Statistical Research on Effect of Desulfurated Parameters on Desulfurization Efficiency

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Abstract. Aluminum electrolysis is an important environmental source of pollution, including carbon anode for aluminum electrolytic aluminum industry. The calcined petroleum coke in the process of burning not only produces the number of amazing soot, but also emits SO\textsubscript{2} emissions. At present, most aluminum carbon, petroleum coke and calcined flue gas require desulfurization treatment, but little of the effect of desulfurization has been reported in the literature. In order to promote the healthy development of aluminum electrolytic green and environmental protection career progress, Origin and SPSS software was used to analyze the calcined flue gas data of aluminum charcoal coke rotary kiln in one aluminum plant in Yunnan Province. We obtained the correlation between the monitoring parameters and SO\textsubscript{2} removal efficiency, and gave some advice on controlling the flue gas flow rate, temperature, humidity or oxygen content to increase flue gas desulfurization efficiency.

1. Introduction

At present, China has entered the period of promoting the overall modernization, accelerating the transformation of economic system reform, especially with the further accelerating the process of modernization. Environmental issues have become increasingly prominent, one of the most notable is the air pollution. More and more researchers focus on flue gas desulfurization, but the studies on influence of flue gas parameters on the desulfurization efficiency are not definite enough.

Some researchers found that increasing the flue gas flow rate can reduce the flue gas residence time in the absorption tower, resulting in SO\textsubscript{2} removal rate decreased. When the flue gas temperature is too high, the absorption liquid temperature also increased and increasing ammonia escape, then this can promote the dissolution of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, while accelerating the decomposition of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3} and making desulfurization efficiency reduced [1]. However, Wang et al pointed out that increasing the gas velocity can increase the mass transfer rate and mass transfer coefficient in the absorption tower, so as to increase the ability of the absorption liquid to absorb SO\textsubscript{2}. Therefore he thought increasing the gas velocity can improve the SO\textsubscript{2} removal rate [2].Jiang et al found that the addition of moist air can increase the amount of condensable water and improve the desulfurization effect [3]. In addition, Yang et al studied the effects of humidity and temperature of flue gas from lime-gypsum boiler desulfurization on the composition of flue gas pollutants in many articles [4-6]. Their research shows that humidity and temperature can indeed affect the dust and SO\textsubscript{2} removal rate, but they also did some quantitative studies on the extent of the impact. Some literatures showed that the addition of oxygen to the desulfurization solution can promote the oxidation reaction of SO\textsubscript{3} and HSO\textsubscript{3}⁻, then the oxidation products would generate precipitation with Ca\textsuperscript{2+}, reduce the mass transfer resistance between gas and...
liquid phase, and promote the dissolution of $\text{SO}_2$ in water, indicating that the oxygen content of flue gas can also affect the removal of $\text{SO}_2$ [7-9].

He B. et al in the study of the effect of temperature on the efficiency of ammonia desulfurization found that $\text{SO}_2$ removal rate at low flue gas temperature is relatively high. With the increase of flue gas temperature, $\text{SO}_2$ removal rate showed a decreasing trend and reached the lowest at 70°C. Then, while the temperature continues to rise, $\text{SO}_2$ removal rate showed an upward trend [10]. However, some researches got the opposite result from He B. They indicated that the initial reaction rate of desulfurization increased with increasing temperature, after a period of time, increasing the temperature resulting in desulfurization reaction rate decreases [11-14]. It shows that flue gas temperature is a complicated parameter, and it may have interaction and restriction relationship with other flue gas parameters [15]. In other words, the study of desulfurization efficiency from a single perspective is often not comprehensive.

By analyzing previous studies, we found that flue gas parameters such as temperature, humidity, oxygen content or flow can indeed affect the composition of pollutants in flue gas. Therefore, it is feasible to control $\text{SO}_2$ emission by artificially controlling flue gas parameters.

2. Data Analysis

2.1. Data sources

This study selected the inlet and outlet flue gas data of ammonia desulfurization system from aluminum charcoal coke rotary kiln in one aluminum plant in Yunnan Province, monitoring gas parameters to get a set of sample data each hour, including flow, temperature, oxygen content and moisture content in inlet flue gas and $\text{SO}_2$ concentration in input and output flue gas during 0 o’clock on January 1st to 23 o’clock on January 5th, 2017.

The anode back calcined kiln specification is $\Phi 2.2\times45$, designed capacity of 5.5t/h, it forms an annual output of 400,000 tons of electrolytic aluminum production scale and an annual output of 180,000 tons of prebaked anode production line.

2.2. Analytical method

We use Origin 8.0 to indicate the trend of changes in sample emissions data. The mathematical expectation and confidence interval of sample emission data were analyzed by SPSS 19.0, then we obtained the normal range of sample emission data for normal system operation. The significance of the correlation between flue gas parameters and $\text{SO}_2$ emissions is explained by the Pearson correlation coefficient. And $\text{SO}_2$ removal rate equals the ratio of reduction of $\text{SO}_2$ concentration and $\text{SO}_2$ concentration in inlet flue gas.

2.3. Analysis of theoretical basis

Confidence interval refers to the estimated interval of the overall parameters constructed by the sample statistics. In statistics, the confidence interval of a probabilistic sample is the interval estimate of some overall parameter of the sample. Confidence interval shows the true value of this parameter has a certain probability of falling around the measurement results. The confidence interval gives the confidence level of the measured value of the measured parameter, which is the “one probability” previously required.

For a given set of sample data with an average of $\mu$ and a standard deviation of $\sigma$, the 100 $(1-\alpha)\%$ confidence interval for the mean of the overall data is $(\mu-Z_{\alpha/2}\sigma, \mu + Z_{\alpha/2}\sigma )$, where $\alpha$ is the coverage area of the non-confidence level in the normal distribution, and $Z_{\alpha/2}$ is the corresponding standard score.

In statistics, the Pearson correlation coefficient, also known as the Pearson product-moment correlation coefficient (PPMCC or PCCs), is used to measure the difference between two variables, X and Y correlated (linearly related) with values between -1 and 1. The Pearson correlation coefficient can be expressed as follows:
Formula (1) defines the overall correlation coefficient, commonly used in lowercase Greek letter \( \rho \) as a representative symbol. Estimating the sample covariance and standard deviation, Pearson correlation coefficient can be obtained:

\[
\rho_{X,Y} = \frac{\text{cov}(X,Y)}{\sigma_X \sigma_Y} = \frac{E[(X-\mu_X)(Y-\mu_Y)]}{\sigma_X \sigma_Y}
\]  

(1)

It can also be estimated from the standard point average of the sample point \((X_i, Y_i)\) to obtain an equivalent expression to the formula (2):

\[
r = \frac{\sum_{i=1}^{n}(X_i-\bar{X})(Y_i-\bar{Y})}{\left[\sum_{i=1}^{n}(X_i-\bar{X})^2\right]^{1/2}\left[\sum_{i=1}^{n}(Y_i-\bar{Y})^2\right]^{1/2}}
\]  

(2)

In the above formulas, \( \bar{X} \) and \( \bar{Y} \) are the average of the sample, and \( \sigma_X \) and \( \sigma_Y \) are the standard deviation of the sample. More generally, the correlation coefficient is positive if both \( X_i \) and \( Y_i \) tend to be larger or at the same time tend to be smaller than their respective mean. If \( X_i \) and \( Y_i \) tend to fall on the opposite side of their mean, the correlation coefficient is negative.

3. Results and discussion

3.1. Trends of samples

There are 120 sets of flue gas parameters and SO\(_2\) samples respectively, which is relatively representative. By analyzing the variety trend of flue gas parameters and SO\(_2\) emission, we can get a general understanding of the flue gas entering the desulfurization system.

![Figure 1. Trend chart of flue gas parameters](image-url)
As shown in Figure 1, the flue gas parameters of the desulfurization system show less obvious correlation with the time change and did not show the expected change with time except flue gas oxygen content. Flue gas flow roughly fluctuates from 80000 m$^3$/h to 140000 m$^3$/h, flue gas temperature is relatively stable distribution from 40°C to 50°C, in addition, flue gas moisture content is relatively stable from 8.9% to 9.1%. As for the flue gas oxygen content, excluding suddenly increased 3.11% at 12 o'clock on the 5th resulting in continued to reach 7.28%~8.18% till 23 o'clock on the 5th, the flue gas oxygen content is generally more stable distribution between 4%~6%.

We can see that there is also no obvious correlation between SO$_2$ concentration and time from Figure 2. SO$_2$ concentration in inlet flue gas is mostly concentrated in 2500 mg/m$^3$~5500 mg/m$^3$. However, the variation of SO$_2$ concentration in outlet flue is more obvious and varies greatly from 0 to 400 mg/m$^3$.

Figure 2. Trend chart of SO$_2$ concentration

3.2. Confidence interval analysis
Confidence interval refers to the estimated interval of the overall parameters constructed by the sample statistics. In statistics, the confidence interval for a probabilistic sample is the interval estimate for one overall parameter of that sample. In this article, the confidence level is 0.95.
After removing a very small number of outliers, the parameters vary around their respective mean during respective confidence intervals when desulfurization system is working properly. As shown in Figure 3, the confidence interval of flue gas flow is $119414.6177 \text{ kg/h} - 126728.7723 \text{ kg/h}$ and 5% trimmed mean is $122551.9220 \text{ kg/h}$. The confidence interval of flue gas temperature is from $44.2866^\circ \text{C}$ to $44.8342^\circ \text{C}$, and $44.6021^\circ \text{C}$ is its 5% trimmed mean. In addition, the confidence interval of flue gas moisture content is from $8.9940\%$ to $9.0058\%$, and the confidence interval of flue gas oxygen content is from $4.7863\%$ to $5.1401\%$, their 5% trimmed mean is $9.0009\%$ and $4.6622\%$ respectively.

Figure 4 indicates that SO$_2$ emission concentration varies around its 5% trimmed mean (92.54 mg/m$^3$) during its confidence interval (from 84.0930 mg/m$^3$ to 118.3852 mg/m$^3$) when desulfurization system is working properly. In addition, SO$_2$ removal rate ranges from 95.28\% to 96.74\%, and the average desulfurization rate is 96.42\%.

3.3. Correlation analysis

In this paper, we used Pearson correlation analysis in SPSS software to analyze the dependence between flue gas parameters and SO$_2$ emissions. We all know that Pearson correlation coefficient is used to measure whether two data sets are in a line and the linear relationship between distance variables.

3.3.1. Correlation analysis of flow to SO$_2$ emissions. As shown in Table 1, there is a significant positive correlation between flue gas flow and SO$_2$ emission concentration, it indicates that increasing the flue gas flow can increase the SO$_2$ emission concentration and vice versa. The same method is used to the dependence of flue gas flow to SO$_2$ removal rate, this indicates there is a significant negative correlation between flue gas flow and SO$_2$ removal rate.
Table 1. Correlations of flue gas flow to SO₂

| Pearson correlation | SO₂ concentration | SO₂ removal rate |
|---------------------|-------------------|-----------------|
|                     | 0.222*            | -0.234*         |
| Sig. (2-tailed)     | 0.015             | 0.010           |
| N                   | 120               | 120             |

*Correlation is significant at the 0.05 level (2-tailed).

We speculate that the increase of flue gas flow leads to the increase of oxygen supplied to the desulfurization system, more sulfur-containing components are oxidized to generate SO₂. At the same time, the larger the flue gas flow, the shorter the time of flue gas stay in the absorption tower. Therefore, increasing the flue gas flow will increase the SO₂ concentration of outlet flue gas and decrease the SO₂ removal rate.

3.3.2. Correlation analysis of temperature to SO₂ emissions. Table 2 suggests that flue gas temperature is significantly related to both SO₂ concentration and SO₂ removal rate. The different part is that flue gas temperature is positively correlated with SO₂ concentration but negatively correlated with SO₂ removal rate.

Table 2. Correlations of flue gas temperature to SO₂

| Pearson correlation | SO₂ concentration | SO₂ removal rate |
|---------------------|-------------------|-----------------|
|                     | 0.253**           | -0.259**        |
| Sig. (2-tailed)     | 0.005             | 0.004           |
| N                   | 120               | 120             |

**Correlation is significant at the 0.01 level (2-tailed).

Increasing the flue gas temperature can provide more energy for the desulfurization reaction and oxidize sulfur component more thoroughly, then produce more SO₂. In addition, increasing flue gas temperature can accelerate decomposition of H₂SO₃. On the other hand, the increase of gas temperature leads to higher temperature of the desulfurization solution with the solubility of ammonia and SO₂ in the desulfurization solution decreasing, this releases more SO₂.

3.3.3. Correlation analysis of moisture content to SO₂ emissions. From Table 3, neither the correlation of moisture content to SO₂ concentration nor the correlation of moisture content to SO₂ removal rate is significant. It means that flue gas moisture content has no significant effect on SO₂ concentration and SO₂ removal rate.

Table 3. Correlations of flue gas moisture content to SO₂

| Pearson correlation | SO₂ concentration | SO₂ removal rate |
|---------------------|-------------------|-----------------|
|                     | -0.117            | 0.050           |
| Sig. (2-tailed)     | 0.205             | 0.587           |
| N                   | 120               | 120             |

In theory, the higher moisture content of the flue gas results in a more moisturized absorbent surface, then more SO₂ will be absorbed. However, in practical applications, there are many other factors may restrict the desulfurization effect besides the moisture content, such as the temperature mentioned.
above. High temperature can promote the evaporation of desulfurization solution, thereby change the flue gas moisture content and may cover up the impact of moisture content. Therefore, the direct impact of moisture content is not significant.

3.3.4. Correlation analysis of oxygen content to SO₂ emissions. There is no significant correlation between flue gas oxygen content and SO₂ emissions (see Table 4).

Similar to the analysis of moisture content, the change of the gas flow caused by oxygen content has a stronger effect on SO₂ emission than oxygen content itself. Therefore, the effect of oxygen content on the desulfurization efficiency is not obvious.

| Table 4. Correlations of flue gas oxygen content to SO₂ |
|-------------------------------------------------------|
| Pearson correlation | SO₂ concentration | SO₂ removal rate |
| Sig. (2-tailed)     | 0.586             | 0.370            |
| N                  | 120               | 120              |

4. Conclusions

From the above analysis, it can be seen that Desulfurization system flue gas parameters can indeed directly affect the desulfurization efficiency, in other words, it is feasible to improve the desulfurization efficiency by controlling the flue gas parameters of the desulfurization system.

(1) The SO₂ removal rate is between 95.28%~96.74% and its 5% trimming average value is 96.42%, this industry requires SO₂ removal rate not less than 95%, so it seems that the desulfurization efficiency of the aluminum plant is relatively satisfactory.

(2) The results of Pearson correlation analysis indicated that SO₂ removal efficiency can be improved by reducing the flue gas flow rate or reducing the flue gas temperature, while changing the flue gas oxygen content or flue gas moisture content has no obvious effect on the flue gas SO₂ removal efficiency.

(3) This paper only qualitatively analyzes the correlation of desulfurization system gas parameters on desulfurization, the quantitative results require further study.

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