Influence of Moisture in Flue Gas after Wet Desulfurization on the Measurement of SO₂ Concentration

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Abstract: Wet desulfurization is dominant in China's coal power industry as flue gas discharged from wet desulfurization is over-saturated, includes lots of moisture, and can bring huge interference to the measurement of SO₂. When using existing SO₂ measuring methods, especially wet desulfurization technology aiming at ultra-low emissions, it is necessary to take into account the impact of water in flue gas. The pH value of condensate water of flue gas after desulfurization with limestone gypsum wet desulfurization is 2, lower than that of desulfurizing slurry, indicating that some SO₂ has been dissolved in the water carried by flue gas after desulfurization. In order to avoid the interference of water, infrared online continuous emission monitoring system (CEMS) is equipped with a water removal device. When a conventional condensate water removal method is applied, condensate water will dissolve SO₂ and then lead to the relatively low concentration of SO₂ in the flue gas measured. When a proper water removal method is adopted, it can effectively avoid the measuring error as a result of SO₂ dissolved in condensate water.

1. Introduction
China adopts coal as its main energy, and the total energy consumption reached 4.64 billion tons of standard coal (tce) in 2018, 59.0% of which was contributed by coal consumption [1]. While providing important support for economic development, coal has also produced huge pollution. After discharging into the air, SO₂ generated from coal combustion produces SO₃ after oxidation and forms H₂SO₄ when combining with water in the air, which reaches the ground with rainfall or snowfall. It is known as acid rain when the pH value of rainfall or snowfall is less than 5.6. Acid rain is extremely dangerous for the environment, buildings, animals and plants, and also endangers the fitness of the general public. Therefore, China has designated acid rain control areas, and made rigid restrictions for the emission concentration of SO₂ from industrial sources [2-5].

In China, thermal power generation industry is the major emission source of SO₂. By the end of 2019, the installed capacity of coal power generation in China has exceeded 1 billion kilowatt (kW). In order to realize the strict emission limit, over 90% of units have applied wet desulfurization, where limestone gypsum wet desulfurization occupies a dominant position. To further cut back on the emissions of coal-burning pollutants, the Ministry of Environmental Protection, the National Development and Reform Commission and the National Energy Administration issued the Work Programme for the Full Implementation of Ultra-low Emissions and Energy-saving Transformation of Coal-fired Power Plants in 2015, requiring that the emission concentration of SO₂ shall be no higher than 35mg/m³ when the benchmark oxygen content of coal-fired units is 6%. As of the end of 2019, coal-fired units realizing ultra-low emissions had reached about 890 million kW.
The ongoing SO\textsubscript{2} control has gained sound results. In 2013, the size of acid rain areas across the country accounted for 10.6\% of the national territorial area, which reduced to 5.5\% in 2018, demonstrating a decline of nearly 50\% \[6\]. By referring to the success stories of coal-fired units in ultra-low emissions, China has started to replicate ultra-low emissions transformation in many fields, including coal-fired boilers, iron & steel and building materials, and limestone gypsum wet desulfurization is also the technology mainly adopted. Despite the high desulfurization efficiency of wet desulfurization which leads to the steady achievement of ultra-low emissions \[7-8\], the water content in the flue gas discharged is very high at an over-saturated condition, and there is liquid drop in the flue gas \[9\], bringing huge interference to the measurement of SO\textsubscript{2}.

2. Issues Existing in the Measuring Methods

2.1. Applicability

The \textit{Emission standard of air pollutants for thermal power plants} (GB 13223-2011) \[10\] specified three measuring methods for SO\textsubscript{2} concentration. Specifically, the range of measurement in the \textit{Determination of sulfur dioxide from exhausted gas of stationary sources Iodine titration method} (HJ/T 56-2000) is 100-6,000mg/m\textsuperscript{3}, with a measuring error of ±6\% \[11\]; the range of measurement in the \textit{Determination of sulfur dioxide from exhausted gas of stationary sources Fixed-potential electrolysis method} (HJ/T 57-2000) is 15-14,300mg/m\textsuperscript{3}, with a measuring error of ±5\% \[12\]; and the detection limit in the \textit{Stationary sources emission-Determination of sulfur dioxide-Non-dispersive infrared absorption method} (HJ 629-2011) is 3mg/m\textsuperscript{3}, with a lower limit of 10mg/m\textsuperscript{3} \[13\]. With the advancement in the understanding about the issues in the measurement and measuring techniques, the \textit{Stationary sources emission-Determination of sulfur dioxide-Fixed potential by electrolysis method} (HJ 57-2017) has been released and implemented, under which the detection limit is 3mg/m\textsuperscript{3} and the lower limit is 10mg/m\textsuperscript{3} \[14\].

The \textit{Emission standard of air pollutants for thermal power plants} (GB 13223-2011) specified the concentration of SO\textsubscript{2} in dry flue gas. When measuring the concentration of SO\textsubscript{2} after desulfurization, many analytical instruments will allocate water removal devices. Instruments using fixed-potential electrolysis method arrange dehydrating units as per new standards, so as to eliminate the coagulation and impact of water on the surface of osmotic membrane of the sensor.

Currently, mainstream online monitoring instruments use the non-dispersive infrared absorption method which features high precision and stability. The theory is that SO\textsubscript{2} selectively absorbs the light with characteristic wavelength, and the concentration of SO\textsubscript{2} is then measured quantitatively based on Lambert Beer's law. The infrared absorption method is vulnerable to the interference of H\textsubscript{2}O, and in order to ensure that flue gas does not generate condensate water during the transmission process in the sampling tube, the online monitoring instruments with the non-dispersive infrared absorption method heat the tracing pipe so that the water in the flue gas in the sampling tube is totally gaseous. After cooling in the condenser, high temperature flue gas enters into the light room for analysis, and the condensate water generated is discharged from the instruments, while the flue gas measured is free from condensate water.

2.2. Impacts of condensate water

SO\textsubscript{2} is soluble in water, and the curve of its solubility in water under different temperatures is shown in Figure 1. When the water temperature is below 80\degree C, SO\textsubscript{2} becomes more soluble in water as the temperature drops, and the highest range of solubility of SO\textsubscript{2} is 0-5\degree C.
Condensate water is collected for test analysis from different point locations of a 330MW coal-fired unit and a 660MW coal-fired unit. Both units are equipped with typical limestone gypsum flue gas wet desulfurization system, but have yet to reach the standards for ultra-low emissions.

According to M4 method [15], the first absorption bottle is changed to an empty bottle, the second and third absorption bottles are added with 100ml deionized water respectively, while the fourth one is added with silica gel or other desiccating agent with equivalent effect. After that, samples are taken. The pH value of condensate water in the flue gas collected in the first absorption bottle is measured. The pH value of condensate water collected from chimney and expansion joint is measured [16-17]. The measured pH value of condensate water at different locations are shown in Table 1.

Table 1. pH value of condensate water at different locations.

| Collection locations of condensate water | pH value | 330MW unit | 660MW unit |
|-----------------------------------------|----------|------------|------------|
| Outlet of the desulfurization system    |          |            |            |
| Average                                 | 2.01     | 2.03       |
| Maximum                                 | 2.50     | 2.40       |
| Minimum                                 | 1.50     | 1.88       |
| Average                                 | 1.79     | 2.01       |
| Chimney and expansion joint             |          |            |            |
| Maximum                                 | 1.88     | 2.25       |
| Minimum                                 | 1.46     | 1.74       |

In order to increase the solubility of CaSO4 generated from the desulfurization process, it is suitable to control the pH value of slurry of the absorption tower at 5.2-5.8 when the limestone gypsum wet desulfurization system uses limestone as the absorbant during real operation; if lime is used as the absorbant, it is suitable to control the pH value of slurry of the absorption tower at 5.2-6.2 [18], while the pH value of condensate water in the flue gas at the outlet of the desulfurization system is about 2, indicating that some acid gas is dissolved in the water carried in the flue gas during the desulfurization process, which then leads to the further decline in the pH value.

As wet desulfurization removes most of the reactive acidic gas, acid gas in the flue gas emitted with wet desulfurization is mainly SO2 and NO, while the solubility of NO in water is rather low. Therefore, the major factor contributing to the reducing pH value of the water carried in the flue gas emitted with wet desulfurization is that SO2 is soluble in water and produces H2SO3, and then generates H2SO4 after oxidation [19].

When flue gas discharges to the air through chimney from the outlet of the desulfurization system, the temperature of the flue gas drops continually, the volume of condensate water in the flue gas is on the rise, while the temperature of condensate water also drops. Figure 1 shows that as the temperature of condensate water reduces, the concentration of SO2 dissolved in the water will rise, and then lead to the lower pH value of condensate water of chimney and expansion joint than that of condensate water in the flue gas at the outlet of the desulfurization system.

The condenser of the online monitoring instrument with the non-dispersive infrared absorption method will cool the flue gas to 2-4 °C, and the over-saturated flue gas will generate condensate water due to temperature decline, while the solubility of SO2 in water is the highest within the temperature range. SO2 will be dissolved in the condensate water largely separated, thus resulting in the decline in
the concentration of SO$_2$ in the flue gas and the minus deviation in the monitoring results$^{[20-21]}$. The higher the humidity and the more the condensate water separated, the lower the concentration of SO$_2$.

In order to reduce the impact of condensate water on the measurement of the concentration of SO$_2$, the Specifications and test procedures for continuous emission monitoring system for SO$_2$, NOx and particulate matter in flue gas emitted from stationary (HJ 76-2017) put forward relevant technique requirements for the amount of loss of SO$_2$ of the CEMS sample gas condensation and dehumidification equipment$^{[22]}$.

3. Measurement results of different methods

The principle of the ultraviolet absorption method is identical with that of the non-dispersive infrared absorption method, but the characteristic wavelengths of both methods are different. The former method is basically free from the interference of H$_2$O, and the flue gas analytical instrument with the ultraviolet absorption method also adopts whole-course heating with high temperature to gasify all liquid drops, but it is not equipped with condenser. High-temperature flue gas directly enters into the light room for analysis, and the flue gas measured also has no condensate water$^{[23]}$. Due to the absence of the condensation process, it can effectively reduce the impact of condensate water on the measurement of SO$_2$ concentration.

(1) Case No. 1

This case measures SO$_2$ concentration after wet desulfurization of a chemical enterprise which has met the standard for ultra-low emissions through desulfurization with the sodium alkali method. The CEMS adopts the non-dispersive infrared absorption method, and deploys the condensation and dehydration device. By selecting the identical measuring points of the CEMS, the concentration of SO$_2$ measured by the CEMS and flue gas analytical instrument with the ultraviolet absorption method is compared. The measurement results are specified in Table 2.

| Serial number | CEMS | Ultraviolet absorption method | Difference |
|---------------|------|-------------------------------|------------|
| 1             | 3.0  | 5.6                           | 2.6        |
| 2             | 3.0  | 5.7                           | 2.7        |
| 3             | 2.9  | 4.3                           | 1.4        |
| 4             | 2.9  | 4.6                           | 1.7        |
| 5             | 3.0  | 5.3                           | 2.3        |
| 6             | 3.0  | 5.3                           | 2.3        |
| 7             | 2.9  | 4.3                           | 1.4        |
| 8             | 2.9  | 4.3                           | 1.4        |
| 9             | 3.0  | 5.0                           | 2.0        |
| 10            | 2.8  | 3.9                           | 1.1        |
| 11            | 2.8  | 3.9                           | 1.1        |
| 12            | 3.0  | 5.0                           | 2.0        |
| 13            | 2.9  | 4.3                           | 1.4        |
| 14            | 2.9  | 4.3                           | 1.4        |
| 15            | 2.9  | 4.3                           | 1.4        |
| 16            | 3.0  | 4.6                           | 1.6        |
| 17            | 3.0  | 5.0                           | 2.0        |
| 18            | 3.0  | 4.6                           | 1.6        |
| 19            | 2.9  | 4.3                           | 1.4        |
| 20            | 3.0  | 4.6                           | 1.6        |

Average: 2.9 | 4.7 | 1.8
The average value measured of the CEMS is $2.9\text{mg/m}^3$, and the average value measured of the flue gas analytical instrument with the ultraviolet absorption method is $4.7\text{mg/m}^3$. The error of average value measured of both methods is less than $2.0\text{mg/m}^3$, which shows the sound consistency of the measurement results of the two methods.

(2) Case No. 2

This case measures SO$_2$ concentration after wet desulfurization of a coal chemical enterprise which has yet to meet the standard for ultra-low emissions through limestone gypsum wet desulfurization. The CEMS adopts the non-dispersive infrared absorption method, and deploys the condensation and dehydration device. By selecting the identical measuring points of the CEMS, the concentration of SO$_2$ measured by the CEMS and flue gas analytical instrument with the ultraviolet absorption method is compared. The measurement results are specified in Table 3.

Table 3. Measurement data of emission concentration of SO$_2$ of the coal chemical enterprise.

| Serial number | CEMS | Ultraviolet absorption method | Difference |
|---------------|------|--------------------------------|------------|
| 1             | 29.7 | 34.6                           | 4.9        |
| 2             | 31.8 | 41.7                           | 9.9        |
| 3             | 33.6 | 46.6                           | 13.0       |
| 4             | 42.9 | 49.1                           | 6.2        |
| 5             | 30.9 | 46.0                           | 15.1       |
| 6             | 33.8 | 42.0                           | 8.2        |
| 7             | 30.0 | 42.0                           | 12.0       |
| 8             | 29.2 | 44.3                           | 15.1       |
| Average       | 32.7 | 43.3                           | 10.6       |

The average value measured of the CEMS is $32.7\text{mg/m}^3$, and the average value measured of the flue gas analytical instrument with the ultraviolet absorption method is $43.3\text{mg/m}^3$. The average value of the emission concentration of SO$_2$ measured through CEMS is $10.6\text{mg/m}^3$ lower than that of the device with ultraviolet absorption method.

(3) Case No. 3

This case measures SO$_2$ concentration after wet desulfurization of a 350MW coal-fired unit which has met the standard for ultra-low emissions through limestone gypsum wet desulfurization. The CEMS adopts the non-dispersive infrared absorption method, and deploys the condensation and dehydration device. By selecting the identical measuring points of the CEMS, the concentration of SO$_2$ measured by the CEMS and two flue gas analytical instruments with the ultraviolet absorption method is compared. One of the flue gas analytical instruments is equipped with the condensation preprocessing unit. The measurement results are specified in Table 4.

Table 4. Measurement data of emission concentration of SO$_2$ of the 350MW coal-fired unit.

| Serial number | CEMS | Ultraviolet absorption method | Difference |
|---------------|------|--------------------------------|------------|
|               |      | With condensation              | Without condensation |
| 1             | 11.8 | 8.9                            | 29.0        |
| 2             | 12.3 | 10.0                           | 30.6        |
| 3             | 13.2 | 10.4                           | 30.7        |
| 4             | 12.3 | 12.1                           | 32.0        |
| 5             | 13.8 | 11.6                           | 31.7        |
| 6             | 13.5 | 11.8                           | 32.8        |
| 7             | 14.4 | 12.3                           | 34.5        |
| 8             | 11.3 | 12.4                           | 33.0        |
| 9             | 12.5 | 16.7                           | 39.3        |
The data measured by the CEMS and the flue gas analytical instrument with the ultraviolet absorption method which is equipped with condensation preprocessing unit is highly consistent, with the error of average value measured less than 1mg/m³, indicating that both the non-dispersive infrared absorption method and the ultraviolet absorption method are applicable to post-desulfurization flue gas which does not contain condensate water, and demonstrate sound consistency.

When measurement is conducted by using the flue gas analytical instrument with the ultraviolet absorption method, the SO₂ concentration of the flue gas drops obviously after it undergoes the treatment by the condensation preprocessing unit, with the average concentration down by 20.6mg/m³ from 32.9mg/m³ to 12.3mg/m³. When the water contained in flue gas is removed by the condensation preprocessing unit, SO₂ dissolved by the water is also removed, leading to the reduction in the concentration of SO₂ in the flue gas after dehydration.

The average value measured of the CEMS is 12.9mg/m³, and the average value measured of the flue gas analytical instrument with the ultraviolet absorption method which is not equipped with the preprocessing unit is 32.9mg/m³. The average value of the emission concentration of SO₂ measured through CEMS is 20.0mg/m³ lower than that of the device with ultraviolet absorption method.

Cases No. 1, 2 and 3 all use wet desulfurization and CEMS with the non-dispersive infrared absorption method which is equipped with condensation and dehydration device. The difference lies in the desulfurization technologies adopted in the three cases: Case No. 1 employs desulfurization with the sodium alkali method, Case No. 2 adopts limestone gypsum wet desulfurization, while Case No. 3 uses limestone gypsum wet desulfurization. These different desulfurization technologies are exactly the direct reasons behind the error of the measurement data.

The desulfurizing slurry with the sodium alkali method is alkaline, and when SO₂ dissolves in the water of the flue gas, it will generate acid-base reaction with sodium hydroxide. When the water of the flue gas does not contain SO₂ and the condensate water it generates also has no SO₂, condensation and dehydration will not affect the concentration of SO₂ in the flue gas. As for the limestone/lime gypsum methods, the desulfurizing slurry is acidic, the water of the flue gas can dissolve some SO₂, and the condensate water it generates dissolve some SO₂, so the process of removing condensate water will lead to the decline in the concentration of SO₂ in the flue gas.

Therefore, when measuring SO₂ concentration after wet desulfurization with the limestone/lime gypsum methods, it is necessary to take into account the measuring error due to the dissolution of SO₂ in the condensate water.

(4) Case No. 4

Currently, many CEMSs with the non-dispersive infrared absorption method have given up the traditional dehydration technology via the condensation method, and adopted new dehydration technologies, such as acid process through condensation and Nafion tube technology, which will not lead to the reduction in SO₂ concentration while removing water in the flue gas.

This case measures SO₂ concentration after wet desulfurization of a coking plant which has met the standard for ultra-low emissions through lime gypsum wet desulfurization. The CEMS adopts the non-dispersive infrared absorption method, and deploys the new dehydration device. By selecting the identical measuring points of the CEMS, the concentration of SO₂ measured by the CEMS and flue gas analytical instrument with ultraviolet absorption method is compared. The measurement results are specified in Table 5.

Table 5. Measurement data of emission concentration of SO₂ of the coking plant.

| Serial number | CEMS | Ultraviolet absorption method | Difference |
|---------------|------|--------------------------------|------------|
| 1             | 13.3 | 11.1                           | -2.2       |
| 2             | 14.7 | 11.1                           | -3.6       |
| 3             | 13.5 | 11.4                           | -2.1       |
| 4             | 13.7 | 11.1                           | -2.6       |
The average value measured of the CEMS is 13.0mg/m$^3$, and the average value measured of the flue gas analytical instrument with the ultraviolet absorption method is 11.5mg/m$^3$. The average value of the emission concentration of SO$_2$ measured through CEMS is 1.5mg/m$^3$ higher than that of the device with the ultraviolet absorption method, which shows the sound consistency of the measurement results of the two methods.

(5) Other cases

By selecting the identical measuring points after wet desulfurization of different enterprises, SO$_2$ concentration measured by the CEMSs and flue gas analytical instruments with the ultraviolet absorption method is compared. The CEMSs adopt the non-dispersive infrared absorption method, and deploy the new dehydration device. The summarized measurement results are indicated in Table 6.

Table 6. Measurement data of emission concentration of SO$_2$ of different enterprises.

| Serial number | Desulfurization technologies | CEMS | Ultraviolet absorption method | Difference |
|---------------|------------------------------|------|-------------------------------|------------|
| 1             | limestone-gypsum method      | 20.0 | 16.7                          | -3.3       |
| 2             | limestone-gypsum method      | 50.5 | 49.0                          | -1.5       |
| 3             | limestone-gypsum method      | 35.0 | 30.1                          | -4.9       |
| 4             | lime-gypsum method           | 4.9  | 5.0                           | 0.1        |

It can be found that after the new dehydration device is allocated, the issue of the reduction in SO$_2$ in the flue gas arising out of dissolution in condensate water can be tackled. The ultraviolet method and the non-dispersive infrared absorption method show sound consistency, and the maximum measuring error of both methods is less than 5mg/m$^3$.

4. Conclusion

The flue gas after wet desulfurization is over-saturated flue gas, and can significantly affect the measurement of SO$_2$ concentration. When being applied in measuring SO$_2$ concentration in high-moisture flue gas, the non-dispersive infrared absorption method should arrange a suitable dehydration device, so as to eliminate the measuring error due to the water in the flue gas.

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