

Effects of Additives on Seawater Flue Gas Desulfurization

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Abstract—This work investigated the technology of seawater flue gas desulfurization. The results show that the liquid-gas ratio and gas-flow rate significantly influence SO₂ removal efficiency. The inlet concentration of SO₂ and temperature of the absorption solution have little effect on the SO₂ removal efficiency. The effects of additives on desulfurization and desulfurization seawater recovery were observed by introducing different concentrations and types of additives. Inorganic and organic additives could increase SO₂ removal efficiency to a certain degree. Organic additives have negative effects on seawater recovery, and inorganic additives have little influence on seawater recovery with increasing SO₂ removal efficiency.

Keywords- seawater; flue gas desulfurization; additive; desulfurization seawater recovery

I. INTRODUCTION

Seawater flue gas desulfurization technology, which uses the natural alkalinity of seawater to remove SO₂ from flue gas, has low operation cost and zero release of solid wastes. The pH of post-desulfurization seawater is ~3–4 and contains excess amounts of sulfite. A common method is to dilute post-desulfurization seawater with fresh seawater and then to subject it to aeration. After aeration, the seawater can be discharged [1, 2]. The pH and sulfite concentration must meet certain requirements prior to discharge. Many power plants use this technology in China, but the relevant technologies are introduced from abroad [3, 4].

The addition of an additive is an important method to increase the SO₂ removal efficiency and the utility ratio of the desulfurizing agent, and to decrease the investment and operation costs for the process [5]. Full seawater has low alkalinity, so its pH is reduced rapidly during desulfurization. Currently, it is adequate for treating flue gas that contains small amounts of SO₂. An additive introduced into the seawater desulfurization process forms new buffer systems with seawater to decrease the pH gradually. Many researchers have performed studies on the influence of additives on desulfurization [6–8]. More studies were done on the influence of additives on the limestone/lime-gypsum flue gas desulfurization [9, 10]. The additives mainly include inorganic or organic substances [11–13]. However, research on the effects of additives on seawater desulfurization is lacking [14].

This work studied seawater flue gas desulfurization technology. By analyzing the factors that affect desulfurization under an orthogonal experiment, the effects of additives on SO₂ removal efficiency and desulfurization seawater recovery were observed. The experiment involved introducing different kinds of additives at different concentrations. This study provides a foundation for the application and engineering design of seawater flue gas desulfurization technology.

II. MATERIALS AND METHODS

A. Materials

Standard SO₂ gas (40.07%, 0.5 MPa, Dalian Special Gas Industry Company, China) was used to prepare simulated flue gas. Seawater which the pH is 8.1–8.4 was extracted from the sea near Dalian Fisheries University. All other chemicals were analytical grade and were used without further purification.

B. Desulfurization experiment apparatus

The packed column was used for the desulfurization experiment which its size is $\phi 40 \times 4$ mm. Ceramic Raschig ring was built-in the packed column with an effective packing height of 280 mm. The flow diagram of the desulfurization experiment facilities is shown in Fig. 1.

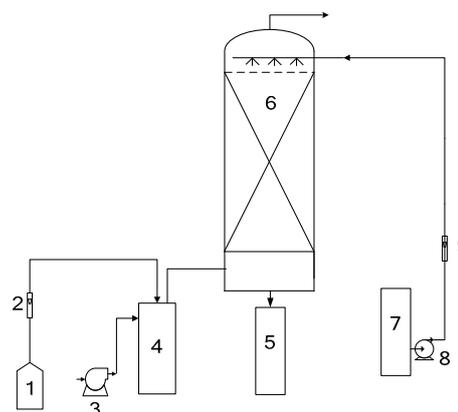


Figure 1. Flow diagram of the desulfurization experiment facilities
1. SO₂ cylinder; 2. Gas rotameter; 3. Air pump; 4. Buffering tank; 5. Desulfurization seawater tank; 6. Packed column; 7. Seawater tank; 8. Magnetic pump; 9. Liquid rotameter.

C. Desulfurization experiment

The orthogonal experiment was designed to study the influence of gas-flow rate, inlet concentration of SO₂, liquid-gas ratio, and temperature of absorption solution on SO₂ removal efficiency. The important factor was determined by using data visual analysis.

D. Desulfurization seawater recovery experiment

Seawater after desulfurization was mixed with fresh seawater at 2:1 volume ratio (fresh seawater:desulfurization seawater). The mixture was aerated in a 1 L graduated cylinder using an air pump (aeration rate was 180 L/h). The pH and the sulfite concentration of the seawater mixture were measured every 2–4 min.

E. Effect of additives on the seawater desulfurization and desulfurization seawater recovery

Seawater solutions (1.5 L) containing a specific concentration of sodium sulfate or magnesium sulfate (0.050, 0.100, 0.150, and 0.200 M), and 1.5 L seawater solutions containing a specific concentration of acetic acid or hexanedioic acid (0.005, 0.010, 0.015, and 0.020 M) were prepared. The SO₂ removal efficiency within 12 min, the pH of the pre/post-desulfurization seawater and sulfite concentration within 8–20 min after adding additives were measured. The desulfurization seawater recovery after adding additives was studied using the method described in Section D.

F. Analytical method

The inlet and outlet concentration of SO₂ were measured using GASBOARD-3000 Air Analyzer (type ZH-1521, from Dailian Zhong Huan Environmental System Engineering Co., LTD). The pH of the pre/post-desulfurization seawater was measured by a pHs-25 Acidometer (Shanghai REX Instrument Factory). The sulfite concentration was measured by standard iodine solution titration.

III. RESULTS AND DISCUSSION

A. Orthogonal experiment

The orthogonal experiment was performed to study the influence of gas-flow rate, inlet concentration of SO₂, liquid-gas ratio, and temperature of absorption solution on SO₂ removal efficiency. The experiment was done using a four-factor three-level orthogonal table. Table 1 shows the experimental factors and levels. Table 2 lists the experimental arrangement data and visual analysis results.

TABLE I. ORTHOGONAL EXPERIMENTAL FACTORS AND LEVELS

Level	Factors			
	Gas-flow rate, m ³ /h	Inlet concentration of SO ₂ , mg/Nm ³	Liquid-gas ratio L/Nm ³	Temperature °C
L 1	0.25	715	8	20
L 2	0.75	2145	12	30
L 3	1.25	3575	16	40

TABLE II. ORTHOGONAL EXPERIMENT AND VISUAL ANALYSIS

No.	Gas-flow rate, m ³ /h	Inlet concentration of SO ₂ , mg/Nm ³	Liquid-gas ratio, L/Nm ³	Temperature, °C	SO ₂ removal efficiency, %
E1	0.25	715	8	20	77.2
E 2	0.25	2,145	12	30	80.8
E 3	0.25	3,575	16	40	84.0
E 4	0.75	715	12	40	71.4
E 5	0.75	2,145	16	20	78.7
E 6	0.75	3,575	8	30	64.4
E 7	1.25	715	16	30	79.3
E 8	1.25	2,145	8	40	71.3
E 9	1.25	3,575	12	20	73.6
Mean1	0.807	0.760	0.710	0.765	
Mean2	0.715	0.769	0.753	0.748	
Mean3	0.747	0.740	0.807	0.756	
Range	0.092	0.029	0.097	0.017	

Based on direct comparison and data visual analysis, the factors are arranged according to the strength of their influence on SO₂ removal efficiency: liquid-gas ratio > gas-flow rate > inlet concentration of SO₂ > temperature of absorption solution. Among the factors, liquid-gas ratio and gas-flow rate have greater influence on SO₂ removal efficiency. The higher is the liquid-gas ratio, the higher is SO₂ removal efficiency. Moreover, the lower are the gas-flow rate and inlet concentration of SO₂, the higher are SO₂ removal efficiency. Higher temperatures of absorption solution have negative desulfurization effects. Nonetheless, the influence of absorption temperature within 20–40 °C is insignificant.

B. Effect of additives on the seawater desulfurization and desulfurization seawater recovery

Four kinds of typical additives were used in this research (inorganic additives, namely, sodium sulfate and magnesium sulfate; and organic additives, namely, acetic acid and hexanedioic acid). By changing the quantities of additives, their effect on seawater flue gas desulfurization and post-desulfurization seawater recovery were measured. The experimental conditions in this study were as follows: gas-flow rate of 0.75 m³/h, liquid-gas ratio of 10 L/Nm³, inlet concentration of SO₂ at 1430 mg/Nm³, and temperature of absorption solution of 30 °C.

1) Magnesium sulfate as additive

The effect of magnesium sulfate on seawater desulfurization and desulfurization seawater recovery were observed. The results are shown in Figs. 2 and 3.

With 0.050 M magnesium sulfate, SO₂ removal efficiency increased by 3.6 % more than that without magnesium sulfate. The pH of desulfurization seawater increased by 0.43 relative to that of full seawater after

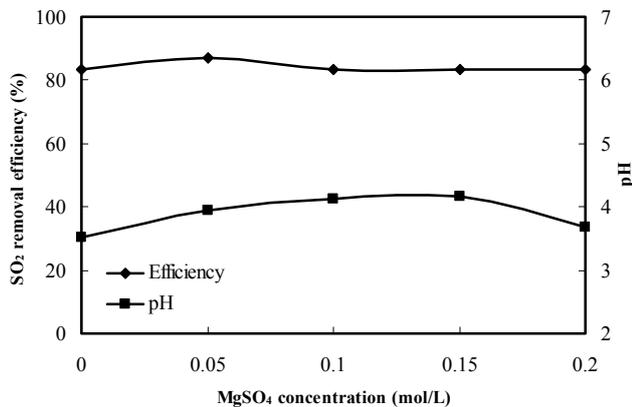


Figure 2. Effect of magnesium sulfate on the SO₂ removal efficiency and pH of desulfurization seawater

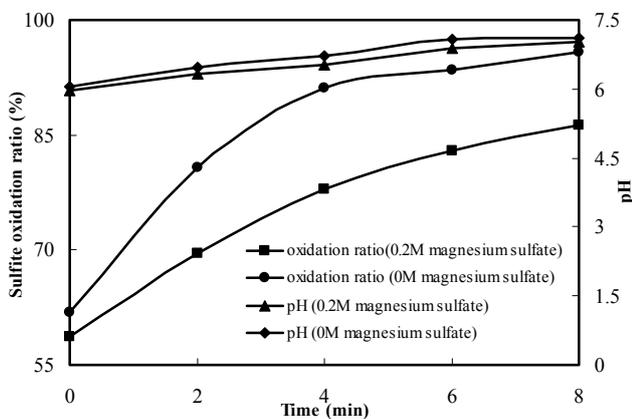


Figure 3. Effect of magnesium sulfate on desulfurization seawater recovery

desulfurization. Magnesium sulfate affects certain chemical reactions during desulfurization. Magnesium ions react with dissociating sulfite ions. In turn, this reduces SO_3^{2-} concentrations in seawater and causes dissolution reaction of SO_2 , thereby increasing SO_2 removal efficiency. When the magnesium sulfate concentration increased again, the SO_2 removal efficiency dropped slightly, almost similar with that without magnesium sulfate. This may be caused by higher concentrations of magnesium sulfate. Increased ionic strength of seawater has a negative effect on the SO_2 solution. Thus, the SO_2 removal efficiency did not increase with the increase in magnesium sulfate concentration. Magnesium sulfate formed a new buffer system by combining with seawater and the pH of the desulfurization seawater kept a high level (Fig. 2).

The pH of desulfurization seawater with 0.200 M magnesium sulfate can be adjusted to 7.03 through aeration for 8 min when the oxidation ratio of SO_3^{2-} is as much as 86.3% (Fig. 3). Therefore, the seawater recovery situation is inferior to that of full seawater. This may be due to the newly introduced ions that strengthen the buffering capacity of seawater, and the higher concentrations of sulfate which have negative effects on the oxidation of sulfite.

2) Sodium sulfate as additive

The effect of different concentrations of sodium sulfate on seawater desulfurization and desulfurization seawater recovery were observed. The results are shown in Figs. 4 and 5.

As shown in Fig. 4, with 0.050 M sodium sulfate, the SO_2 removal efficiency increases by 6.2% more than that without sodium sulfate. The SO_2 removal efficiency dropped slightly with the increase in sodium sulfate concentration, almost similar with that without sodium sulfate. This variation tendency is similar to that when magnesium sulfate was used as additive. Seawater recovery was high, with pH up to 7.23, by aeration treatment for 8 min (Fig. 5) when the oxidation ratio of SO_3^{2-} was 90.9%. The results show that sodium sulfate at certain concentrations used as additive has a slight influence on desulfurization seawater recovery. The introduction of sodium sulfate increases SO_2 removal efficiency and has slight influence on desulfurization seawater recovery; therefore, it is an optimal additive.

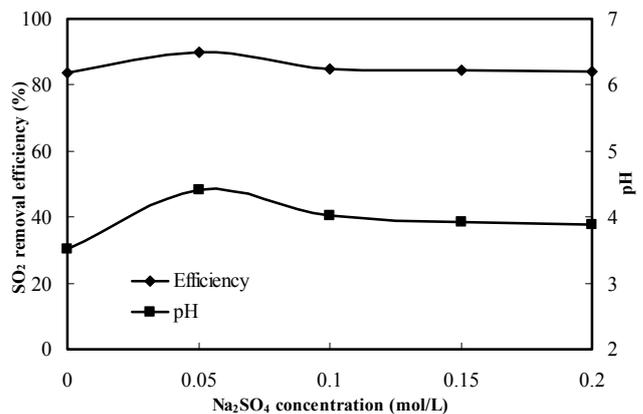


Figure 4. Effect of sodium sulfate on the SO₂ removal efficiency and pH of desulfurization seawater

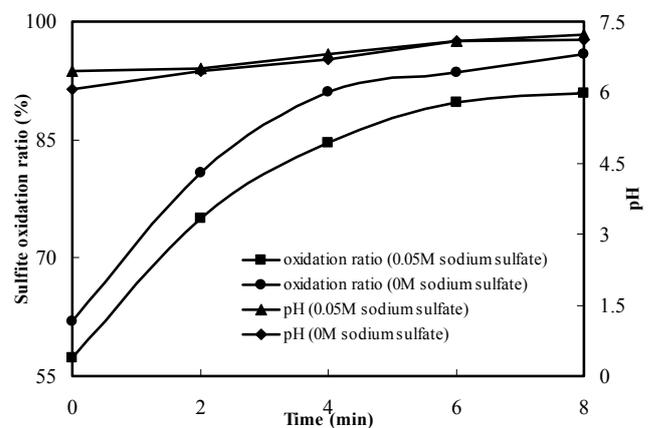


Figure 5. Effect of sodium sulfate on desulfurization seawater recovery

3) Acetic acid as additive

The effect of different concentrations of acetic acid on seawater desulfurization and desulfurization seawater recovery were observed. The results are shown in Figs. 6 and 7.

Fig. 6 shows that SO₂ removal efficiency increased when 0.005–0.020 M acetic acid was the additive. With 0.005 M acetic acid, the SO₂ removal efficiency increased by 7.2% more than that without acetic acid. The results show that desulfurization degree decreases with an increase in acetic acid concentration. Adding acetic acid strengthens the buffering capacity of seawater. There is a slight difference in seawater pH between pre-desulfurization and post-desulfurization; therefore, acetic acid has positive effects on desulfurization. However, with increasing acetic acid concentration, the pH of seawater dropped significantly, and the concentration of hydrogen ions increased sharply. The pH₀ of mixed seawater before desulfurization dropped to 3.69 when the concentration of acetic acid was 0.020 M. Acetic acid at that concentration has negative effects on the SO₂ solution, thus the increase in SO₂ removal efficiency was lower than that of low acetic acid concentration.

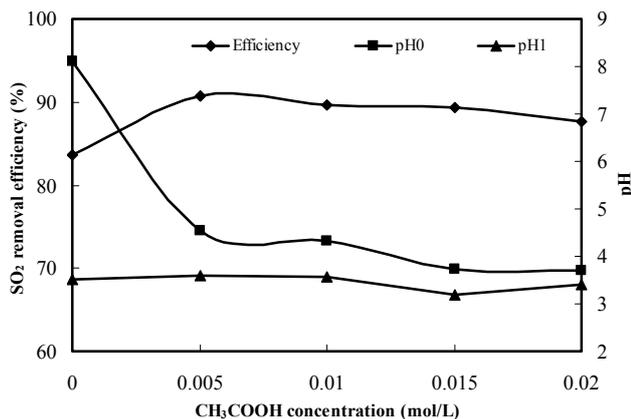


Figure 6. Effect of acetic acid on the SO₂ removal efficiency and pH of desulfurization seawater

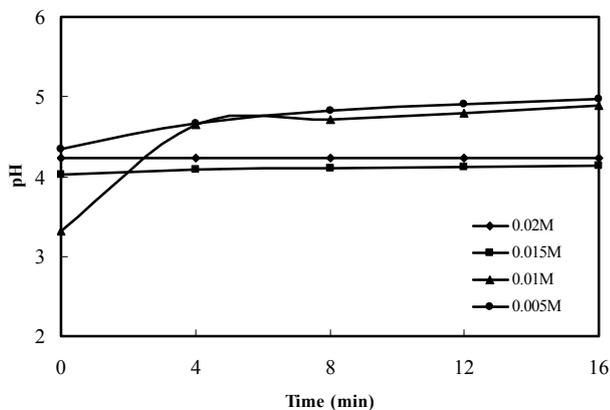


Figure 7. Effect of acetic acid on desulfurization seawater recovery

Adding acetic acid has negative effects on post-desulfurization seawater recovery, especially at higher concentrations (Fig. 7). The pH of seawater was still 4–5 after the seawater mixture underwent aeration treatment for 16 min. This is possibly because the acidity of acetic acid dropped the pH of seawater and the system that combines acetic acid with seawater has stronger buffering capacity. Therefore, the pH of desulfurization seawater cannot be recovered and cannot meet discharge requirements.

4) Hexanedioic acid as additive

The effect of hexanedioic acid on seawater desulfurization and desulfurization seawater recovery were observed. The results are shown in Figs. 8 and 9.

Fig. 8 shows that lower concentrations of hexanedioic acid promote seawater desulfurization. With 0.005 M hexanedioic acid, the SO₂ removal efficiency increased by 2%. Moreover, with 0.020 M hexanedioic acid, the SO₂ removal efficiency was 76.0%, which dropped by 7.6% relative to full seawater. Higher concentrations of hexanedioic acid lowered the pH of the seawater solution significantly. With 0.020 M hexanedioic acid, the pH₀ of pre-desulfurization seawater was 3.44 and pH₁ of post-desulfurization seawater was 3.08. Hexanedioic acid has a negative effect on SO₂ solution, which results in decreased SO₂ removal efficiency.

Hexanedioic acid has negative effects on post-desulfurization seawater recovery, especially at higher concentrations (Fig. 9). With 0.005 M hexanedioic acid, the pH of seawater was 4.17 after the seawater mixture was aerated for 20 min. With 0.020 M hexanedioic acid, the pH of seawater was 4.02. This is possibly because the system that combines hexanedioic acid with seawater has stronger buffering capacity, which is enhanced by the acidity of hexanedioic acid. Therefore, hexanedioic acid has negative effects on desulfurization seawater recovery.

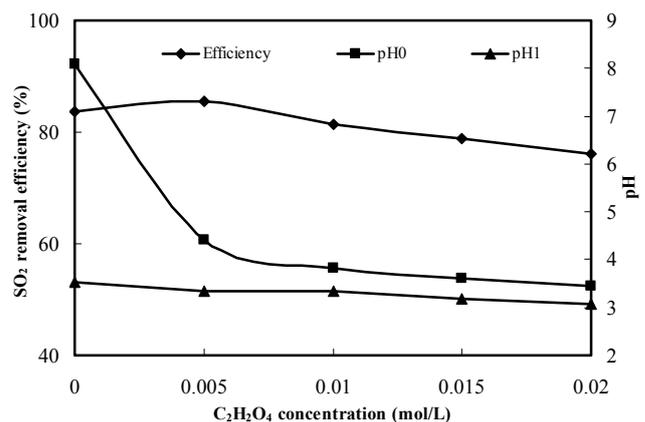


Figure 8. Effect of hexanedioic acid on the SO₂ removal efficiency and pH of desulfurization seawater

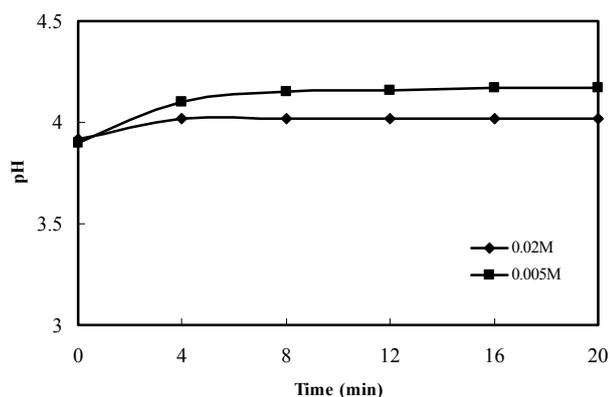


Figure 9. Effect of hexanedioic acid on desulfurization seawater recovery

IV. CONCLUSIONS

1) The factors are arranged according to the strength of their influence on SO_2 removal efficiency: liquid-gas ratio > gas-flow rate > inlet concentration of SO_2 > temperature of absorption solution. Liquid-gas ratio and gas-flow rate had significant influence on SO_2 removal efficiency. Liquid-gas ratio was the most important factor. Higher liquid-gas ratio had better desulfurization degree. Seawater consumption increased with an increase in liquid-gas ratio, and the corresponding operation costs may also increase. Gas-flow rate had a distinct effect. Lower gas-flow rate was efficient at absorbing sulfur dioxide. However, decreased gas-flow rate will require larger absorption equipment, thereby resulting in an increase in investment costs. Therefore, optimal operating conditions must be selected by integrating all factors.

2) Lower concentrations of inorganic additives (magnesium sulfate and sodium sulfate) increase the SO_2 removal efficiency and have little effect on desulfurization seawater recovery. After aeration treatment for 8 min, the pH of desulfurization seawater and oxidation ratio of sulfite can meet the discharge requirements. In particular, lower concentrations of sodium sulfate have no influence on desulfurization seawater recovery along with increasing SO_2 removal efficiency. Hence, it is worthy of tentative application in seawater flue gas desulfurization. Organic additives (acetic acid and hexanedioic acid) have promoting effects on seawater desulfurization at lower pH, but they have negative effects on post-desulfurization seawater recovery. Therefore, they are inappropriate for use in

practical applications because the pH of seawater cannot recover to higher levels for a long aeration time.

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