

Calculation and Treatment Measures of Sulfur Dioxide Emission in Waste Gas of Ceramic Industry

Yan Luo¹, Hubin Bai^{2*}, Kaifang Wang², Xianbian Mao²

¹Candle Light Middle School of the Guangyuan Democratic League, Zhaohua District, Guangyuan, Sichuan, 628021, China

²China Building Material Test & Certification Group (Shaanxi) Co. Ltd, Xi'an, Shaanxi, 710049, China

Abstract: The emission index of sulfur dioxide in the exhaust gas of the ceramic industry is an important indicator of the green production of enterprises and the green development of society. This article analyzes the emission sources of sulfur dioxide in the exhaust gas of the ceramic industry, and gives the calculation method for calculating the sulfur dioxide emissions in raw materials and fuels. At the same time, it compares the two-alkali wet desulfurization, limestone-gypsum wet desulfurization, and semi-dry desulfurization. The three governance measures provide references for ceramic companies to evaluate sulfur dioxide emissions and treatment.

1 Introduction

The ceramic industry is an industry with high energy consumption, high emissions and high pollution, especially the pollution of the atmospheric environment is very serious. The fossil fuel combustion process in the ceramic powder preparation and kiln firing process will produce particulate matter, SO₂, NO_x, CO₂ and other atmospheric pollutants, among which particulate matter poses a threat to human health; SO₂ and NO_x are the main causes of acid rain; CO₂ is a greenhouse gas, it is the main factor leading to global warming [1]. With the advancement of the national ecological construction strategy, the national emission control standards and requirements for air pollutants have become more stringent. The calculation of exhaust gas pollutants in the ceramic industry, especially the calculation of sulfur dioxide emissions in the exhaust gas and the study of treatment measures, will help enterprises achieve green and sustainable development has important guiding significance.

2 Sulfur dioxide emission source in the ceramic industry

The SO₂ in ceramic industry exhaust gas mainly comes from the oxidation of sulfur in coal, diesel oil and other fuels and the sulfur in ceramic raw materials [2]. Among them, the amount of SO₂ produced by the combustion of fossil fuels is directly related to the amount of sulfur content, which generally originates from the combustion of organic sulfur compounds and combustible sulfur compounds in the fuel. The SO₂ produced during the firing of ceramic raw materials partly comes from the oxidation of coarse-grained pyrite in the high-temperature stage raw materials, and part comes from the decomposition of natural sulfate auxiliary minerals (including Fe₂(SO₄)₃,

CaSO₄, Na₂SO₄, etc.) in the raw materials [3-4]. The contribution of sulfur in the fuel to the amount of SO₂ produced in the exhaust gas is much greater than the contribution of the amount of SO₂ produced by the oxidation of sulfur in the raw material.

The research of Fang H.X [5] and others on the sulfide emission in ceramic firing showed that the SO₂ emission concentration of ceramic roller kilns using coal, heavy oil, diesel and other fuels is about 800~5 000 mg/m³, and coal is used as fuel The concentration of SO₂ produced is about 2 000 mg/m³, the concentration of SO₂ produced by burning heavy oil as fuel is about 1 000 mg/m³, and the concentration of SO₂ before spray drying tower treatment is generally about 500 mg/m³.

The SO₂ emission concentration in the spray drying tower and kiln flue gas of the ceramic industry is mainly affected by the type of fuel. The order of the SO₂ concentration produced by different fuels is: coal>fuel>coal water slurry>gas. Different kiln types also have an important impact on the SO₂ emission concentration. In the latest "Emission standard of pollutant for ceramic industry" (GB 25464-2010), the SO₂ limit of spray drying towers and ceramic kilns in the ceramic industry is adjusted to 50mg/m³. In the actual ceramic production process, the SO₂ concentration in the flue gas emitted by the spray drying tower and the ceramic kiln is much higher than the new standard, so it is necessary to carry out the prediction of sulfur dioxide emissions and take effective control measures.

3 Calculation of sulfur dioxide emission in waste gas of ceramic industry

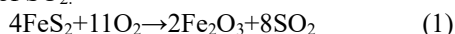
Currently, sulfur dioxide emissions in ceramic waste gas are mainly monitored by online monitoring equipment [6]. Such online monitoring equipment is expensive and

*Corresponding author's e-mail: baihu2007@aliyun.com

requires high maintenance, which cannot meet the needs of small and medium ceramic enterprises in my country. The emission of sulfur dioxide pollutants from ceramic waste gas can be established through the principle of material balance to establish a practical method for predicting air pollutants from ceramic kilns.

3.1 Calculation of sulfur dioxide emissions in raw materials

The main impurities of sulfur in ceramic raw materials include FeS_2 , $\text{Fe}_2(\text{SO}_4)_3$, CaSO_4 and Na_2SO_4 . In the high-temperature firing process, a series of oxidation-reduction reactions occur in the raw materials, releasing gases such as SO_2 . A large amount of SO_2 emissions in the raw materials are produced by the oxidation of FeS_2 . The chemical reaction equation of FeS_2 oxidation decomposition reaction is shown in formula (1)^[7]. According to the principle of chemical equilibrium, every gram of FeS_2 reacts completely at high temperature to produce 1.07g of SO_2 .



The SO_2 emissions caused by the raw materials also include the high-temperature decomposition of natural sulfate-assisted minerals in the raw materials. The content of sulfate in the raw materials is relatively low. The main sulfates are: $\text{Fe}_2(\text{SO}_4)_3$, CaSO_4 and Na_2SO_4 . According to the principle of chemical equilibrium, every gram of $\text{Fe}_2(\text{SO}_4)_3$, Na_2SO_4 and CaSO_4 completely react at high temperature to produce 0.6g, 0.45g and 0.47g SO_2 .

3.2 Calculation of sulfur dioxide emissions in fuel

The pulverized coal, water gas, and natural gas used in the ceramic drying and firing process produce sulfur dioxide during the combustion process. Generally, for building ceramics and special ceramics that are formed by dry pressing (with spray drying towers), the calculation of sulfur dioxide production or emissions mainly includes spray drying towers and kilns. For daily-use ceramics, sanitary ceramics, non-dry-pressed building ceramics and special ceramics, the calculation of the amount of sulfur dioxide produced or emitted only includes the furnace part^[8].

According to the "Technical guidelines of accounting method for pollution source intensity ceramics products manufacturing" (HJ 1096-2020), the calculation methods for the sulfur dioxide emissions of organized waste gas are: analogy, material balance algorithm and actual measurement method. The analogy method is applicable to the same type of raw and auxiliary materials and fuels, similar components related to pollutant emissions, the same production process, similar pollution control measures, and the design removal efficiency of pollutants is not lower than the removal efficiency of analog objects, and the design production capacity difference of a single production line No more than 20% of the production line. The actual measurement method is to calculate the pollutant emissions based on the actual exhaust gas emissions and the corresponding pollutant emission concentrations, which is suitable for existing engineering

pollution sources with effective automatic monitoring or manual monitoring data. The calculation formula of the material balance algorithm is as follows:

$$D_{\text{SO}_2} = 2 \times \left(A \times \frac{K_{\text{TRS}}}{100} \times K_\alpha + B \times \frac{K_{\text{YRS}}}{100} \times K_\beta + \sum_{i=1}^n G_i \times \frac{K_i}{100} - D \times \frac{K_{\text{CS}}}{100} \right) \quad (2)$$

Where:

D_{SO_2} —The amount of sulfur dioxide produced during the accounting period, t.

A—The fuel consumption of hot blast stoves during the accounting period, where producer gas is used as the fuel based on the coal input when it is produced, t or m^3 .

K_{TRS} —The sulfur content of hot blast stove fuel, solid/liquid fuel is the received base sulfur content, %; gas fuel (except cold gas) is calculated by sulfur content, $\text{mg}/\text{m}^3 \times 10^{11}$.

B—The fuel consumption of the kiln during the accounting period. When producer gas is used as fuel, it is calculated based on the coal input when it is produced, t or m^3 .

K_{YTS} —Sulfur content of kiln fuel, solid/liquid fuel is received base sulfur content, %; gas fuel (except cold gas) is calculated by sulfur content, $\text{mg}/\text{m}^3 \times 10^{11}$.

K_α , K_β —The coefficient of sulfur in the fuel to generate sulfur dioxide, which is taken according to the type of fuel: 0.85 for coal or coal water slurry, 1.0 for other fuels.

α , β —Values according to different types of hot blast stove and kiln fuel: when the fuel is producer gas, the desulfurization efficiency at the time of its preparation needs to be considered, take $(1 - \eta_1 / 100)$, 1 is the desulfurization efficiency of producer gas station, %; other fuels take 1.0.

G_i —The consumption of the i-th raw material (including raw materials, glazes and pigments, etc.) in the accounting period, on a dry basis, t.

K_i —The sulfur content of the i-th raw material (calculated as elemental sulfur), %.

D—Product output in the accounting period, calculated on a dry basis, t.

KCS—Sulfur content in fired products (calculated as elemental sulfur), %.

4 Sulfur dioxide treatment measures in the exhaust gas of the ceramic industry

The current treatment of sulfur dioxide emissions in ceramic flue gas is based on desulfurization technology. Common desulfurization technologies include: double-alkali wet desulfurization, limestone-gypsum wet desulfurization, semi-dry desulfurization, etc.^[9].

4.1 Two-alkali method for flue gas desulfurization.

The dual-alkali flue gas desulfurization technology uses calcium hydroxide and sodium carbonate as desulfurizers. In the initial stage, sodium sulfite, which is the reaction product of sodium carbonate and SO_2 in the flue gas, is used to dissolve in water and put in calcium hydroxide to desulfurize the sodium sulfite and hydrogen in the circulating water. The calcium oxide reacts to form

sodium hydroxide and calcium sulfite. Through precipitation and separation, the insoluble calcium sulfite can be removed from the circulating water. Sodium hydroxide is easily soluble in water and can be recycled. The desulfurization process only consumes calcium hydroxide^[10].

The calcium-sodium double-subtractive desulfurization technology has the advantages of simple process and low initial investment. At present, more than 80% of ceramic enterprises use the calcium-sodium double-alkali method for flue gas desulfurization. Due to the high oxygen concentration in the flue gas of the ceramic kiln (usually around 16%), it will oxidize part of the Na_2SO_3 in the desulfurization solution and generate Na_2SO_4 , and the Na_2SO_4 cannot be replaced by calcium ions. After multiple cycles, the SO_4^{2-} ion concentration is too high, the peak concentration can reach up to 5000mg/L, which will eventually put a huge pressure on the wastewater treatment of the enterprise.

4.2 Limestone-gypsum flue gas desulfurization

The reaction of the limestone-gypsum flue gas desulfurization process can be roughly divided into two processes: absorption and oxidation. First, limestone powder is added with water to make a slurry, which is pumped into the absorption tower as an absorbent to fully contact and mix with the flue gas to absorb sulfur dioxide to generate calcium sulfite, and then oxidize with the air blown from the lower part of the tower to form calcium sulfate. After calcium sulfate reaches a certain degree of saturation, it crystallizes to form gypsum [11]. The gypsum slurry discharged from the absorption tower is concentrated and dehydrated to make its water content less than 10%, and then sent to the gypsum storage bin by a conveyor for stacking. The flue gas after desulfurization is passed through a mist eliminator to remove droplets, and then heated by a heat exchanger. After the temperature rises, it is discharged into the atmosphere through the chimney [12].

Due to the large initial investment, this method is less applied in the ceramic industry. From the perspective of application effects, this method can meet the requirements of current emission standards, but wet desulfurization has its own flue gas humidity and obvious white fog.

4.3 Semi-dry flue gas desulfurization

The process of semi-dry flue gas desulfurization is a comprehensive process including mass transfer, heat transfer and chemical reaction. The semi-dry desulfurization technology is to spray lime slurry directly into the flue gas, or spray lime powder and soot into the flue after being humidified and mixed to produce a mixture of calcium sulfite, calcium sulfate dry powder and soot. The desulfurization in the wet state is used because the alkaline absorbent hardly reacts with SO_2 under dry conditions, and the desulfurization reaction can only proceed in the presence of water^[13]. In the dry state, the desulfurization product is processed mainly by using the heat of the flue gas itself to evaporate the moisture of the

absorption liquid while the acid-base reaction is proceeding, so that the final product appears in a "dry state".

Semi-dry desulfurization is less used in the ceramic industry due to its low desulfurization efficiency, high calcium-sulfur ratio, uncommercialized by-products, and increased dust removal load. Judging from the operation of a small number of companies that currently exist, due to the low initial SO_2 emission value of the ceramic industry, it can meet the emission requirements of the ceramic industry, and there is no waste water and white smoke generated, which is fully in line with the current environmental protection policy. Therefore, semi-dry desulfurization technology is likely to become the next mainstream technology for desulfurization in the ceramic industry.

5 Conclusion

The calculation and treatment of sulfur dioxide emissions in the waste gas from the production of ceramic products have become an important evaluation element for companies to carry out clean production and green development. Ceramic enterprises can finally meet the requirements of national standards, improve their production methods, and promote the green development of society by analyzing the pollution sources generated by their own sulfur dioxide, choosing correct and reasonable calculation methods, and taking effective waste gas treatment measures.

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