

## Article

# Effect of Metal Oxides and Smelting Dust on SO<sub>2</sub> Conversion to SO<sub>3</sub>

Haipeng Liu, Qin Zhang \*, Hongying Yang, Yanan Wu, Jiacheng Chen and Shen Hu

School of Metallurgy, Northeastern University, Shenyang 110819, China; longfeilhpli@163.com (H.L.); yanghy@smm.neu.edu.cn (H.Y.); wu724553614@126.com (Y.W.); chjch123321@163.com (J.C.); 1871273@stu.neu.edu.cn (S.H.)

\* Correspondence: zhangq@smm.neu.edu.cn; Tel.: +86-0248-3673-932

**Abstract:** The purpose of this study was to investigate the effects of metal oxides and smelting dust on the formation of sulfur trioxide during copper, lead, zinc smelting process and flue. Focusing on the effects of SO<sub>2</sub> concentration, O<sub>2</sub> concentration, and temperature on SO<sub>2</sub> oxidation conversion rate under homogeneous test conditions, and under various metal oxide oxidation conditions, further in dust (mainly electric dust removal ash in copper, lead, zinc smelting process), which were studied by single factor experiment test. The results showed that the effect of heterogeneous catalytic oxidation on SO<sub>2</sub> conversion rate is much greater than that of pure gas phase oxidation. The addition of five pure metal oxides such as Fe<sub>2</sub>O<sub>3</sub>, CuO, Al<sub>2</sub>O<sub>3</sub>, ZnO, and CaO obviously promoted the SO<sub>2</sub> conversion rate under different conditions. At different temperatures, the ability of metal oxides to promote SO<sub>2</sub> conversion is ranked: Fe<sub>2</sub>O<sub>3</sub> > CuO > CaO > ZnO > Al<sub>2</sub>O<sub>3</sub>. The catalytic oxidation of copper, lead, and zinc smelting dust to SO<sub>2</sub> conversion rate was studied, and the conclusion was drawn that the metal oxides that promoted SO<sub>2</sub> conversion rate in copper smelting dust were Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, CaO, and the main substance was Fe<sub>2</sub>O<sub>3</sub>; the metal oxides that promoted SO<sub>2</sub> conversion in zinc smelting dust were Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, CaO, CuO, and the main substances were Fe<sub>2</sub>O<sub>3</sub> and ZnO; the metal oxides that promoted SO<sub>2</sub> conversion rate in lead smelting dust were Fe<sub>2</sub>O<sub>3</sub>. Whether metal oxides or copper, zinc, lead smelting dust in the experiment, Fe<sub>2</sub>O<sub>3</sub> displayed the strongest catalytic oxidation capacity.

**Keywords:** SO<sub>2</sub>; SO<sub>3</sub>; conversion rate; metal oxides; boiler and flue dust



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## 1. Introduction

During the non-ferrous smelting process and flues, it is inevitable that sulfur dioxide (SO<sub>2</sub>) will be generated, together with low levels of sulfur trioxide (SO<sub>3</sub>). While the formation of SO<sub>3</sub> is counter-productive, it not only may cause low-temperature corrosion, but also fireside corrosion if deposits with low melting points are formed [1]. SO<sub>3</sub> will combine with water vapor in the flue to form a sulfuric acid mist. After the flue gas containing sulfuric acid mist is exchanged by the waste heat boiler, the temperature will decrease to produce sulfuric acid, which will cause serious corrosion to the waste heat boiler and the dust collecting equipment. Therefore, the suppression and elimination of SO<sub>3</sub> in flue gas from non-ferrous smelting sources has gradually become an urgent problem to be solved in the development of the industry.

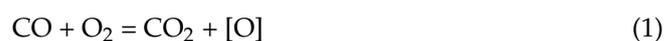
Due to the presence of large amounts of sulfur-containing species in the feedstock, the process of gas in a copper flash smelting heat recovery boiler typically contains around 30 vol pct SO<sub>2</sub>, which can be oxidized to sulfur trioxide (SO<sub>3</sub>) during the process. In addition to the high SO<sub>2</sub> concentration in the flue gas, roughly 5 vol pct H<sub>2</sub>O is also present, reacting with SO<sub>3</sub>, which enables sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) formation under suitable conditions.

Much effort has been made to clarify the SO<sub>3</sub> formation mechanism during the combustion process by both experimental measurement and modeling methods [2–6]. However,

the internal environment of the non-ferrous smelting furnace and flue is more complex, under the combined action of the gas phase composition of the flue gas and the solid phase catalysis of the boiler and flue smoke and dust, a series of physical and chemical changes occur, and some of the SO<sub>2</sub> in the flue gas is gradually converted into SO<sub>3</sub>. In the non-ferrous smelting flue gas treatment system, the SO<sub>3</sub> formation sites are dispersed, the generation routes are diverse, and the generation mechanism is more complex.

SO<sub>3</sub> formation under oxy-CFB combustion conditions was researched and came to the conclusion that N<sub>2</sub> and CO<sub>2</sub> do not change the SO<sub>3</sub> formation levels while the addition of water enhances SO<sub>3</sub> formation. The increased O<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>O concentrations along with increasing temperature are favorable for enhancing SO<sub>3</sub> formation. Fe<sub>2</sub>O<sub>3</sub>, CuO, and V<sub>2</sub>O<sub>5</sub> are able to catalyze SO<sub>2</sub> conversion to SO<sub>3</sub>. Fly ash can either catalyze the SO<sub>3</sub> formation or absorb SO<sub>3</sub>, depending on the temperature and the alkalinity of the ash [7–9].

At present, a generally accepted theory is that the conversion of SO<sub>2</sub> to SO<sub>3</sub> is divided into two processes according to the formation site, one is the smelting process, high-temperature combustion occurs in the smelting furnace, and high-temperature reaction between CO and O<sub>2</sub> in the flue gas occurs, generating atomic oxygen, active atomic oxygen oxidizes SO<sub>2</sub> in the flue gas to SO<sub>3</sub>. The more intense the combustion, the higher the smelting temperature, and the higher the atomic oxygen concentration, the more SO<sub>3</sub> is formed. The reaction process is as follows [10,11]:



where, M is solid-phase metal oxides, in particular, the paper M is Fe<sub>2</sub>O<sub>3</sub>, CuO, CaO, ZnO, Al<sub>2</sub>O<sub>3</sub>, and various smelting dust.

The second part is produced in the waste heat boiler and flue. When smelting flue gas passes through the waste heat boiler and flue, in addition to the SO<sub>3</sub> generated in the early stage, some SO<sub>2</sub> will be gradually converted into SO<sub>3</sub>. Lawrence P. Belo et al. found that SO<sub>2</sub> concentration, O<sub>2</sub> concentration (leakage), temperature, and residence time have a greater impact but have little to do with H<sub>2</sub>O content. Some data indicate that H<sub>2</sub>O combines with free [O] to form [OH], which promotes the adsorption of SO<sub>2</sub> oxidation and reduces the oxidation rate of SO<sub>2</sub>. Related studies show that MeO (Me represents metal) in smelting dust has a significant effect on the oxidation of SO<sub>2</sub>, among which the iron oxides with good effect [12–14] reduction of SO<sub>3</sub> by H-radicals,



and secondary formation of SO<sub>3</sub> via HOSO<sub>2</sub>,



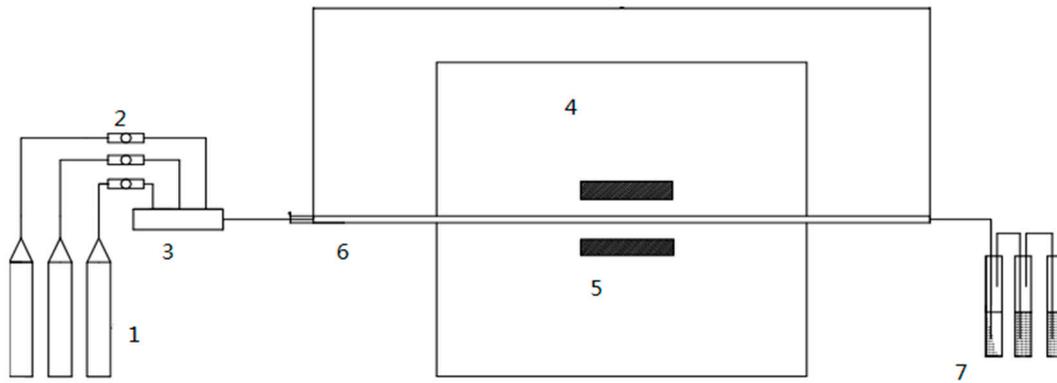
In order to better understand the relationship between the formation of SO<sub>3</sub> and the solid oxides and dust in the non-ferrous smelting flue gas, the following experiments are proposed to provide a helpful theory for reducing SO<sub>3</sub> in the actual production of non-ferrous smelting.

## 2. Experiment and Method

### 2.1. Experiment Setup

The experimental setup mainly consists of 5 parts: gas distribution and gas mixed equipment, reaction equipment, gas absorption apparatus, and detection apparatus. The experimental gas was obtained from the high-pressure gas cylinder gas after passing through the gas distribution system and the gas mixing equipment (automatic concentration gas distribution cabinet, LFIX-6000, Laifeng Technology Co., Ltd, Chengdu, China). The mass

flow meter was used to accurately control the flow rate, and the gas rate of each gas path was adjusted according to the experimental requirements. The reaction equipment (single temperature zone tube furnace, GSL-1200X, Kejing Co., Ltd, Zhenzhou, China) was mainly performing an oxidation reaction of  $\text{SO}_2$ , and mainly consisted of a tube furnace, a quartz tube, and a sealing device. The temperature zone control range was 200~1200 °C, and the temperature control accuracy was  $\pm 1$  °C. The quartz tube used had an inner diameter of 8 mm, an outer diameter of 12 mm, and a length of 1000 mm, as shown in Figure 1.



**Figure 1.** Experiment tube furnace reactor system 1. High-pressure gas cylinders 2. Gas flowmeters 3. Gas mixer 4. Tube furnace 5. Heated zone 6. Quartz-glass reactor 7.  $\text{SO}_3$  Absorbent.

## 2.2. Test Cases

The amount of  $\text{SO}_3$  and  $\text{SO}_2$  present in the hydrogen peroxide solution was quantified through a titration method using barium perchlorate with a thoron indicator, according to the U.S. Environmental Protection Agency method 8A [15].

The detection of sulfate was carried out by absorption of 80% isopropanol solution and titration of the barium–thorium complex. The detailed operation process was as follows: collect the absorption liquid in the absorption bottle of the porous glass plate and the connecting tube between the absorption bottles and record the volume of the solution as  $V_a$  mL. Take 20 mL of the collected absorption solution and place it in a conical flask and dilute it by adding 40 mL of 80% isopropanol solution. First, titrate with a concentration of 0.025 mol/L of strontium perchlorate titration solution. If the titration was finished, it will not change color, or the color change effect will not be obvious. The titration solution concentration was halved, and the above operation was repeated. Take 3 titrations and take the average and record the volume of the titrant consumed as  $V_b$  mL.

Bring the above data into the following formula to obtain the amount of  $\text{SO}_3$  generated in each set of experiments.

$$n_{\text{SO}_3} = c \times b \times \frac{a}{20} \quad (6)$$

where  $n_{\text{SO}_3}$  is the number of moles of  $\text{SO}_3$  produced during the experiment, and  $c$  is the concentration of the titrant used.

Based on the titration results, the amount of  $\text{SO}_3$  produced in each set of experiments was calculated in order to compute the  $\text{SO}_2$  conversion rate. The calculation formula is:

$$\delta = \frac{n_{\text{SO}_3}}{n_{\text{SO}_2, \text{in}}} \times 100\% \quad (7)$$

where,  $\delta$  represents the conversion rate of  $\text{SO}_2$ ,  $n_{\text{SO}_3}$  represents the amount of  $\text{SO}_3$  production, and  $n_{\text{SO}_2, \text{in}}$  represents the total amount of  $\text{SO}_2$  access. Three experiments are performed under each condition. Calculate these average values separately.

### 2.3. Materials

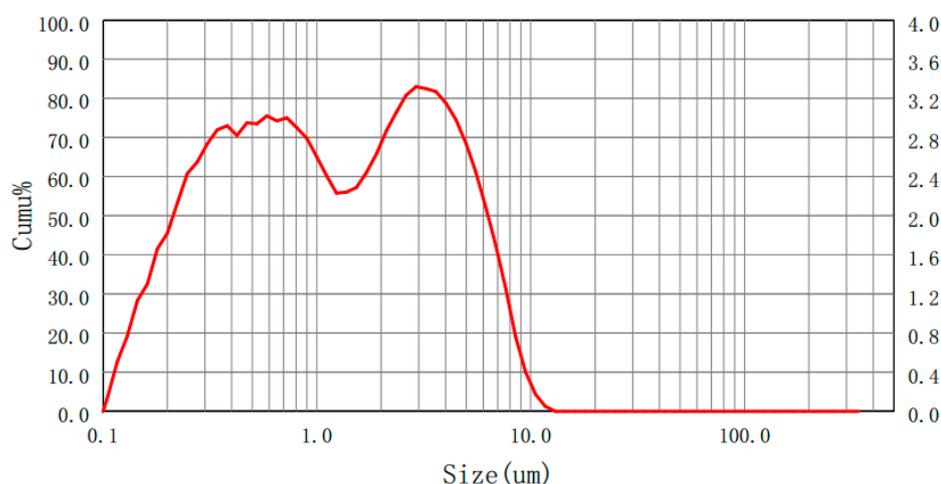
The main reagents used in the experiment were isopropanol, hydrogen peroxide, potassium hydroxide, barium perchlorate trihydrate, thorium reagent, which were all excellent grade purity, from Chinese reagents.

In addition to that high-pressure gas SO<sub>2</sub> (99.9%), O<sub>2</sub> (99.9%), N<sub>2</sub> (99.9%).

For metal oxides, Fe<sub>2</sub>O<sub>3</sub>, CuO, Al<sub>2</sub>O<sub>3</sub>, CaO, ZnO, the physical and chemical character are listed in Table 1, particle size analysis used in experiments by laser particle size analyzer (MS2000, Malvern Instruments Ltd., Malvern, UK). For example, using the laser particle size analyzer to analyze the particle size of Fe<sub>2</sub>O<sub>3</sub>. The analysis result is shown in Figure 2.

**Table 1.** The physical and chemical character of Fe<sub>2</sub>O<sub>3</sub>, CuO, Al<sub>2</sub>O<sub>3</sub>, CaO, ZnO.

Metal Oxides	Median Diameter (um)	Specific Surface Area (m <sup>2</sup> /kg)	97% Granularity (um)	Purity
Fe <sub>2</sub> O <sub>3</sub>	1.105	3580	<7.051	99.0%
CuO	6.190	452.2	<19.5	99.0%
Al <sub>2</sub> O <sub>3</sub>	77.20	38.12	<196.2	99.0%
CaO	55.82	139.7	<187.7	99.0%
ZnO	17.27	698	<112.4	99.0%



**Figure 2.** Particle size analysis of Fe<sub>2</sub>O<sub>3</sub>.

Thus, the Fe<sub>2</sub>O<sub>3</sub> powder particles used in the experiment had a median diameter of 1.105 μm and a specific surface area of 3580 m<sup>2</sup>/kg, of which <7.051 μm particle size accounted for 97%. The same method analyses were used for CuO, Al<sub>2</sub>O<sub>3</sub>, CaO, ZnO, zinc, lead, copper dust, with results listed Tables 1 and 2.

**Table 2.** The composition and physical character of Zinc, lead, copper dust.

Dust	CuO	PbO	ZnO	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	CaO	CdO	Median Diameter (um)	Specific Surface Area (m <sup>2</sup> /kg)	97% Granularity (um)
zinc	9.26	12.28	15.46	3.88	0.81	5.03	0.53		15.06	343.6	<41.06
copper	1.58	2.57	55.16	0.98		10.27	0.92		5.504	1161	<25.56
lead	0.24	37.7	0.31			0.09		22.86	2.294	1768	<5

The copper dust was collected from the electrostatic precipitation of dust to a silver furnace in a smelter in Shandong, the lead and zinc dust were collected from a lead-zinc

smelter in Henan. They were all obtained by on-site sampling. The composition and physical characteristics of zinc, lead, copper dust are listed in Table 2.

#### 2.4. Experiment

There were many factors affecting the formation mechanism of SO<sub>3</sub>, such as the physicochemical effect and interaction of all components in the smoke and dust, and the effects of complex distributed temperature and flow fields, and mass or heat transfer in the gas-solid phase or gas-liquid phase interface. However, the influence on the more significant factors and available conditions such as temperature, main gas phase components, and solid-phase metal oxides, and various smelting dust to SO<sub>2</sub> conversion rate was investigated in the experiment [12,16].

Firstly, a catalytic experimental platform was built, and a single factor experiment was conducted using simulated flue gas. The effects of pure gas phase to SO<sub>2</sub> conversion rate under different conditions were investigated by homogeneous experiments, then the effects of pure metal oxides contained in non-ferrous smelting dust to SO<sub>2</sub> conversion rate were investigated compared to the homogeneous experiments in the same conditions. Secondly, by means of particle size analysis, particle size characteristics of metal oxides and non-ferrous smelting dust were obtained; XRD analysis, elemental quantitative analysis to determine the composition of the non-ferrous smelting dust. Finally, the flue dust was used to carry out the catalytic conversion experiment, the effects of non-ferrous smelting dust to SO<sub>2</sub> conversion ratio were investigated, and a comparison between several metal oxides on the SO<sub>2</sub> convert to SO<sub>3</sub>, and the influence law of several flue dust on the oxidation process of SO<sub>2</sub> was studied.

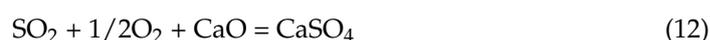
For the above experiment, the effects of temperature, initial O<sub>2</sub> concentration, initial SO<sub>2</sub> concentration, a series of single-factor experimental conditions as follows: temperature range 673~1273 K, assumed total gas flow rate to 200 sccm/min, O<sub>2</sub> concentration in the flue gas to be 40%, N<sub>2</sub> concentration was 40% and SO<sub>2</sub> concentration 20%; when the temperature was 873K, O<sub>2</sub> concentration increased from 2% to 40%, SO<sub>2</sub> concentration was 20%, and N<sub>2</sub> concentration was changed; when the temperature was 873K, in the range of 5~30% SO<sub>2</sub> concentration, O<sub>2</sub> concentration was 40%, and N<sub>2</sub> concentration was changed.

The flue gas components of each group were simulated, and N<sub>2</sub> was used as the balance gas. When investigating the influence on the change of the O<sub>2</sub> or SO<sub>2</sub> concentration on the SO<sub>2</sub> conversion ratio, the other gas fraction was fixed, and the N<sub>2</sub> flow rate was adjusted thus that the total flow rate remained unchanged. Each reaction time was about 10 min.

### 3. Result and Discussion

It is generally believed that the SO<sub>3</sub> in the smelting flue gas is mainly derived from two processes. One is in the melting furnace—high-temperature combustion occurs in the melting furnace, and the CO in the flue gas reacts with O<sub>2</sub> at a high temperature to generate atomic oxygen, and the active atomic oxygen will smoke. The SO<sub>2</sub> in the gas was oxidized to SO<sub>3</sub>. The other is that when smelting flue gas passes through the waste heat boiler and flue, in addition to the SO<sub>3</sub> generated in the early stage, some SO<sub>2</sub> will be gradually converted into SO<sub>3</sub> [17,18].

The possible reactions between SO<sub>2</sub>, O<sub>2</sub> gas phase component and various metal oxides in the smelting flue gas are as follows:

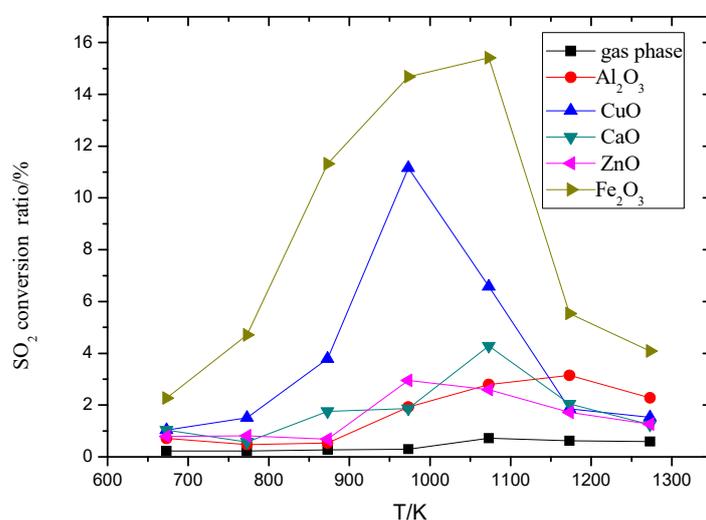




### 3.1. The Influence on Temperature to SO<sub>2</sub> Conversion Ratio

The effect of temperature on the smelting flue gas balance components is obvious. H<sub>2</sub>O will combine with SO<sub>3</sub> to form H<sub>2</sub>SO<sub>4</sub> in smelting flue gas when lower than 773 K. In the range of 673~1273 K, the concentration of SO<sub>2</sub> and O<sub>2</sub> in the smelting flue gas increases with the increase of temperature, and the content of SO<sub>3</sub> decreases gradually. In the range of 1373~1573K, SO<sub>3</sub> is basically absent. This is because the temperature rise promotes SO<sub>3</sub>. The decomposition of SO<sub>3</sub> is substantially completely decomposed into SO<sub>2</sub> and O<sub>2</sub> above 1373K.

In this set of experiments, the total gas flow rate was set to 200 sccm/min, and the O<sub>2</sub> concentration in the simulated flue gas was 40%. The effect of temperature change on SO<sub>2</sub> conversion rate was investigated in the pure gas phase atmosphere and the presence of Fe<sub>2</sub>O<sub>3</sub>, CuO, Al<sub>2</sub>O<sub>3</sub>, CaO, ZnO in the range of 673~1273 K, as shown in Figure 3.



**Figure 3.** The influence of temperature on SO<sub>2</sub> conversion rate for each metal oxide.

The measured SO<sub>2</sub> to SO<sub>3</sub> conversion rate in the different temperatures in Figure 3 showed the SO<sub>2</sub> conversion rate in the presence of metal oxides was higher than that of the pure gas phase homogeneous condition at the corresponding temperature. The later SO<sub>2</sub> conversion rate was relatively low and less variable, lower than 0.8%, while the metal oxides added, the conversion rate significantly increased, which indicates that the metal oxides have a significantly catalytic oxidation effect on its reaction. Even the conversion rate 21 times at the present of Fe<sub>2</sub>O<sub>3</sub> than pure gas phase at 1073 K.

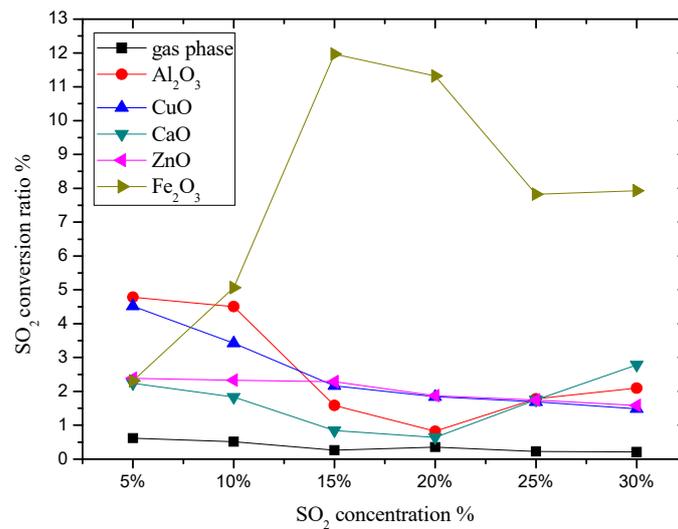
The SO<sub>2</sub> conversion rate former increased and then decreased with the temperature increasing, the peak rate occurred around 973~1173 K, such as Fe<sub>2</sub>O<sub>3</sub> to 1073 K and maximum rate 15.41%; CuO to 973 K and maximum value 11.16%; CaO to 1073 K and 4.28%; ZnO to 773 K and 2.95%; Al<sub>2</sub>O<sub>3</sub> to 773 K and 3.27%.

The ability of metal oxides to promote SO<sub>2</sub> conversion rate at different temperatures was roughly trend ranked: Fe<sub>2</sub>O<sub>3</sub> >> CuO > CaO > ZnO > Al<sub>2</sub>O<sub>3</sub>. The catalytic oxidation strength of the metal oxides was related to the particle size, specific surface area or surface porosity, and its properties. From Table 1, there were minimum particle size and maximum specific surface area to Fe<sub>2</sub>O<sub>3</sub>.

It was reported that the Fe<sub>2</sub>O<sub>3</sub> particle size determines the corresponding temperature when it exhibits the strongest catalytic activity. The peak of the catalytic activity of micron-sized Fe<sub>2</sub>O<sub>3</sub> appears at 923 K, while the peak of the catalytic activity of nanoscale Fe<sub>2</sub>O<sub>3</sub> corresponds to 723 K [19,20].

### 3.2. The Influence on Initial SO<sub>2</sub> Concentration to SO<sub>2</sub> Conversion Rate

The SO<sub>2</sub> concentration in non-ferrous smelting flue gas varied greatly according to different smelting furnace and methods, some were less than 1%, and some were as high as 30%. Thus, the variation of SO<sub>2</sub> conversion rate was investigated SO<sub>2</sub> initial concentration in the range of 5~30% at 873 K in the experiment, and the total gas flow rate was set to 200 sccm/min, and the O<sub>2</sub> concentration in the simulated flue gas was 40%. The measured result is shown in Figure 4.



**Figure 4.** The influence of SO<sub>2</sub> concentration on SO<sub>2</sub> conversion rate for each metal oxide.

The same as temperature, SO<sub>2</sub> conversion rate was also relatively low and less variable with SO<sub>2</sub> concentration increasing, thus the change of SO<sub>2</sub> concentration had no obvious effect on the SO<sub>2</sub> conversion rate under the homogeneous experimental conditions. Different from the conversion polylines of temperature, the rate was found to be gradually decreasing with SO<sub>2</sub> concentration increasing.

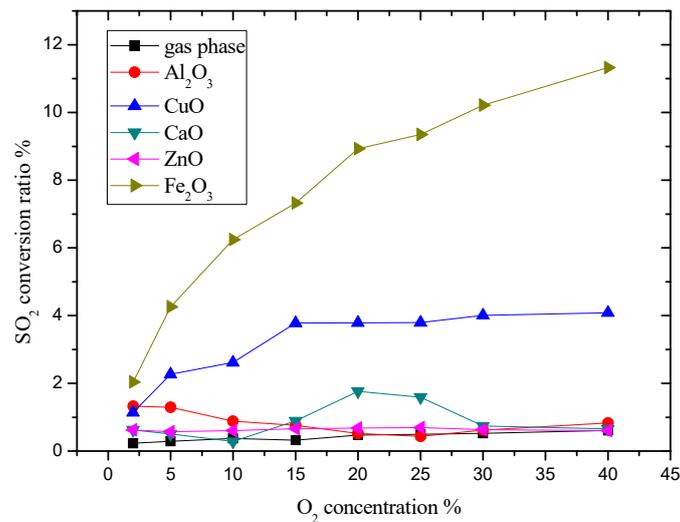
Similarly, SO<sub>2</sub> conversion rate in the presence of metal oxides was higher than that of the pure gas phase homogeneous condition at corresponding SO<sub>2</sub> concentration. While adding the metal oxides, the result of SO<sub>2</sub> conversion rate becomes complicated. For CuO, ZnO, a similar trend of homogeneous experiments was observed in Figure 3, besides, added Fe<sub>2</sub>O<sub>3</sub>, the SO<sub>2</sub> conversion rate former increased and then decreased with the SO<sub>2</sub> concentration increasing, but for CaO, Al<sub>2</sub>O<sub>3</sub>, present the opposite trend. Such as Fe<sub>2</sub>O<sub>3</sub> maximum rate 11.97% at the 15% SO<sub>2</sub> concentration.

The reason for the phenomenon perhaps Fe<sub>2</sub>O<sub>3</sub> had significant catalytic activity to SO<sub>2</sub> converse to SO<sub>3</sub>, but CaO, Al<sub>2</sub>O<sub>3</sub> had a stronger adsorption capacity to SO<sub>3</sub>, forming the CaSO<sub>3</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, decreasing the SO<sub>3</sub> concentration [21,22].

It should be noted SO<sub>3</sub> concentration in the system display generally increasing trend, with SO<sub>2</sub> concentration increasing both the pure gas phase condition and presence of the metal oxides.

### 3.3. The Influence on Initial O<sub>2</sub> Concentration to SO<sub>2</sub> Conversion Rate

Due to different smelting furnace and methods, particularly different working segments in the production process, the O<sub>2</sub> concentration in non-ferrous smelting process varied greatly, such as the rich oxygen smelting process, the O<sub>2</sub> concentration in furnace reached 90%, but the furnace outlet cut down to 3% or less, then it increased even to 40% in the flue. Thus, the variation of SO<sub>2</sub> conversion rate was investigated in the range of 2%~40% O<sub>2</sub> at 873 K in the experiment, and the total gas flow rate was set to 200 sccm/min, and the SO<sub>2</sub> concentration in the simulated flue gas was 20%. The results are shown in Figure 5.



**Figure 5.** The influence of O<sub>2</sub> concentration on SO<sub>2</sub> conversion rate for each metal oxide.

Similarly, O<sub>2</sub> concentration had no obvious effect on the SO<sub>2</sub> conversion rate under the homogeneous experimental conditions, the rate from 0.23% for 2% O<sub>2</sub> to 0.61% for 40% O<sub>2</sub>. Same as above, the added metal oxides significantly improved the SO<sub>2</sub> conversion rate, among Fe<sub>2</sub>O<sub>3</sub>, CuO addition better than others, even 19 times than the pure gas phase condition.

Corresponding to O<sub>2</sub> concentration increase, SO<sub>2</sub> conversion rate increased in the presence of Fe<sub>2</sub>O<sub>3</sub>, CuO. While other metal oxides presented different trends, for CaO, its former increase and then decrease, for Al<sub>2</sub>O<sub>3</sub>, the conversion rate was lower and lower with O<sub>2</sub> concentration increasing, for ZnO, a little change and very small value similar as Al<sub>2</sub>O<sub>3</sub>.

### 3.4. The Influence on Flue Dust to SO<sub>2</sub> Conversion Rate

For the actual production process, in order to reduce the sulfur trioxide (SO<sub>3</sub>) in the flue of the non-ferrous metallurgical production process, the effect on the formation of sulfur trioxide and the strength of catalytic oxidation has to be investigated on the flue dust in the actual production. Thus, collected copper, lead, zinc smelting dust, mainly electrostatic precipitation of dust, particle size analysis, XRD analysis, elemental quantitative analysis, and other means to determine the composition and characteristics of these dust. The composition and physical characteristics of zinc, lead, copper dust are listed in Table 2.

The SO<sub>2</sub> catalytic experiments were carried out on copper, lead, and zinc smelting dust. The effects of different temperatures, different O<sub>2</sub> concentrations, and different SO<sub>2</sub> concentrations on the SO<sub>2</sub> conversion rate were investigated, simultaneously compared with the effects of above the same mass single metal oxidation. The results are shown in Figures 6–8.

Comparing the effects of these three kinds of dust and pure oxide on the conversion rate, it can be seen that the SO<sub>2</sub> conversion rate influence polyline of copper dust was approximately trended to Fe<sub>2</sub>O<sub>3</sub> and CuO but was lower in the 973~1173 K range. The influence polyline of zinc dust was basically the same as ZnO with the increase of temperature below 973 K, but more than 973 K, which was totally different may be the result of various oxides. The effect of lead dust on the conversion rate of SO<sub>2</sub> was relatively flat, which may be due to the fact that the Fe<sub>2</sub>O<sub>3</sub> mainly increasing the SO<sub>2</sub> conversion rate was less.

Above, Figure 7 indicates that the effect of copper smelting dust on SO<sub>2</sub> conversion rate was also mainly Fe<sub>2</sub>O<sub>3</sub> with the SO<sub>2</sub> concentration increasing. In addition, basically same polyline trend as that of Fe<sub>2</sub>O<sub>3</sub> but lower. The other metal oxides influenced polyline below it, and thus have a relatively small effect on SO<sub>2</sub> conversion rate. The effect of SO<sub>2</sub>

concentration on the SO<sub>2</sub> conversion rate to zinc smelting dust was more similar to the ZnO polyline trend but higher, which indicates the catalytic effect of Fe<sub>2</sub>O<sub>3</sub> on SO<sub>2</sub> conversion rate was much stronger than that of ZnO to zinc smelting dust, and thus does lead dust.

For copper dust, the SO<sub>2</sub> conversion rate increased gradually with the O<sub>2</sub> concentration from 2% to 20%, and then gradually decreased with O<sub>2</sub> concentration from 20% to 40%, which indicates the effect of copper smelting dust on SO<sub>2</sub> conversion rate was mainly Fe<sub>2</sub>O<sub>3</sub> and CuO, due to lower effect on the conversion rate with the O<sub>2</sub> concentration increasing to Al<sub>2</sub>O<sub>3</sub> and ZnO, and ignored. Thus, the effect of O<sub>2</sub> concentration on the SO<sub>2</sub> conversion rate to zinc smelting dust was Fe<sub>2</sub>O<sub>3</sub>, which increased with O<sub>2</sub> concentration, similar to the Fe<sub>2</sub>O<sub>3</sub> polyline trend but lower. The effect of lead dust on the SO<sub>2</sub> conversion rate was relatively flat and small.

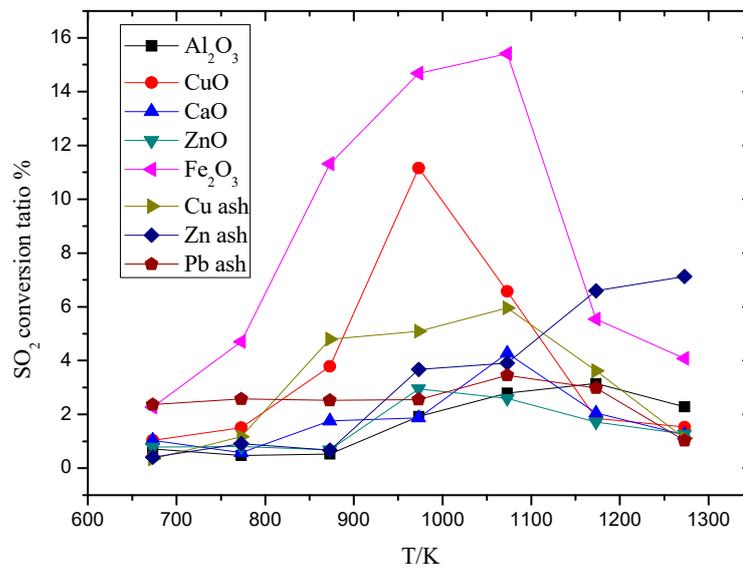


Figure 6. The influence of temperature on SO<sub>2</sub> conversion rate for Cu, Zn, Pb ash.

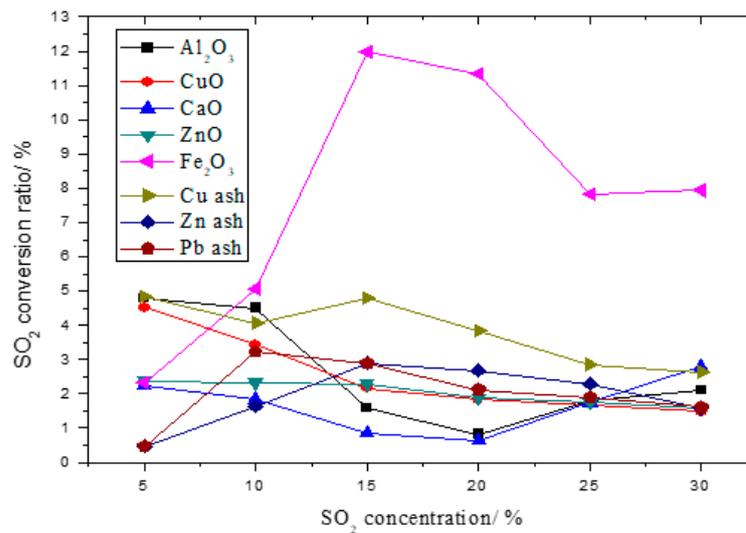


Figure 7. The influence of SO<sub>2</sub> concentration on SO<sub>2</sub> conversion rate for Cu, Zn, Pb ash.

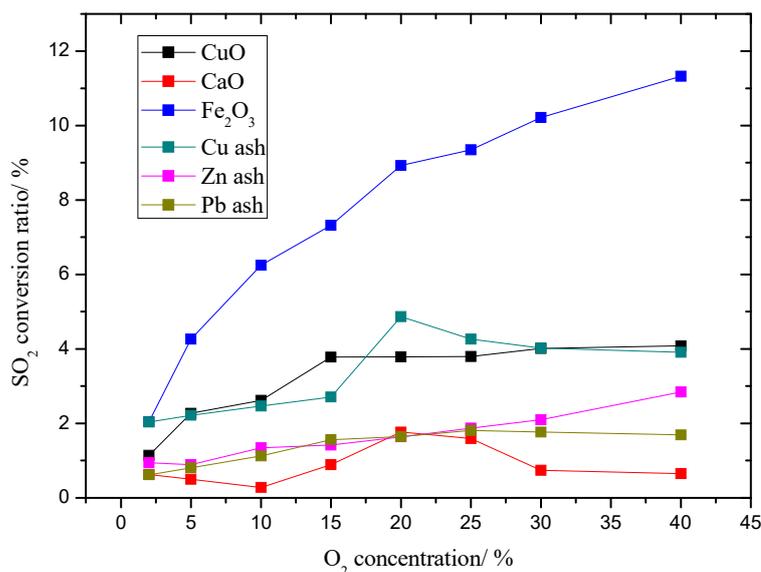
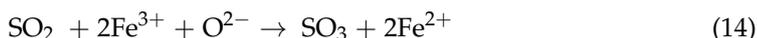


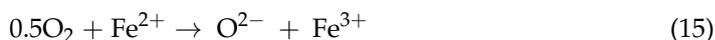
Figure 8. The influence of O<sub>2</sub> concentration on SO<sub>2</sub> conversion rate for Cu, Zn, Pb ash.

Based on the above experimental results and analysis, we can see that the effect of heterogeneous catalytic oxidation on SO<sub>2</sub> conversion rate is much greater than that of pure gas phase oxidation, whether it is metal oxide or various smelting dust, because of providing the large surface area necessary for rapid SO<sub>2</sub> oxidation, and largely enhancing the rate of mass and heat transfer at the metal oxides and dust gas-solid interface [23,24].

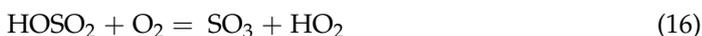
Wherein the above metal oxides and copper, zinc, lead smelting dust, Fe<sub>2</sub>O<sub>3</sub> displayed the strongest catalytic oxidation capacity. The reasons may be as follows [25–28]: first, the catalytic oxidation strength of the metal oxides or smelting dust is related to the particle size, specific surface area or surface porosity, and itself properties, there were minimum particle size and maximum specific surface area to Fe<sub>2</sub>O<sub>3</sub>; second maybe follow reaction involves: (a) absorption of SO<sub>2</sub>, reduction of iron ions from Fe<sup>3+</sup> to Fe<sup>2+</sup>, and formation of SO<sub>3</sub> from SO<sub>2</sub> and O<sup>2-</sup> ions,



and (b) absorption of oxygen, re-oxidation of the iron ions, and formation of O<sup>2-</sup> ions:



third, according to the Xiao research report density, functional analysis found that



is a key step forming SO<sub>3</sub> reaction in the gas phase. The required energy barrier of 187.70 kJ/mol, Fe<sub>2</sub>O<sub>3</sub> for the catalytic reaction of SO<sub>2</sub> is 57.357 kJ/mol. The energy barrier required for the gas phase reaction is much higher than the solid catalytic energy barrier, thus Fe<sub>2</sub>O<sub>3</sub> has a good catalytic effect on the formation of SO<sub>3</sub>, we think that the mechanism of Fe<sub>2</sub>O<sub>3</sub> on the catalytic oxidation of SO<sub>2</sub> is similar to that of V<sub>2</sub>O<sub>5</sub>, but the catalytic ability is not as strong as that of V<sub>2</sub>O<sub>5</sub>, the specific differences need to be further studied.

From the above experimental results, it can be seen that the solid phase metal oxides have a great catalytic oxidation effect on the formation of SO<sub>3</sub> in the non-ferrous smelting fume. Even the amount of SO<sub>3</sub> produced by the trace dust may be tens or hundreds of times than the amount of homogeneous oxidation. While in the actual smelting flue, there are many smoke components, the complex dust composition affects each other, the

temperature and velocity distribution of the flue gas are not uniform, and so on, thus making it difficult to study the generation of SO<sub>3</sub> and reduce its productivity.

The impact of SO<sub>3</sub> generation inside the flue is not just the content involved in this study, and the above studies have considerable limitations simulated flue environment. However, the research involved in this heterogeneous study catalysis of metal oxides in smelting dust is an important factor affecting the generation of SO<sub>3</sub>. A series of experimental results were obtained and enriched basic theoretical research. These have greatly helped to reveal the formation mechanism of SO<sub>3</sub> in the actual smelting flue, laying the foundation for further research.

#### 4. Conclusions

The effect of heterogeneous catalytic oxidation on SO<sub>2</sub> conversion rate is much greater than that of pure gas phase oxidation. The addition of five pure metal oxides such as Fe<sub>2</sub>O<sub>3</sub>, CuO, Al<sub>2</sub>O<sub>3</sub>, ZnO, and CaO can promote the SO<sub>2</sub> conversion rate under different conditions. The ability of metal oxides to promote SO<sub>2</sub> conversion rate at different temperatures is ranked: Fe<sub>2</sub>O<sub>3</sub> > CuO > CaO > ZnO > Al<sub>2</sub>O<sub>3</sub>, and for five metal oxides, the optimum temperature range for SO<sub>2</sub> conversion rate is 973~1173K, particularly for Fe<sub>2</sub>O<sub>3</sub> the SO<sub>2</sub> conversion rate at 1073 K is significantly higher than that of SO<sub>2</sub> under pure gas phase experimental conditions. Under different SO<sub>2</sub> and O<sub>2</sub> concentrations experiment conditions, Fe<sub>2</sub>O<sub>3</sub>, CuO addition to SO<sub>2</sub> conversion rate batter than others, shown obvious catalytic oxidation.

The metal oxides that promote SO<sub>2</sub> conversion rate in copper smelting dust are Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, CaO, and the main substance is Fe<sub>2</sub>O<sub>3</sub>. The metal oxides that promote SO<sub>2</sub> conversion in zinc smelting dust are Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, CaO, CuO, and the main substances are Fe<sub>2</sub>O<sub>3</sub> and ZnO. The metal oxides that promote SO<sub>2</sub> conversion rate in lead smelting dust are Fe<sub>2</sub>O<sub>3</sub>.

Wherein the above metal oxide and copper, zinc, lead smelting dust, Fe<sub>2</sub>O<sub>3</sub> displayed the strongest catalytic oxidation capacity, analyzed the reasons no longer repeat. Thus, reducing SO<sub>3</sub> in flue requires reducing the amount of Fe<sub>2</sub>O<sub>3</sub> or lower O<sub>2</sub> concentration.

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