Evaluation and calculation on the source of sulfur dioxide in waste gas of ceramic products manufacturing industry

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Abstract

The purpose of this study was to explore whether the sulfur content in the raw materials could affect the sulfur dioxide production in the exhaust gas produced by the whole system in the ceramic production process. Through the comparison with the proportion of sulfur in the fuel, it can provide the basis for the calculation method of pollution source intensity in the ceramic industry. In this sampling, the samples of construction ceramic enterprises were obtained from Jingdezhen Jin Yitao Company, Jingdezhen Y Company and Jinjiang M Company; the samples of sanitary ceramics were from X Sanitary Ware Company, and the samples of daily ceramics were from Jingdezhen Hongye Ceramics Factory. After familiarizing themselves with the production processes of various ceramic factories, X-ray fluorescence analysis was carried out on the collected samples to obtain the concentrations of sulfur during each transfer process. After understanding the approximate consumption of fuel and raw materials in one production cycle in the first production line, the ratio of total sulfur in the raw materials to the exhaust gas emitted by the whole system and the total sulfur in the fuel to the exhaust gas emitted by the whole system were finally obtained by using the material balance algorithm. The results showed that the calculation results of raw material proportion for the two Jin Yitao were 50.08% and 23.66%, respectively; the calculation results of raw material proportion for the two Y Company were 32% and 33.55%, respectively; the raw material proportion for Jinjiang M Company was 42.01%, the raw material proportion for X Sanitary Ware was 95.32%, the Hongye Ceramic Factory did not discharge sulfur dioxide to the outside, and all sulfur elements were enriched in the products. It was concluded that the influence of sulfur content in raw materials and fuel should be considered for building ceramics. For sanitary ceramics, it was urgent to consider the influence of raw materials; for daily ceramics, sulfur in fuel and raw materials was enriched into products, and sulfur content discharged into flue gas was ignored, so it was not considered.

Keywords Ceramics · Sulfur dioxide · Blank and glaze · Material balance · X ray fluorescence · Percentage

1 Introduction

In the ceramic production process, it is necessary to burn fuel and clay and billets, glazes, etc., and generate a large amount of harmful gases such like CO, SO₂, NO_x, fluoride and soot at high temperatures, while the exhaust emissions are large in ceramic enterprises. The free SiO₂ content is high in air and dust, and the dust dispersion is high in

the exhaust gas. It indicates that the consequences will not be unfamiliar. It could cause air pollution, acid rain, plant failure, etc.; more serious consequences would lead to greenhouse effect, sea level rise, climate anomalies, which is one of the global closely watched question since the industrial revolution [1–3].

SO_x includes SO₂ and SO₃. SO₂ is a colorless and odorous strong irritating acid gas. Its combination with water

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vapor in the air produces sulfurous acid and sulfuric acid which are very hazard for crops, buildings, cultural relics, livestock and other living organisms and humans. According to statistics, 8 of the 10 typical public hazards in the history of the world are caused by the pollution of harmful gases such as SO_2 . At present, the annual losses caused by environmental pollution are as high as several hundred million Yuan in China [4].

There are two sources of sulfur. One is fuel, including solid, liquid and gas, such as coal, gas and heavy oil. The second is sulfurous raw materials such as pyrite (FeS_2) and sulfate in the billet. It is a coal-fired, fuel-fired or gas-fired spray drying tower or ceramic kiln. Because they contain sulfur in the raw materials, they can cause SO_2 emission of atmospheric pollutants during the high-temperature firing of ceramics [5, 6].

(1) Fuel-induced SO_x emissions

SO_x emissions are mainly from the combustion of solid, liquid and gaseous fuels. If coal is used as fuel, sulfur exists in coal in three forms: organic sulfur (combined with C, H, etc., into complex compounds), pyrite sulfur and sulfate sulfur. Sulfate cannot be reoxidized and can be counted as ash. Organic sulfur and pyrite sulfur have a complex reaction form when coal is burned, and eventually almost 100% are converted to SO_x . The release of sulfur during coal combustion can be divided into rapid and slow release. After the coal is sent into the furnace, its structure is destroyed and volatile substances are released as the temperature rises. Most of the FeS and some organic sulfur are released in the form of H_2S and COS [7, 8]. The reaction is as follows:

The remaining small amount of FeS and the formed FeS and part of the organic sulfur remain in the semi-coke, and at the same time, the sulfur released with the volatile matter can also be absorbed by the plastomer formed during the pyrolysis process and converted into organic sulfur to remain in the semi-coke. In addition, a small amount of oxygen diffuses to the coal surface during coal pyrolysis, so that a small amount of FeS and organic sulfur are directly oxidized and released in the form of SO_2 . This stage is a rapid release of sulfur. It is characterized by pyrolysis and oxidized sulfur release is secondary. As the amount of volatiles released decreases, the amount of oxygen diffused to the surface of the coal increases, and FeS_2 , FeS and organic

sulfur in the oxidized semi-coke are released in the form of SO_2 . At this stage, sulfur is mainly used for oxidizing semi-coke, and only about 40% of sulfur is released over a long period of time, which is a slow release of sulfur [9, 10].

The combustion of heavy oil also produces SO_x . The heavy (slag) oil is the residual oil after the crude oil distilled under reduced pressure. The combustion in the ceramic kiln also produces smoke pollution. The high-grade heavy oil has a high sulfur content and also generates harmful gases such as SO_x and black smoke during combustion [11].

The sulfur in the gas exists in the form of hydrogen sulfide and organic sulfur, respectively, and oxidizes to form SO_x when burned at a high temperature. The content of different gas organic sulfur and hydrogen sulfide varies greatly, so the concentration of SO_x pollutants generated during discharge varies greatly [12].

The SO_x content in the flue gas increases significantly as the sulfur content of the fuel increases. Generally, natural gas and liquefied petroleum gas contain little sulfur, while liquid fuels (such as industrial diesel and heavy oil) and water gas (processed from solid coal) have higher sulfur content.

(2) SO_x emissions generated during firing of ceramic raw materials [13].

In recent years, people have gradually realized that in the firing process of traditional ceramics, some sulfur-containing raw materials also cause a large amount of SO_x emissions. A large amount of SO_x emissions in heavy clay plants is caused by the oxidation of pyrite FeS_2 in the raw materials, and the pyrite is oxidatively decomposed between 400 and 600 °C. The decomposition of pyrite proceeds through two stages [14, 15]. Firstly, FeS_2 is oxidized to FeS, and then, FeS is oxidized to Fe_2O_3 .

The reaction process is as follows:

The sulfates contained in the raw materials are also decomposed to produce sulfur dioxide during high-temperature combustion. The reaction equation is:

Among them are RO—CaO, MgO, K_2O , Na_2O , etc.

In the clay system, the initial decomposition temperature of calcium sulfate is 950 °C, magnesium sulfate decomposes above 750 °C, sodium sulfate decomposes between 500 and 600 °C, and potassium sulfate decomposes between 650 and 700 °C. SO_x is not only an

environmental pollutant emitted from the flue gas, but also can cause damage to production when they are circulated in the kiln. For example, when SO_x is combined with H₂O, an acid can be formed which combines with an alkaline element (such as Pb, Ca, Mg, etc.) in a green body (especially glaze) to form a sulfate. Due to the high decomposition temperature of some sulfates, if incomplete or improper decomposition occurs, it may cause defects such as color cast or bubbles on the surface of the bad body (especially glazed) [16–18].

In this study, the strong calculation of sulfur dioxide source in the exhaust pollutants of ceramic industry was taken as the research object, and the influence of sulfur content in the raw material in the ceramic production process on the amount of sulfur dioxide generated in the exhaust gas was investigated, and the sulfur content in the fuel was occupied by the fuel. The comparison of the proportion of total sulfur dioxide emissions in the gas provided a basis for the strong accounting method of sulfur dioxide pollution sources in the ceramic industry. To improve the scientific and accuracy of environmental impact assessment and prediction, we standardized the environmental impact assessment of pollutants in construction projects and further improved the environmental impact assessment technical guidelines system. The experiment conducted on-site investigations and discussions in ceramic enterprises in Jiangxi, Guangdong and Fujian, focusing on the production process of building ceramics, household ceramics and sanitary ceramics, smoke control measures of ceramic enterprises and unorganized emission control measures. We discussed the utilization factors of raw materials, glaze and auxiliary materials, raw material and product standards, drying and firing parameters, kiln activity levels, natural gas or other fuel use, unorganized emission laws, etc. Based on the data related to sulfur dioxide emissions, sampling and sample delivery testing, data collation and processing analysis, this study provides the basis for compiling and forming the “Technical Guide for Pollution Source and Strength Accounting for Ceramic Products” (draft for soliciting opinions) and its preparation instructions and focuses on improving the accounting methods for the source strength of ceramic raw materials and fuels during the combustion process.

The strong accounting methods for pollution sources are mainly considered in the following four perspectives. From the perspective of equipment, we analyzed the production process, discharged characteristics and emission rules of major production equipment for different types of ceramic products and clarified the main production equipment involved in fuel combustion pollution discharge, fuel combustion consumption under different working conditions and pollution-related

conditions (such as temperature), oxygen, etc. From the perspective of industry-based sewage disposal, through the literature, we analyzed typical enterprise fuels and raw materials, the contribution rate of smoke pollutant emissions, one of the main contributors to fuel combustion for kiln and spray drying tower flue gas pollution. From the fuel point of view, we analyzed the types of fuels and energy use, the types of fuels used in spray drying towers and furnaces, the source strength calculation method for fuel combustion links: the classification of solid/liquid/gas fuels when using the material balance algorithm to calculate sulfur dioxide emissions. From the perspective of activity level, this time we strived to find out the characteristics of pollutant discharge in the industry by combining the activity level of each major production equipment (spray drying tower, kiln, gas generator) for ceramic products and achieved establishment to improve environmental quality. It laid a solid foundation for the overall goal of the core source strength, elements and thematic technical guidance system.

2 Materials and methods

2.1 Sample

TC “3.2.1 SiO₂包覆纳米铁制备方法” of C\I “3” On September 25, 2018, the billets, glazes and products of Jingdezhen Jin Yitao Company, Jingdezhen Y Company, Jinjiang M Company, X Sanitary Ware and Hongye Ceramics Factory were sampled, respectively. These samples were tested and analyzed by Huaxia Ceramic Testing Center in Foshan, Guangdong, China.

On December 20, 2018, and on March 4, 2019, the fine coal, coal cinder and slurry of Jingdezhen Jinyitao Company and Jingdezhen Y Company were supplemented and sampled. A total of 6 samples were analyzed and tested in the Building Ceramic Engineering Center in Jingdezhen Ceramic Institute.

On April 4, 3.2019, in the same process of production and time, respectively, 15 samples of coal powder, coal cinder, slurry, glaze and products of Jingdezhen Jin Yitao Company and Jingdezhen Y Company were separately sampled. The same raw materials, process and product conditions were sent to Huaxia Ceramic Testing Center for testing and analysis. On the 12th of the same month, the coal powder, coal cinder and slurry of Jinjiang M Company were sampled in the same process production and time. These sample were tested and analyzed by Huaxia Ceramic Testing Center in Foshan, Guangdong, China. See Tables 1 and 2 for details.

Table 1 Introduction of experiment sample

No.	Company name	Product name	Body glaze ratio	Granulation or firing condition	Firing temperature	Firing cycle
1#	Guangdong, Foshan X Sanitary Ware Co., Ltd. China	Sanitary ceramics	Body: Glaze = 92–93: 7–8 (wt%)	Natural gas for kiln	1280 °C	24 h
2#	Guangdong, Foshan Lihua Building Ceramics Co., Ltd.	Brick	Body: top glaze: polished glaze = 16.5: 0.382: 0.339 (wt)	Coal slurry for spray drying, coal gas for kiln	1215 °C	48 min
3#, 9#	Fujian, Jinjiang M Building Ceramics Co., Ltd.	Brick	Body: glaze = 71:1	Coal for spray drying, Natural gas for kilns	1200 °C	60 min
4#, 8#	Jiangxi, Jingdezhen Jinyi Tao Building Ceramics Co., Ltd.	Brick	Body accounts for 96–96.5% of the product	Pulverized coal direct firing system	1160 °C	75 min
5#	Jiangxi Jingdezhen Ceramics Factory (Hongye Daily Ceramics)	Daily ceramics	Body accounts for 95.5–96% of the product	Natural gas for shuttle kiln,	Plain firing temperature 700 °C, glaze firing 1330 °C, roasting flower temperature 800 °C	
6#, 7#	Jiangxi Jingdezhen Y Company	Wall tiles	Body accounts for 96–96.5% of the product	Spray drying and kiln are used of coal gas,	1190 °C	58 min

2.2 Accounting method

This study does not consider the adsorption–desorption mechanism of sulfur in the spray drying tower or kiln material itself nor determine the actual emission concentration of sulfur.

2.2.1 ContentTC“3.5 不同投加量制备的Fe@SiO₂对Pb²⁺处理的动力学研究”\f C\I“2”

- (1) Coal powder, coal cinder, slurry, billet, glaze and product were tested analytical data;
- (2) Natural gas content according to the requirements of China National Standard GB 17802-1999“Natural Gas” for the second type of gas: sulfur content is 200 mg/m³;
- (3) Jin Yitao direct-fired fine coal containing sulfur amount = $\frac{A}{B} \times 100\%$
A = the amount of sulfur in the burned coal powder = the amount of containing sulfur × 1 – coal cinder containing sulfur amount × 15%. B = the total amount of burned coal powder = 1 – 15%. 15%—the amount of coal cinder;
- (4) The amount of sulfur in the Y Company coal water slurry was similar to that of Jin Yitao coal powder; Water gas sulfur content (mass content) = $\frac{C}{D} \times 100\%$
C = fine coal containing sulfur amount × 1 – coal cinder containing sulfur amount × 15%. D = (1 – 15%) × 2.8. 2.8—1 unit of coal powder produces 2.8 units of water gas;
- (5) According to the formula:

$$\text{ppm} = \frac{24.5}{M} \cdot (\text{mg}/\text{m}^3);$$

24.5—the molar volume of the gas in the new state (L/mol); M—molar mass (g/mol); Converting the water gas mass percentage ppm into a mass concentration kg/m³;

2.2.2 Dosage

- (1) Raw material dosage

The proportion of raw materials and products used by each company was as follows:

Slurry dosage: billet dosage: glaze dosage: product dosage

= 96:96:4:100 (Jin Yitao and Y Company architectural ceramics)
= 93:93:7:100 (X Bathroom ceramics),
= 95.5:95.5:4.5:100 (red leaves household ceramics)

Note: The slurry dried when the sulfur content was measured, so the slurry to blank ratio approximately was 1:1.

- (2) Fuel consumption

- (1) Total energy consumption of spray drying tower and kiln

Table 2 Sample sampling stages

Sampling time	Company	Sample number	Test unit	Test method and standard
September 25, 2018	1#	Injection slurry 1-1	Huaxia Ceramic Testing Center in Foshan, China	Chemical analysis of refractory products by fluorescence analysis (XRF) BS EN ISO 12677-2011
		Glaze 1-2		
		Product 1-3		
	2#	Blank powder 2-1		
		Glaze 2-2		
		Polishing glaze 2-3		
	3#	Product 2-4		
		Blank 3-1		
		Glaze 3-2		
	4#	Product 3-3		
		Blank 4-1		
		Glaze 4-2		
	5#	Protective glaze 4-3		
		Product 4-4		
		Blank 5-1		Total sulfur in coal test methods GB/T 214-2007.
	6#	Burnt body 5-2		
		Glaze 5-3		
December 20, 2018	4#	Product 5-4	Building Ceramic Engineering Center in Jingdezhen Ceramic Institute	Silicate rock test methods (GB/T 14506.28-2010)
		Powder 6-1		
		Glaze 6-2		
March 4, 2019	7#	Product 6-3		
		Slurry		
		Fine coal		
April 4, 2019	7#	Coal cinder	Huaxia Ceramic Testing Center in Foshan, China	Chemical analysis of refractory products by fluorescence analysis (XRF) (BS EN ISO 12677-2011)
		Desulfurization mixed mud cake		
		Coal block for coal gasifier 7-1		
		Gas generator coal cinder 7-2		
		Spray drying tower coal powder 7-3		
		Pray drying tower coal cinder 7-4		
		Slurry 7-5		
		Glaz 7-6		
		Product 7-9		
		Spray drying tower powder 7-7		
		Desulfurization mixed mud cake 7-8		
	8#	Fine coal powder 8-1		Total sulfur in coal test methods (GB/T 214-2007)
		Coal cinder 8-2		
		Slurry 8-3		
		Glaze 8-4		
		Powder 8-5		
		Product 8-6		
April 12, 2019	9#	Spray drying tower powder 7-7		
		Desulfurization mixed mud cake 7-8		
		Fine coal powder 9-1		
		Coal cinder 9-2		
		Slurry 9-3		

Table 3 Calculation basis of ceramic energy consumption

Product type	Kiln type	Total energy consumption (kcal/kg)	Calculated value (kcal/kg)†
Sanitary ceramic daily ceramics	Tunnel kiln	800–1500	1000
	Shuttle kiln	2000–3000	2000
Tile (water absorption rate < 0.5%)	Roller kiln	800–1200	1012
Tile (water absorption rate > 0.5%)			

Table 4 Fuel calorific value

Fuel type	Calorific value range	Calculated value
Fine coal	5000–7000 (kcal/kg)	6000 (kcal/kg)
Water gas	1800–2600 (kcal/m ³)	2595 (kcal/m ³)
Coal water slurry (based on fine coal)	5000–7000 (kcal/kg)	6000 (kcal/kg)
Natural gas	7800–8600 (kcal/m ³)	8000 (kcal/m ³)

1:2 data source—Jin Yitao production actual relevant data

In actual production, 55 kg of fine coal is required for each ton of powder produced in the spray drying tower (the fine coal used in the factory is 5700 kcal/kg), and 2.2 m³ of natural gas/m² building ceramic products is required in the kiln

Product weight: the specification is 600×600 mm², the product weight is 28 kg/m²

The specification is 800×800 mm², and the product weight is 29 kg/m²

The specification is 1000×1000 mm², and the product weight is 30 kg/m²

E.g.: The product is 100 kg, the natural gas required for the furnace is 7.8 m³

Kiln: 3.2–3.5 kg coal/m², taking 3.5, the required amount of coal powder is 12.5 kg

Spray drying tower energy consumption/kiln energy consumption = $5.5 \times 5700 / (7.8 \times 8000) = 5.5 / 12.5 \sim 1:2$

(2) In Table 4, the amount of spray drying tower or kiln fuel = $\frac{\text{corresponding total energy consumption}}{\text{corresponding fuel heating value}} \times 100$

The heat was used to spray the tower fuel according to the empirical value: the heat used in the kiln fuel = 1:2; the detailed process is shown in the note below. Set to 100 kg porcelain, the total energy consumption of each manufacturer = the total energy consumption per unit of the furnace type × 100%, and the total energy consumption of the spray drying tower = $\frac{1}{3} \times$ total energy consumption, the total energy consumption of the furnace = $\frac{2}{3} \times$ total energy consumption;

Table 3 of calculation basis of ceramic energy consumption and Table 4 of fuel calorific value data are derived from actual data related to Jin Yitao production.

2.2.3 Material balance algorithm

When we calculated the SO₂ emission ratio, the transfer process of SO₂ was directly regarded as the transfer process of S. In the calculation, when the generated flue gas was not considered in the desulfurization state, the analysis process illustrated the sulfur balance from the subsystem and the overall system, as shown in Figs. 1 and 2, respectively.

For the construction of ceramics, the process was more complicated. Figures 1 and 2 illustrated the sulfur balance diagram from the two aspects of the subsystem and the whole system. When analyzing the sulfur transfer, it should be noted that the billet was the intermediate produced by the slurry through the spray drying tower instead of raw materials. As for the sanitary ceramics and the daily-use

Fig. 1 Schematic diagram of system sulfur balance

Fig. 2 Schematic diagram of sulfur balance in the overall system

ceramics, the process flow was relatively simple, and only the spray drying tower part needed to be removed, and the blanks only passed through the kiln firing, which affected the sulfur balance, so the blank can be regarded as the raw material. The material balance formula was as follows:

- (1) Sulfur-to-emission ratio in raw materials $= \frac{E}{F} \times 100\%$
 E = amount of sulfur in raw materials = slurry sulfur content $\times$ slurry material + glaze sulfur content $\times$ glaze amount – product sulfur content $\times$ product amount.
 F = total amount of flue gas sulfur produced by spray drying and kiln = slurry sulfur content $\times$ slurry material + glaze sulfur content $\times$ glaze amount – product sulfur content $\times$ product dosage + spray drying tower fuel sulfur content $\times$ spray drying tower fuel consumption + kiln fuel sulfur content $\times$ kiln fuel consumption;
- (2) Sulfur-to-emission ratio in fuel $= \frac{G}{H} \times 100\%$
 G = amount of sulfur in fuel = spray drying tower fuel sulfur content $\times$ spray drying tower fuel consumption + kiln fuel sulfur content $\times$ kiln fuel dosage.
 H = total amount of fumes and sulfur produced by spray drying and kiln = slurry sulfur content $\times$ slurry material + glaze sulfur content $\times$ glaze amount – product sulfur content $\times$ product dosage + spray drying

Fig. 3 Distribution chart of sulfur percentage in the previous stage of experiment

tower fuel sulfur content $\times$ spray drying tower fuel consumption + kiln fuel sulfur content $\times$ kiln fuel consumption

3 Discussion

3.1 Pre-stage results and analysisTC “4.1 TEM, XRD 表征分析”\f C \l “2”

Seventeen samples were analyzed by the China Monitoring Center On September 5–13, 2018; 3 samples of Jin Yitao of building ceramics company were analyzed by the Ceramics University Engineering Center On December 20, 2018 and March 2019, respectively. The calculation results of sulfur emission are listed in Table 5. The distribution chart of sulfur percentage in the previous stage of experiment as Fig. 3.

As can be seen from Fig. 3, for ceramic raw materials (slurry and glaze)

- (1) As for building ceramics, the sulfur content in raw materials has an effect on the proportion of SO_2 emitted into the atmosphere when ceramic floor tiles (the requirement of sulfur content in raw materials is extremely stringent) with water absorption less than 0.5% and ceramic tiles with water absorption greater than 0.5% are burned at high temperature.
- (2) For sanitary ceramics: Although the requirements for ceramic raw materials and glazes were relatively high, the content of sulfur contained was very low, but the fuel used natural gas, so that the content of sulfur in the raw materials accounted for a large proportion of sulfur in the flue gas, which should be considered. The effect of sulfur in the raw materials on atmospheric emissions should be considered, and the experiment is only for Hongye ceramics.
- (3) For daily-use ceramics: Sulfur in the raw materials was all enriched in the product, so it was not discharged into the atmosphere. The experiment was only for the case of Hongye ceramics.

Fuel for building ceramics: spray drying, kiln was used, whether it was fine coal, coal water slurry, coal gas; the fuel part accounted for a large proportion, Jinyi ceramic fuel accounted for 49.92%, Ou Shennuo fuel ratio was 67.22%, and because spray drying towers currently used less natural gas, most of them used fine coal direct burning or coal water slurry, so the impact of S on the flue gas emissions in fuel was also considered.

For sanitary ceramics or household ceramics, since the fuel used in the kiln part was mostly natural gas, the fuel part was not considered.

Table 5 Calculation results of sulfur emission proportion

Company	Item	S content (%)	S mass concentration (kg/m ³)	Dosage	Proportion (%)
4#	Fine coal	0.46			
	Coal cinder	0.128			
	Direct burning fine coal	0.5186		5.7 (kg)	49.92
	Natural gas		0.0002	7.8 (m ³)	
	Slurry	0.028		96 kg	50.08
	Blank powder			96 kg	
	Glaze	0.0917		2 kg	
	Protective glaze	0.1304		2 kg	
	Product	< 0.001		100 kg	
6#	Fine coal	0.22			
	Coal cinder	0.104			
	Water coal slurry	0.2405		6 kg	67.22
	Water gas	0.0859	0.001122	25 m ³	
	Slurry	0.032		96 kg	32.78
	Blank powder			96 kg	
	Glaze	< 0.001		4 kg	
	Product	0.010		100 kg	
2#	Natural gas		0.0002	12.5 m ³	4.68
	Slurry	0.0548		93 kg	95.32
	Glaze	< 0.001		7 kg	
	Product	< 0.001		100 kg	
5#	Natural gas		0.0002	25 m ³	–
	Blank	< 0.001		95.5 kg	–
	Raw billet	< 0.001		忽略不计	
	Glaze	< 0.001		4.5 kg	
	Product	0.00816		100 kg	

3.2 Post-stage results and analysis

Fifteen samples of Jin Yitao and Y Company of building ceramics company On April 4, 2019 and 3 samples of Jinjiang M of building ceramics company on April 12, 2019 were analyzed by Huaxia Ceramic Testing Center in Foshan, China. The calculation results of S on the proportion of emissions are shown in Table 6. The distribution diagram of sulfur proportion in later stage experiment as Fig. 4. As can be seen from Fig. 4, for ceramic raw materials.

Ceramic raw materials (slurry and glaze) for building ceramics: Whether it is a ceramic floor tile with a water absorption rate of less than 0.5% (the requirements for S in the raw material are very strict) or a ceramic tile with a water absorption rate of more than 0.5%, through high-temperature combustion, the S in the raw material discharged to the proportion of SO₂ in the atmosphere has an impact. The sulfur content of the slurry was compared: M > Y > Jin Yitao, while Jinjiang M raw materials accounted for 42.01%, Jin Yitao raw materials accounted for 26.66%, and Y raw materials accounted for 33.55%. The ratio was M > Y > Jin Yitao. Because the M and Jin Yitao ceramic

kiln used natural gas, the sulfur content was very low, so the proportion of raw materials was higher; for building ceramics, no matter whether coal powder, coal–water slurry, or coal-to-gas is used for spray drying and kilns, the fuel component accounts for a larger proportion, with Jinjiang M fuel accounting for 57.99% and Jin Yitao fuel accounting for 73.34%. The proportion of fuel was 66.45%, and since the spray drying tower currently used less natural gas, most of them used fine coal direct burning or coal water slurry, so the influence of sulfur in the fuel on flue gas emissions was also considered.

3.3 Comprehensive analysis

In the early stage of the experiment, the entire process of building ceramic material balance was not fully considered, which led to the long span of the first two experimental periods, so the subsequent experiments were verified as supplementary experiments. The lowest value of raw materials accounted for about 30%, and the highest value was about 50%. As far as the results were concerned, the experimental results of the two-stage

Table 6 Calculation results of sulfur emission proportion

Company	Item	Sulfur content (%)	Sulfur mass concentration (kg/m ³)	Dosage	Proportion (%)
3#	Fine coal	0.68			57.99
	Coal cinder	0.35			
	Direct burning fine coal	0.7382		5.8 (kg)	
	Natural gas		0.0002	7.7 (m ³)	
	Slurry	0.032		98.6	42.01
	Blank	0.1014		98.6	
	Glaze	0.0486		1.4	
	Product	<0.001		100	
4#	Fine coal	0.62			
	Coal cinder	0.228			
	Direct burning fine coal	0.6892		5.7 (kg)	73.34
	Natural gas		0.0002	7.8 (m ³)	
	Slurry	0.0152		96 kg	26.66
	Blank	0.0592		96 kg	
	Glaze	0.0188		4 kg	
	Product	0.0005		100 kg	
6#	Spray drying tower fine coal	0.49			66.45
	Spray drying tower coal cinder	0.32			
	Coal water slurry	0.52		6 kg	
	Gas generator coal block	0.12			
	Gas generator coal cinder	0.21			
	Water gas	0.0372	0.000485	25 m ³	
	Slurry	0.0232		96 kg	33.55
	Blank powder	0.0492		96 kg	
	Glaze	0.0004		4 kg

Fig. 4 Distribution diagram of sulfur proportion in later stage experiment

building ceramics were consistent, that is considering the influence of the sulfur content of the fuel, the influence of the sulfur content of the raw materials must be considered. In the two-stage experiment, the proportion of fuel and raw materials in Jingdezhen Jin Yitao Company fluctuated greatly. The proportion of fuel in

Jingdezhen Y Company was basically the same as that of raw materials.

The main research work of this thesis was to investigate the emission of sulfur dioxide in the atmosphere of different types of ceramics, and compare the effects of sulfur in fuel and raw materials on sulfur dioxide emissions from flue gas. Firstly, we analyzed the production process, discharged characteristics and emission rules of the main production equipment in the manufacture of ceramic products, the contribution rate of fuel and raw materials to the emission of flue gas pollutants, calculated the sulfur dioxide by using the material balance algorithm, and calculated the ratio of the raw materials of the two Jin Yitao (respectively 50.08%, 23.66%). The calculation results of the two Y raw materials were 32% and 33.55%, respectively, Jinjiang M Company accounted for 42.01% of the raw materials, X sanitary ware materials accounted for 95.32%, Hongye Ceramics Factory does not emit sulfur dioxide.

Sulfate in ceramic raw materials (blanks, glazes) decomposes and oxidizes to SO₂ at high temperature, and the green body powder absorbs the sulfur and oxygen

compounds generated during the combustion of the fuel in the hot air furnace in the spray drying tower, and the sulfur-containing compounds are fired in the kiln inside; high-temperature combustion produces SO₂ gas. The SO₂ in the kiln flue gas mainly comes from sulfur-containing fuels (coal, petroleum, etc.) and secondly comes from sulfur-containing impurities in the raw materials. Whether it is domestic or foreign, there is only a qualitative description of the effect of sulfur content in ceramic raw materials and fuels (coal, oil and natural gas) on atmospheric pollutants SO₂. Thus no comparison can be made [19, 20]. Therefore, the following conclusions were drawn:

4 Conclusion

- (1) The raw material proportion for the two Jin Yitao was 50.08% and 23.66% and for the two Y were 32% and 33.55%, respectively; the raw material proportion for Jinjiang M Company was 42.01%, the raw material proportion for X Sanitary Ware was 95.32%, so for building ceramics and sanitary ceramics, it is necessary to consider the effect of sulfur in raw materials and fuels on sulfur dioxide emissions of atmospheric;
- (2) For daily-use ceramics as Hongye Ceramics Factory, since all the sulfur in the raw materials were enriched in the product, they were not discharged into the atmosphere, and there was no need to consider the influence of sulfur in the raw materials and fuel (experiment only for X and Hongye ceramics cases);
- (3) Fuel of for building ceramics, spray drying, kiln, whether it is fine coal, coal water slurry, coal gas, fuel part accounts for a larger proportion, Jinjiang M fuel accounted for 57.99%, Jin Yitao ceramic fuel accounted for 73.34%, Y proportion of fuel is 66.45%, and since the spray drying tower currently uses less natural gas, most of them use fine coal direct burning or coal water slurry, so the influence of S in the fuel on flue gas emissions is also considered. At present, the fine coal direct burning system, gas generator and spray drying tower of the building ceramics factory did not use desulfurization facilities. Only the flue gas of the kiln used desulfurization facilities and can discharge to the standard.
- (4) This study is just a mass balance based on fuel and raw materials characterization, but the gas emissions were not measured and the discussion is not deep enough for instance the mechanisms of sulfur emission-adsorption inside the kiln; these issues are quite complex and need further study.

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Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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