of gas–liquid absorption progress of sodium-alkali desulfurization system in a packed column, and reported the minimum supply rate of absorption liquid was $75.8 \text{ dm}^3/\text{m}^3$ for 4.0 MW diesel engines [7]. Caiazzo et al. set up a seawater SA with focus to desulfurization of marine engine exhaust gas, and confirmed that the desulfurization performance was improved by increasing the liquid flow rate and the gas residence time and decreasing the SO_2 concentration [6]. Tang et al. performed MgO -seawater desulfurization in a SA installed on the “Binghe” container ship, and ranked the significance of different factors for MgO -seawater desulfurization efficiency [8].

Specific requirements for maritime SO_2 scrubbing systems include low energy consumption and pressure drop, simplicity and adaptability to existing equipment, and stability and easiness of control [6]. More important is that the volume of the scrubber should be as small as possible owing to the ship’s narrow space. However, the volumes of packed columns or SAs are generally larger owing to lower gas velocity or lower mass transfer coefficient, which poses a challenge to installation of flue gas desulfurization (FGD) in a ship.

Compared to packed columns and SAs, the volumes of TCAs are relatively smaller owing to higher working gas velocity. At present, Jahanmiri et al. developed a mathematical model for the absorption of SO_2 from flue gas using lime slurry in a TCA [9]. Rubin et al. developed a simulation model to compute energy requirements of FGD (where 3.4% of the total energy was required for a TCA limestone slurry FGD of a “base case” plant of 500 MW) and performed the sensitivity analyses [10]. Wen et al. analyzed the data of limestone slurry scrubbing SO_2 from flue gas using two TCAs (a bench scale and a large scale) under flooding or non-flooding conditions [11]. Zhou et al. conducted a series of experiments of treating low concentration CO_2 flue gas with NaOH solution

in a TCA [12]. Li et al. put a TCA with the filler static altitude of 180 mm as a deduster and conducted the cold dedusting test with the dedusting efficiency of more than 99.5% and the pressure loss of less than 1000 Pa [13].

However, it has been found that very few studies have been made using seawater scrubbing of SO₂ in TCAs. The present work was to investigate the characteristics of seawater scrubbing of SO₂ in TCAs and SAs, and compare these two kinds of absorbers, and meanwhile evaluate whether the TCAs are suitable for FGD of marine diesel.

2. EXPERIMENTAL

Seawater desulfurization in a turbulent contact absorber was performed in a self-designed TCA set-up (Fig. 1). The experimental process was the following: SO₂ gas from SO₂ cylinder was blown into lower part of the TCA tangentially with air, meanwhile the artificial seawater stored in seawater tank was pumped and splashed into upper part of the TCA treated chamber.

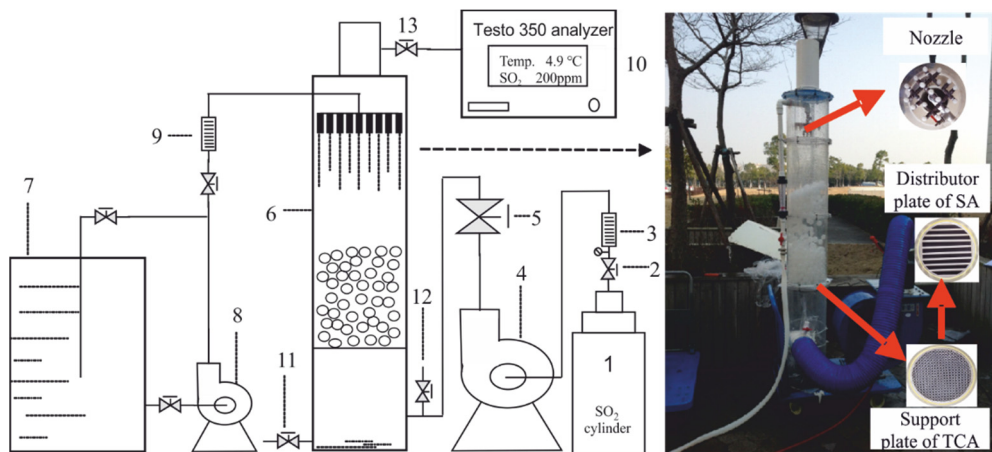


Fig. 1. Schematic diagram of seawater desulfurization on a turbulent contact absorber:
 1 – SO₂ cylinder, 2 – needle valve, 3 – gas flowmeter, 4 – air blower, 5 – outlet valve,
 6 – turbulent contact absorber, 7 – seawater tank, 8 – screw pump, 9 – liquid flowmeter,
 10 – flue gas analyzer, 11 – discharge valve, 12 and 13 – measuring points

The effluent water is discharged from the discharge valve. The inlet and outlet concentrations of SO₂ were measured by the Testo-350 gas analyzer at two measuring points and then converted into the SO₂ partial pressure according to measured pressure. The gas velocity (m/s) was measured by Testo-435 anemometer and then converted into gas flow rate (m³/h) according to the cross-section area of the inlet pipe and the average flow velocity being the half of maximum flow velocity in the pipe. The flow rate of

seawater and SO₂ gas were measured by the liquid and gas flowmeter, and the determination of alkalinity in seawater solution was conducted using potentiometric titration. pH of effluent water was measured using a Mettler Toledo-Delta 320 pH meter.

The TCA column was operated at a counter-current mode, the fluidized bed height was 600–700 mm at the gas velocity of 1.58 m/s. Intensive turbulization and agitation of flows were provided, which led to an increase in the kinetic coefficients of mass exchange and phase contact surface. On the basis of TCA set-up, SA experiments were implemented by removing turbulent ball and support plate and adding distributor plate. Specifications of designed absorbers and operation conditions are shown in Table 1.

Table 1

Specifications of designed absorbers and operation conditions

Element	Parameter	Value
Tower	height	2000 mm
	inner diameter	284 mm
	nozzle height	1800 mm
	inlet gas duct height	300 mm
Nozzle	number	17
	cone angle	30°
	bore diameter	1/8"
	working pressure	0.7–6 Pa
	flow rate per nozzle	0.4–1.3 dm ³ /min
Turbulent bed section of TCA	support plate height	700 mm
	support plate thickness	8 mm
	opening ratio of the support plate	35%
	diameter of the turbulent ball	35 mm
	static bed height	300 mm
	flooding gas velocity	2.86 m·s ⁻¹
Distributor plate of SA	thickness	2 mm
	opening ratio	65%
Operating conditions	flow rate of liquid	0.6 (0.4–1.0) m ³ /h
	flow rate of gas	360 (326–604) m ³ /h
	SO ₂ partial pressure	20 (4.6–23) Pa
	seawater salinity	3.2 wt. %
	gas temperature	4.9 °C
	liquid temperature	10.2 °C

In the experiments, η_{SO_2} is defined as the desulfurization efficiency

$$\eta_{\text{SO}_2} = \left(1 - \frac{P_{\text{SO}_2 \text{ out}}}{P_{\text{SO}_2 \text{ in}}} \right) \times 100\% \quad (1)$$

where $P_{\text{SO}_2 \text{ in}}$ and $P_{\text{SO}_2 \text{ out}}$ are the inlet and outlet partial pressures of SO₂, respectively.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF SO₂ PARTIAL PRESSURE

Seawater desulfurization was performed under various SO₂ partial pressures (Fig. 2). Upon the SO₂ partial pressure increasing, the desulfurization efficiency and pH of effluent water decrease. The reason is that the absorption driving force increases with the increase of SO₂ partial pressure, which makes more SO₂ absorbed by unit volume seawater solution and produces more H⁺ ions consequently by hydrolyzing.

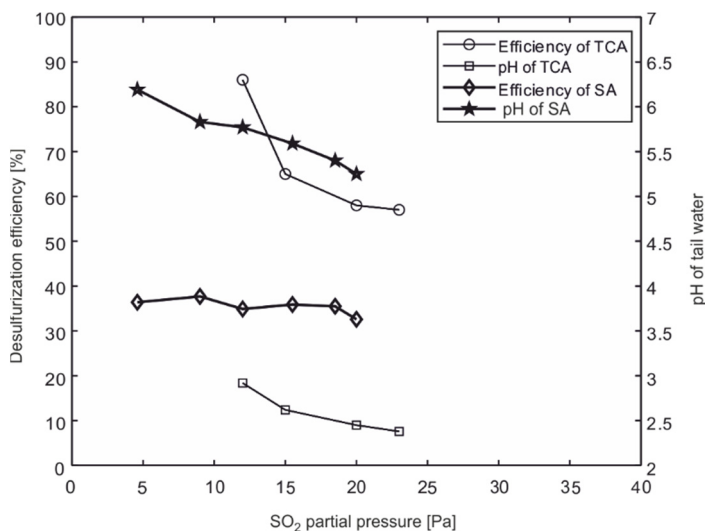


Fig. 2. Effect of SO₂ partial pressure on desulfurization

pH 2.84 of effluent was acquired for seawater scrubbing of SO₂ in a SA at the gas temperature of 250 °C [6]. The range of pH was 2.5–2.6 at the temperature of 10–40 °C in Ghazi et al. [14], and calculated pH was in the range of 2.5–3.0 at the seawater temperature of 45 °C in Anders et al. [5]. While the pH of effluent water in this TCA is 2.34 at the SO₂ partial pressure of 22 Pa. Lower temperature, which can increase the Henry and dissociation equilibrium constants, is kept at 10.2 °C in this experiment, which contributes to the lower pH. In addition, Fig. 2 also shows the drop rate of pH of effluent water is slower and slower with increase of SO₂ partial pressure. Li et al. also reported that pH of sodium alkali solution decreased slowly when it was less than 3 [15]. According to Rahmani et al., the possible reason is that the solvent is close to saturation at high SO₂ concentrations [16]. When pH is less than 3, a little the pH reduces, a lot the concentration of H⁺ increases.

It is thought that there are enough reactant molecules to react with SO₂ molecules at the low feed gas concentration. However, the number of reactant molecules is limited

to react with the SO₂ molecules fed at the high feed concentration, so that the removal efficiency decreases [16]. The extent of absorption decreases with an increase in the concentration of SO₂, which can be explained by the mass-action law. Under the conditions of constant pH and liquid to gas ratio, SO₂ concentration of flue gas is higher, and then per unit mass of SO₂ obtains less absorption solution [17]. The higher the SO₂ concentration is, the faster the concentration of SO₂ in the solution increases. Correspondingly, the decrease of the mass transfer driving force of SO₂ between gas and liquid phases is also more prompt, and thus the removal rate of SO₂ falls more sharply too [15]. Gao et al. reported the SO₂ absorption rate increase from 1.13×10^{-4} mol/(m²·s) to 3.6×10^{-4} mol/(m²·s), when the SO₂ inlet concentration increased from 2.857×10^{-3} kg/m³ to 11.429×10^{-3} kg/m³, and the relationship between the absorption rate of SO₂ and its concentration in the inlet gas was nearly linear when the other parameters were held constant [18]. Though the increasing SO₂ inlet concentration leads to an increase in the driving force and finally in the absorption rate, the increased amount of SO₂ is larger than that needs to be absorbed, which makes removal efficiency to decrease [10, 16].

There is a stable stagnation film between the gas and liquid phase in SA. In the case of countercurrent absorption, the gas–film control is dominated in the upper part of SA, where SO₂ partial pressure is lower and the alkalinity in liquid phase is sufficient to absorb SO₂. Whereas the gas–film control will turn into a combination of both gas–film and liquid–film diffusion controls in the middle part of SA, and a liquid–film control in the lower part of SA owing to the changes of SO₂ partial pressure in gas phase and alkalinity in liquid phase. As seen from Fig. 2, the pHs of effluent water of SA are all above 5, and there are some alkalinities unconsumed in liquid phase according to the potentiometric titration, so the gas–film control is dominated in the overall mass transfer of the SA, and the removal efficiency of SA is affected mainly by gas–liquid contact time. Owing to the smaller contact time (about 1s), the removal efficiencies are all small at different SO₂ partial pressure.

As regards TCA, the desulfurization efficiency of TCA is about two times of SA in the same conditions (Fig. 2). For TCA, the main mass transfer occurs in a turbulent ball fluidized bed in which the gas–liquid interface updates quickly because of intense turbulence of turbulent ball, and hence there is no obvious gas–liquid film, and correspondingly no obvious control of gas film or liquid film, which is the main difference between TCA and SA. El-Dessouky Hisham reported the mass transfer coefficient of the three-phase fluidized bed cooling tower was much higher than that of packed-bed cooling towers with higher packing height [19]. Li et al. explain that the larger gas–liquid contact area forms by innumerable bubbles, which is produced by washing liquid and plastic ellipsoid. Thus, the gas film mass transfer resistance is less, and the gas–liquid contact is consolidated [13].

3.2. EFFECT OF LIQUID TO GAS RATIO

The liquid to gas ratio was adjusted by changing liquid flow rate and gas flow rate, respectively. Two scenarios of regulating liquid to gas ratio are presented:

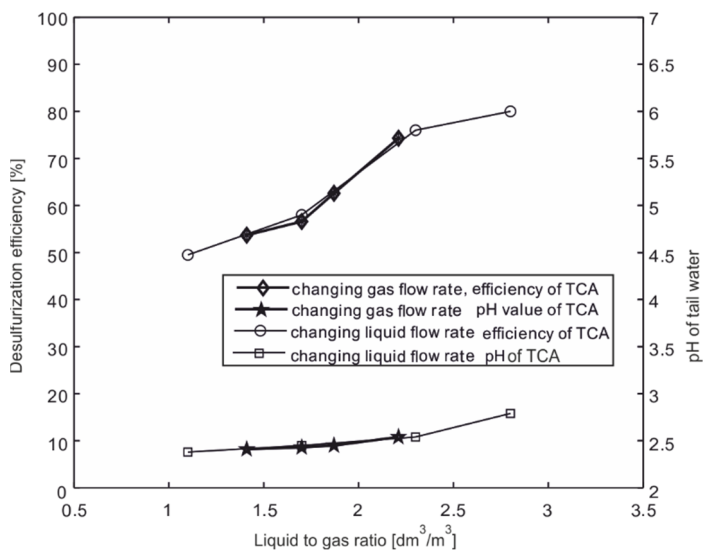


Fig. 3. Effect of liquid to gas ratio on desulfurization of turbulent contact absorber

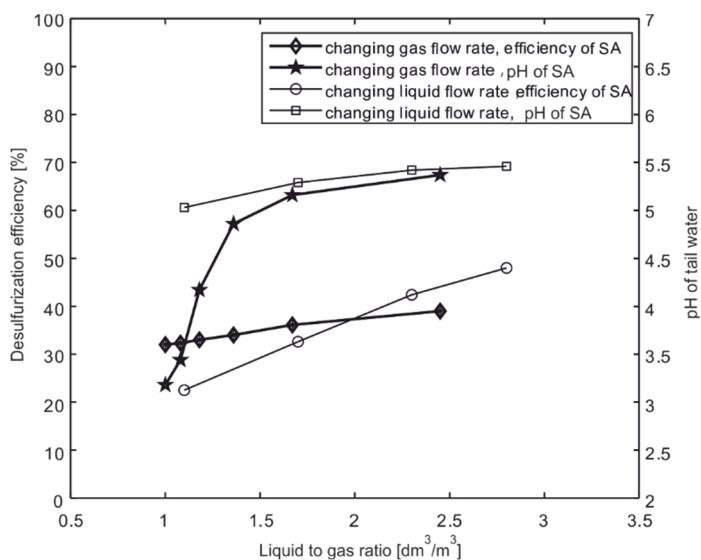


Fig. 4. Effect of liquid to gas ratio on desulfurization of spray absorber

The gas flow rate was 360 m³/h and liquid flow rate increased from 0.4 to 1 m³/h (1), the liquid flow rate was 0.6 m³/h and the gas flow rate decreased from 600 to 245 m³/h (2). The effect of liquid to gas ratio on the desulfurization is shown in Figs. 3 and 4. It can be seen that the pH of effluent water and desulfurization efficiency increased with increasing liquid to gas ratio.

Effect of liquid flow rate. With increase of the liquid flow rate, the amount of SO₂ absorbed by per unit volume seawater solution decreases, and the concentrations of S(IV) and H⁺ in effluent water decrease correspondingly, which leads to the increase of pH of effluent water. In addition, the liquid disturbance is enhanced and the boundary layer between the solution and gas becomes thinner with the increasing liquid flow rate, which leads to the increase of the mass transfer coefficient and enhancement of SO₂ removal efficiency.

Rahmani et al. reported that when SO₂ concentration and temperature were 1400 ppm and 298 K respectively, and L/G was increased from 0.007 to 0.008, the rate of SO₂ removal increased from 72.9% to 83.7%, in which liquid flow rate affected the absorption rate through the liquid film thickness [16]. With increasing the liquid flow rate, more seawater substances can contact SO₂ in unit time and effective gas–liquid interface for mass transfer increases subsequently [8], or the effective wetting of packing increases [20], or the bubble–water interfacial contact area increases [21], which is favorable to SO₂ absorption. Jiang et al. conclude that the relative velocity between liquid elements and packing is higher, then vigorous impingement and uniform dispersion of the liquid occur, which results in excellent mixing and higher mass transfer rate [20].

Effect of gas flow rate. With decreasing gas flow rate, the gas disturbance decreases and the thickness of the gas boundary layer increases subsequently, which lead to the decrease of mass transfer coefficient being unfavorable to SO₂ absorption. But on the contrary, the total amount of SO₂ entering the scrubber in unit time also decreases in the same time, which means the desulfurization load decreases per volume absorbent, so pH of seawater solution decreases slowly, which has a positive effect on the absorption enhancement factor. In addition, the gas–liquid contact time will increase with the decreasing gas flow rate. Increased contact time and absorption enhancement factor make removal efficiency increase.

Lv et al. reported, when the solution flow rate was controlled at 18 cm³/min and the gas flow rate decreased from 250 to 50 cm³/min, the mass transfer coefficient of SO₂ decreased about 3 times, which could be attributed to the increase in gas boundary layer thickness [22]. Jiang et al. [20] and Sarkar et al. [21] also point out that with decreasing gas flow rate, gas–liquid mass transfer area and coefficient slightly decrease owing to increased gas film thickness, but the gas–liquid contact time is increasing, which is dominant in increasing desulfurization efficiency. Other authors report similar facts [15, 17].

Other results. As regards SA, desulfurization efficiency of increasing liquid flow rate is better than that of decreasing gas flow rate (Figs. 3, 4). In this test, increased liquid flow rate is derived from higher outlet pressure of water pump, which leads to the smaller droplet diameter. A fast camera showed that the droplet mean size reduced from 0.9 to 0.4 mm when the liquid flow rate increased from the 0.1 to 0.4 m³/h; furthermore, too small droplets (<0.2 mm) should be avoided, since the gas flow would be able to entrain the droplets out of the column from the top [6]. Finer droplets will have more bubble–liquid interfacial contact area, which in turn enhances the mass transfer [21]. Chien et al. reported, when liquid to gas ratio increased from 4 to 10 dm³/m³, the mean droplet size decreased from 1085 to 595 μm and specific surface area increased from 6.5 to 12.5 m²/dm³ [23].

The gas–liquid contact superficial area increases with increasing liquid flow rate, which contributes to the increase of desulfurization efficiency. On the other hand, decreasing gas flow rate can increase gas–liquid contact time, which also makes desulfurization efficiency increase. Desulfurization efficiency of increasing liquid flow rate is better than that of decreasing gas flow rate (Fig. 4). Therefore, increasing the gas–liquid contact superficial area is better than increasing gas–liquid contact time in improving desulfurization efficiency. Other authors report similar experimental phenomenon [6, 8], which is shown in Table 2.

Table 2

Comparison of the effect of liquid to gas ratio on desulfurization in various papers

	Flow rate [m ³ /h]		L/G ratio [dm ³ /m ³]	Efficiency [%]	Increased efficiency /increased liquid to gas ratio	Result
	Liquid (L)	Gas (G)				
A	0.3	60	5	62%	$\frac{72\% - 62\%}{6.67 - 5} > \frac{76\% - 62\%}{7.5 - 5}$	effect of increased liquid flow rate greater than effect of decreased gas flow rate
	0.4	60	6.67	72%		
	0.3	60	5	62%		
	0.3	40	7.5	76%		
B	gas velocity 0.5 m/s, liquid to gas ratio increased from 5.5 to 14.3			Increased from 43 to 85%	$\frac{85\% - 43\%}{14.3 - 5.5} > \frac{92\% - 43\%}{24.6 - 6.58}$	
	liquid flow rate 40 dm ³ /m ³ , gas velocity decreased from 0.75 to 0.2 m/s, the cross-sectional area of SA 2.25 m ²			Increased from 43 to 92 %		

A refers to [6], Figs. 2, 3 and SO₂ contents of 700 ppm, B to [8], Figs. 2, 3 and SO₂ contents of 280–300 ppm.

Desulfurization efficiency of SA is much smaller than that of TCA. In the scenario of changing liquid flow rate, the desulfurization efficiencies of TCA and SA were 75.9% and 42.4%, respectively, at the L/G of 2.3 dm³/m³. Therefore, the volume of TCA is

much smaller than that of SA under the same removal efficiency. The gas velocities of SAs are generally 0.2–0.8 m/s [6, 8], whereas the gas velocity of this SA is as high as 1.58 m/s which leads to shorter gas–liquid contact time. The SO₂ removal efficiency is 39% under the gas velocity of 1.07 m/s in this SA and close to 43% removal efficiency under 0.75 m/s gas velocity exhibited in a practical SA [8].

As for TCA, the desulfurization efficiency and pH of effluent water are 49.5% and 2.4, 76% and 2.54, 80% and 2.8, respectively, when the liquid to gas ratios are controlled at 1.1, 2.3 and 2.8 dm³/m³, respectively. The desulfurization efficiency of TCA was mainly dependent on the value of L/G and irrelevant to the changing way of L/G, because the mass transfer of TCA is mainly dependent on the intense turbulence of turbulent fluidized bed ball.

The appropriate operation liquid to gas ratio of this TCA is 2.3 dm³/m³ in the experimental condition, because the height of turbulent ball fluidized bed is about 0.6 m, and the gas–liquid contact superficial area and time is limited, so the gas–liquid contact is inadequate under higher liquid to gas ratio, which makes the desulfurization efficiency increase slowly when liquid to gas ratio is larger than 2.3 dm³/m³. Wang et al. reported the increase of desulfurization rate when L/G was greater than 3 [17].

3.3. EFFECT OF THE ALKALINITY OF SEAWATER

The alkalinity of seawater often varies with the change of sea area, so this section test simulates the change of alkalinity of seawater, which is adjusted by adding sea salt into tap water. The relations between the salinity and alkalinity are shown in Table 3. Desulfurization efficiency and pH of effluent water increase with the increase of alkalinity (Fig. 5).

Table 3

Salinity, pH and alkalinity in seawater solution

Salinity, %	1.9	2.3	2.8	3.2
pH	7.96	7.99	8.03	7.9
Alkalinity (mol·m ⁻³)	1.48	1.59	1.72	1.84

With increasing alkalinity of seawater solution, the absorption enhancement factor increases, which leads to the increase of mass transfer coefficient. The SO₂ absorption in seawater can be divided into physical and chemical ones, which are mainly dependent on temperature and alkalinity, respectively. So increasing alkalinity of seawater solution will increase the chemical absorption.

As for this TCA, in the conditions of SO₂ partial pressure and liquid to gas ratio are 20 Pa and 1.67 dm³/m³, respectively, the relationship between the increased desulfurization efficiency and increased alkalinity is nearly linear, in which the desulfurization efficiency increases by 6.8% as alkalinity of seawater solution increases by 0.36 mol/m³. In other words, the mole increase of alkalinity in seawater solution is approximately

equal to the mole decrease of SO₂ in outlet in unit time, i.e. the increased alkalinity can fully take part in the absorption of SO₂. It can be said that liquid-film control is dominant, to be more precise, the mole ratio between alkalinity and sulfur content is the main factor for seawater scrubbing of SO₂ in TCA. However for SA, the pH of effluent water is generally higher, the gas-film control is dominant in absorption process, so the influence of increased alkalinity on SO₂ removal efficiency is little.

Sun et al. found, owing to the existence of complex CO₂-H₂O-HCO₃⁻-CO₃²⁻ equilibrium system, the seawater had a higher overall mass transfer coefficient than tap water, and the mass transfer coefficient of seawater was about twice as large as that of aqueous NaOH solution with pH of 8.35 [24]. Gao et al. reported that when the (NH₄)₂SO₃ concentration increased from 0.03 to 0.05 mol/dm³, the SO₂ absorption rate increased from 2.65×10⁻⁴ to 3.53×10⁻⁴ mol/(m²·s) at 40 °C. However, as the (NH₄)₂SO₃ concentration increased above 0.05 mol/dm³, the SO₂ absorption rate became nearly constant, and the reaction might be mainly influenced by gas-film, and be zero-order with respect to (NH₄)₂SO₃ concentration [18]. But for seawater scrubbing of SO₂ in TCA, the above so-called gas-film and zero-order reaction is unlikely owing to limited alkalinity in natural seawater. In addition, at the higher temperature, alkalinity of seawater seems to be the most important factor in increasing the SO₂ uptake [5].

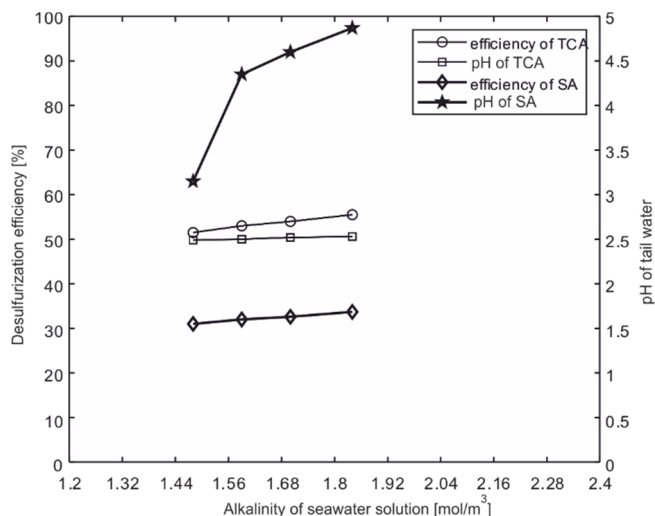


Fig. 5. Effect of alkalinity of seawater on desulfurization

3.4. EFFECT OF INITIAL pH OF SEAWATER

According to Tang et al. magnesium-base seawater has better adaptability to environment and a relatively broader suitable extent [8]. NaOH solution can be used as absorbent for scrubbing of SO₂ from marine engine because it is unsatisfied for seawater

scrubbing of SO_2 with medium-high concentration [7]. So this section test simulates the change of pH of seawater when sodium hydroxide is added into seawater solution. SO_2 partial pressure is controlled at 22 Pa in this section test, and the purpose is making the difference more obvious between high and low pH. The effect of initial pH of seawater solution on desulfurization is shown in Fig. 6. The desulfurization efficiency and pH of effluent water increase with increasing initial pH of seawater solution.

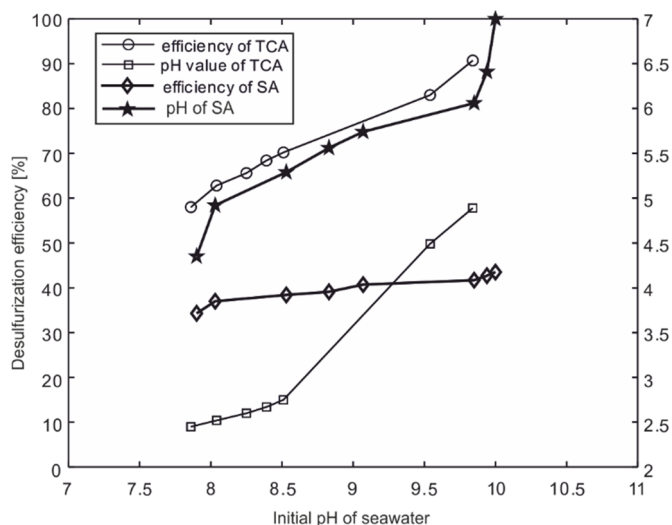


Fig. 6. Effect of initial pH of seawater on desulfurization

The concentration of OH^- in solution increases rapidly with increasing pH when it is close to 10, which makes desulfurization efficiency of TCA increasing quickly at higher pH. Under higher pH, most of SO_2 is absorbed chemically, so the pH of effluent water is above 4.5. The efficiency increases as the liquid becomes more basic. This is due to the affinity of the acidic SO_2 towards a basic solution [21]. SO_2 is an acidic gas, so the increase of pH of absorption solution is favorable to the absorption [20]. At high pH, SO_2 dissolved in the liquid converts to HSO_3^- fast and the chemical absorption reaction is almost complete, and at pH lower than 5 only the physical absorption of SO_2 takes places [15]. According to Wang et al., there was a critical pH for various operating conditions. When pH of sodium alkali solution was less than the critical one, SO_2 in gas phase could not be completely removed and pH would decrease sharply [17]. At higher pH, the liquid film keeps larger enhancement factor of the absorption process, and higher removal efficiency the DFG is achieved. Orthogonal experiments were designed to detect the priority of different factors, for magnesium base-seawater methods, the significance of different factors for desulfurization efficiency could be ranked as below: $\text{pH} > \text{liquid to gas ratio} > \text{empty container gas velocity}$ [8]. Darake et al. report that the

pH of seawater (8–9.5) is not significant for seawater desulfurization [25], which is consistent with this test.

3.5. EFFECT OF TEMPERATURE

Some parameters including diffusivity, chemical reaction, Henry and dissociation constants, solubility, as well as liquid evaporation and removal efficiency depend on temperature. The diffusivity of SO₂ in solution increases with the increase of temperature [16]. In addition, increasing the temperature of a chemical reaction generally increases the rate of the reaction. The reaction between the SO₂ and the absorbent can be treated as instantaneous reactions with a rate constant of 3.4×10^6 (s⁻¹) or more, which shows that the effect of temperature on chemical reaction is very small. Based on the above positive impact, Gao et al. revealed that the mass transfer of SO₂ in the solution increased with the increase of temperature, in which the absorption rate increased from 3.3×10^{-4} to 3.6×10^{-4} mol/(m²·s), as the temperature increased from 20 to 50 °C at the SO₂ inlet concentration of 11.429×10^{-3} kg/m³ [18].

Some negative influences of temperature can also be seen. The Henry constant, dissociation constant and SO₂ solubility decrease with the increase of temperature [5, 18]. Temperature can also enhance liquid evaporation [16, 26], which is unfavorable to absorption. Relative humidity and absolute humidity of desulfurated flue gas enhanced from 54% and 25.9 g/kg to 85% and 98.5 g/kg, when liquid temperature increased from 25 °C to 60 °C [26]. In addition, the absolute humidity of desulfurated flue gas increased evidently with increasing inlet flue gas temperature from 80 °C to 102 °C, while the relative humidity decreased slightly.

In general, the negative effects of temperature on SO₂ solubility and evaporation are slightly higher than its positive effect on diffusivity. So Rahmani et al. reported that the SO₂ removal efficiency decreased from 83 to 77% as the temperature increased from 298 to 333 K at the SO₂ concentration and liquid to gas ratio 1400 ppm and 8 dm³/m³, respectively [16]. Darake et al. also report that an increase in gas temperature causes a decrease in the removal efficiency [25].

3.6. DROP PRESSURE

The drop pressure of this TCA and SA are 690 and 260 Pa, respectively, when the gas flow rate is 360 m³/h and liquid flow rate is 0.6 m³/h. So the drop pressure difference of 430 Pa corresponds to turbulent ball bed. The two biggest two-stroke marine engine manufacturers in the world (MAN and Wärtsilä) rule that the drop pressure after the turbine charger should not exceed the 3000 Pa. So the drop pressure of this TCA meets requirement of marine engine. In addition, multistage TCA can be used according to requirements, in which increasing a stage of turbulent ball bed means the drop pressure increase by 430 Pa.

Correlations are developed to relate the pressure drop and the liquid holdup of a TCA, showing that the pressure drop of a single stage bed of TCA is independent of gas velocity [27]. El-Dessouky Hisham reported that the air-side pressure drop increased very slowly with increase in air velocity, and the minimum fluidization velocity was found to be independent of the static bed height [19]. In general, the bed pressure drop increases linearly with the gas velocity and then remains constant, and an increase in the liquid flow rate increases liquid holdup, which leads to an increase in bed pressure drop [28].

4. CONCLUSION

In this paper, the experiments of seawater scrubbing of SO₂ were performed in a TCA and SA. The desulfurization efficiency of SA was much smaller than that of TCA, and sometimes maybe half of it, so the volume of TCA was much smaller than that of SA under the same removal efficiency. In addition, the drop pressure of turbulent ball bed with static bed height of 300 mm is about 430 Pa when the gas velocity in the absorber is 1.58 m/s, which means increasing a stage of turbulent ball bed will make the total drop pressure increase by 430 Pa as multistage TCA is used. Such data indicate the TCA can be used as absorber in scrubbing of SO₂ from marine engine, and meanwhile, it has an advantage in volume. Furthermore, owing to intense turbulence of turbulent ball, the desulfurization efficiency of TCA is mainly dependent on the value of L/G, and the mole ratio between alkalinity and sulfur content is dominant for seawater scrubbing of SO₂ in TCA. In the experimental conditions, the appropriate operation liquid to gas ratio of this TCA is 2.3 dm³/m³. Unlike TCA, desulfurization efficiency of increasing liquid flow rate is better than that of decreasing gas flow rate in SA.

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