Feasibility Study on Application of Seawater Flue Gas Desulfurization (SWFGD) in Ultra-low Emission (ULE)*

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Abstract. As an economical and energy-saving environmental protection technology, seawater desulfurization technology is widely used in environmental protection facilities of coal-fired power plants. With the introduction of the ULE management, the traditional seawater desulfurization technology can no longer meet the increasingly stringent environmental requirements. Based on the theory of gas-liquid mass transfer and nozzle atomization size distribution analysis, this paper investigates the effect and limitation of desulfurization performance enhancement by adding spray layer. The research results show that the design efficiency of the fifth layer spray is only 31.94%, and the export SO2 is only reduced to 98mg/m3. The concentration level is far from the ULE standard (35mg/m3), and the spray layer does not fully meet the requirements of ULE standards. Therefore, further considerations need to be taken from other ways of increasing efficiency.

1. Introduction
Seawater flue gas desulfurization is a desulfurization process that utilizes the natural alkalinity of seawater to absorb SO2 in flue gas. Figure 1 is the typical schematic diagram of SWFGD system.

In this process, the following main reactions occur in the contact of SO2 with seawater in the flue gas:

\[ \text{SO}_2 \text{(gas)} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \rightarrow \text{H}^+ + \text{HSO}_3^- \]  
\[ \text{HSO}_3^- \rightarrow \text{H}^+ + \text{SO}_3^{2-} \]  
\[ \text{SO}_3^{2-} + 1/2\text{O}_2 \rightarrow \text{SO}_4^{2-} \]

The above reaction is an absorption and oxidation process. The seawater absorbs gaseous SO2 in the flue gas to form H2SO3. With instability the H2SO3 will be decomposed into H+ and HSO3-, and the HSO3- will continue to decompose into H+ and SO32-. then SO32- combines with dissolved oxygen in
water to oxidize to SO$_4^{2-}$. However, the dissolved oxygen in the water is very small, generally around 7~8mg/L, and it is far from being able to oxidize SO$_3^{2-}$ generated by SO$_2$ to SO$_4^{2-}$[1].

The concentration of H$^+$ in the seawater after SO$_2$ absorption increases, the acidity of seawater is enhanced; and the pH value is generally around 3, which is strongly acidic. It needs fresh alkaline seawater to increase the pH value by neutralization between fresh seawater and the seawater after FGD. Meanwhile, the carbonate progress reacts as follows[2]:

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 \uparrow + H_2O$$ (4)

While carrying out the above neutralization reaction, a large amount of air is blown into the seawater for aeration, and the main functions thereof are: (1) oxidation of SO$_3^{2-}$ to SO$_4^{2-}$; (2) generation of neutralization reaction by using mechanical force, and large amount of CO$_2$ is driven out of the water; (3) The dissolved oxygen in the discharge seawater increases to reach the standard discharge[3,4].

![Figure 1. Schematic diagram of typical SWFGD system](image)

2. Analysis of efficiency intensified measures

According to the general experience of ultra-low emission (ULE) modification of coal-fired thermal power units, the main ways of improving quality and efficiency can be summarized as two parts: 1) increase the mass transfer area (increasing the spray layer, adding mass transfer strengthening structure); 2) strengthening the mass transfer rate (Strengthen the pH of the slurry and enhance the mass transfer rate). The specific field application methods of the two synergistic pathways can be summarized as follows: 1) Add trays to increase the liquid holding capacity in the absorption tower, thereby effectively increasing the gas-liquid mass transfer liquid-gas ratio and prolonging the residence time of the flue gas in the absorption zone; 2) The height of the spray area can be increased by adding a top spray layer, and the gas-liquid mass transfer time can last longer; 3) Improve the quality of the absorption liquid (in the seawater FGD process, the absorbent is taken from the ocean and does not circulate in the tower, so the seawater quality cannot be changed.).

3. Experiment and analysis

3.1. Analysis of spray droplets character

Taking the atomization characteristics of the nozzle for seawater desulfurization of a typical 600MW unit as the research object, the particle size distribution characteristics of seawater spray atomization were investigated by laser measurement method, which provided the basic technical parameters for the derivation of the mass transfer specific surface area of the subsequent spray atomization layer.

The spray layer in FGD tower is arranged in a rotating cross, and the intersection angle between each main spray tube is 22.5$^\circ$, and the four main spray tubes are evenly distributed in the 90$^\circ$ sector. In the spray area, the upper and lower two-way spray nozzles are arranged in the central area of the 1/2/3
spray layer, the double-head solid cone nozzle is arranged near the wall nozzle, and the double-head hollow cone nozzle is arranged in the central area of the fourth spray layer. The spray head is facing down and the double-headed solid cone nozzle is also placed close to the wall nozzle. Figure 2 is a schematic diagram of the spray nozzle layout.

![Diagram of spray layer nozzle distribution](image)

Figure 2. Diagram of spray layer nozzle distribution

The number of spray nozzles arranged is shown in Table 1. There are 37 solid cone nozzles on the 1/2/3 layer edge, 140 in the bidirectional hollow cone nozzle, 37 solid cone nozzles on the 4th layer edge, 140 hollow cone nozzles in the middle area.

| Spray level   | Equilateral full nozzle | Equilateral hollow nozzle | Bidirectional hollow nozzle | Total number |
|---------------|-------------------------|---------------------------|-----------------------------|--------------|
| IV(upper)     | 37                      | 140                       | 0                           | 177          |
| III           | 37                      | /                         | 140                         | 177          |
| II            | 37                      | /                         | 140                         | 177          |
| I             | 37                      | /                         | 140                         | 177          |

The most common average diameter at present is the Sauter-mean diameter SMD ($d_{32}$), and the conversion formula is as shown in the formula (5), and the average diameter (the average diameter of the Souter) is obtained according to the principle of keeping the total surface area of the original liquid mist constant, which reflects the ratio of the volume occupied by the liquid to the total surface area of the liquid. Obviously, at the same volume, the smaller SMD means larger surface area of the liquid, so be the better atomization quality.

Volume-surface area average diameter:

$$d_{32} = \frac{\sum n_i D_i^3}{\sum n_i D_i^2}$$  \hspace{1cm} (5)

Where $D_i$ represents the i-th size particle size and $n_i$ represents the number of droplets having a particle size of $D_i$.

During the test, the SMD distribution of the droplets at different distances from the nozzle was tested to understand the characteristics of the SMD distribution of the droplets at different spray distance levels. The test results are shown below (Figure 3).

It can be seen from the results that as the distance between the atomization section and the nozzle increases, the SMD of the droplet at the center of the section increases, the SMD of the edge droplet decreases, and the uniformity of the SMD distribution of the section droplet increases. It can be seen from the figure that the atomization of the test nozzle is a hollow atomization ring. The closer the distance from the nozzle is, the more obvious the annular atomization is. As the distance increases, the droplets diffuse to the entire section to form a solid atomization. The droplet SMD distribution tends
to be uniform. As the diameter of the nozzle increases, the cross-section droplet SMD decreases. Under the pressure of 3.6MPa, the SMD range of the nozzle section is 40~150μm, and the nozzle section SMD range is 90~180μm under the pressure of 3.0MPa. Therefore, at higher nozzle pressure, the SMD tends to be smaller, so for the same spray flow rate, a larger mass transfer specific surface area can be obtained.

**Figure 3. SMD of droplets at different atomization cross-section distances (nozzle pressure 3.8/3.4/3.0 MPa)**

### 3.2. Analysis of mass transfer intensification

According to the double membrane theory, the rate equation in the absorption process can be expressed by the diffusion rate equation of gas and liquid membrane in the form of molecular diffusion by solute.

**Gas-film:** \[(N_A)_g = K_g(P_g - P_i)\]  \hspace{1cm} \text{(6)}

**Liquid film:** \[(N_A)_l = K_l(C_i - C)\]  \hspace{1cm} \text{(7)}

In the formula: \((N_A)_g, (N_A)_l\)--mass transfer flux of solute through the gas film and liquid film, kmol/(m²·s); \(P_g, P_i\)--respectively, the partial pressure of the solute component at the gas phase body and phase interface, kPa; \(C_i, C_p\)--the concentration of the solute component at the liquid phase interface and the main body, respectively, kmol/m³; \(K_g\)--gas phase mass transfer coefficient and liquid phase mass transfer coefficient, kmol/(m²·s·kPa); \(K_l\)--liquid phase mass transfer coefficient, kmol/[m²·s·(kmol/m³)], or m/s.

The test case is designed according to the typical 3+1 arrangement of the spray FGD tower. The calculation of the SO₂ mass transfer rate and the desulfurization efficiency is carried out according to the conditions in which the four layers of spray are all enabled under the BMCR condition. The stratified calculation data was extracted separately for fitting, and the degree of synergy of the addition of the 5th spray layer to the SO₂ removal performance is predicted. The relevant data is shown in Table 2 and Figure 4.
Table 2. Mass transfer rate and SO2 removal efficiency of five layer spray seawater desulfurization system

| Layer | Inlet SO2 (mg/m³) | Outlet SO2 (mg/m³) | DeSO2 (%) | Mass transfer (mol) | Transfer rate (N_A) (mol/(m²·s)) |
|-------|------------------|-------------------|-----------|---------------------|---------------------------------|
| 1     | 1450             | 614               | 57.66     | 5.2                 | 9.93811E-07                     |
| 2     | 614              | 347               | 43.49     | 1.7                 | 3.17401E-07                     |
| 3     | 347              | 217               | 37.46     | 0.8                 | 1.5454E-07                      |
| 4     | 217              | 144               | 33.64     | 0.5                 | 8.67801E-08                     |
| 5(add) | 144              | 98                | 31.94     | 0.3                 | 5.46834E-08                     |

Figure 4. Effect of adding spray layer on SO2 removal and efficiency

From the results in the figure, it can be seen that with the continuous absorption of SO2, the SO2 concentration level in the high-level spray area is low, and after the three spray layers’ absorption, the relevant SO2 mass transfer rate has dropped to the order of 10^-8 compared to the other three spray layers, and the mass transfer rate of the leaching decreased by one order of magnitude. Therefore, according to the inversion calculation of the relevant data, the effect obtained by adding the fifth layer of the spray layer is limited, and the design efficiency of the fifth layer spray is only 31.94%, and the discharge concentration of SO2 has only dropped to 98mg/m³, which is still far from the ULE standard (35mg/m³).

4. Conclusion
Consequently, the existing SWFGD technology cannot fully meet the requirements of ULE. When the inlet SO2 concentration is at 1450mg/m³, the FGD system can only achieve a discharge concentration of 98mg/m³ by adding a spray layer, and there is still a certain gap from the limit of ultra low emission 35mg/m³. Therefore, further considerations need to be taken from other ways of increasing efficiency.

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