An experimental study on effect of coke ratio on SO$_2$ and NO$_x$ emissions in sintering process

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Abstract. By using the sinter cup experiment, the effects of different coke ratios of 0%, 25%, 50%, 75%, and 100% on the formation and total emissions of SO$_2$ and NO$_x$ in the sintering process were studied with the Testo350 flue gas analyzer. The experimental results show that the emissions of SO$_2$ and NO$_x$ are closely related to sintering process. With the increase of the coke proportion, the sintering temperature changes and the maximum peak time appears earlier. SO$_2$ concentration has a bimodal distribution and NO$_x$ concentration has a triple peak. Besides, the both maximum peaks appear at the end of sintering. In addition, due to the increasing of the S and N contents in the fuel with the coke ratios from 0% to 100%, the amounts of SO$_2$ and NO$_x$ emissions are raised respectively at 10.82 mg, 11.42 mg, 13.84 mg, 13.69 mg, 20.36 mg and 3.11 mg, 3.39 mg, 4.44 mg, 4.31 mg, 6.16 mg.

1. Introduction
As the two major air pollutants, sulfur dioxide (SO$_2$) and nitrogen oxide (NO$_x$) can lead to the formation of acid rain, haze and photochemical smoke, and can also cause serious harm to human health [1]. SO$_2$ and NO$_x$ in the atmosphere are mainly derived from the combustion of industrial and fossil fuels. Steel industry is one of the most important sources of industrial pollution. There were 820,000,000 tons of crude steel produced in China in the year of 2014, making a year-on-year increase of 0.9%, and accounting for 49.3% of the global crude steel production. The SO$_2$ and NO$_x$ emissions in 2014 were 1.807 million tons and 566,000 tons, i.e. respectively 4% and 7% of the total emissions of industrial source [2]. As an important part during the pollution process of steel enterprises, the emission of SO$_2$ and NO$_x$ in the sintering head flue gas is about 60% and 50% of the total emission in steel production. Therefore, how to reduce the emission of SO$_2$ and NO$_x$ in sintering flue gas is the most important step to control the air pollution in iron and steel industry [3, 4].

Due to SO$_2$ and NO$_x$ in the sintering flue gas mainly come from the S and N in sintering raw materials, it is possible to reduce the content of pollutants in sintering flue gas by means of source reduction, that is, to reduce pollutants in sintering flue gas by controlling the composition of sintering raw materials [5-10]. Through the different proportion of coke, Pan J [11] found that the ratio of coke seriously affected the sulfur removal during sintering and the emission concentration of SO$_2$ in sintering flue gas. When sintering air reached to certain amount, the ratio of coke directly affected the highest temperature level and sintering atmosphere in the sinter layer. By controlling the different ratio of coke that were added, Su Y [12] found in the sintering cup experiment that the content of N in the
mixture increased with the increase of the proportion of coke, and the amount of NO produced by the combustion of coke also increased accordingly.

Among all the sintering raw materials in the fuel, coke and pulverized coal have a higher content of S and N, compared with other sintered materials. Once the ratio between the coke and pulverized coal in the fuel is changed, it would have a direct impact on the content of SO$_2$ and NO$_x$ in the flue gas [13-15]. Due to the deducted cost of coke and its pretty good chemical nature and composition, the use of coke is more conducive to the production of sinter. Therefore, it is important to study the influence of coke on the characteristics of the SO$_2$ and NO$_x$ emission in sintering flue gas.

2. Materials and methods

2.1. Experimental device and sampling equipment

The size of the sinter cup equipment selected in this study was 100 kg/cup, which belonged to pilot scale and had industrial application significance. The sampling point was shown in figure 1.

For the determination of flue gas parameters, such as temperature, O$_2$, SO$_2$ and NO$_x$ content, the Testo350 flue gas analyzer was used in this study. The device was measured by electrochemical sensors, with low detection limits and long-time measurement. Besides, the device had a recording interval of 1 s.

![Figure 1. The schematic diagram of sinter cup system.](image)

2.2. Experimental material

Sintering raw materials included iron powder, coke, pulverized coal and dust removing powder which were taken from a sintering plant of iron and steel enterprise. The proportioning of sinter raw materials was based on actual production. And the carbon content of the sinter fuel, included coke and pulverized coal, were stable at 3.6%, which was also based on actual production. The chemical composition of coke and pulverized coal was shown in table 1.

| Table 1. The industrial analysis of sintering fuels. |
|-----------------------------------------------|
| **Fuel** | C (%) | S (%) | N (%) | Ash content (%) | Ash composition |
|---------|-------|-------|-------|----------------|----------------|
| Coke    | 81.50 | 0.74  | 1.08  | 14.50          | SiO$_2$ 45.00  |
|          |       |       |       |                | Al$_2$O$_3$ 30.00 |
|          |       |       |       |                | CaO 4.00              |
|          |       |       |       |                | MgO 0.60              |
| Pulverized coal | 78.50 | 0.30  | 0.38  | 8.94           | SiO$_2$ 81.54  |
|          |       |       |       |                | Al$_2$O$_3$ 8.95   |
|          |       |       |       |                | CaO 6.82              |
|          |       |       |       |                | MgO 2.68              |

The S content of fuel coke and pulverized coal was 0.74% and 0.30%, respectively. The S content of coke was 2.47 times that of pulverized coal. The N content of fuel coke and pulverized coal was respectively 1.08% and 0.38%. The N content of coke was 2.84 times that of pulverized coal.
2.3. Experimental method
The coke and pulverized coal were used as the sintering fuel, and 5 different coke ratio experiments, i.e. 100%, 75%, 50%, 25% and 0%, were studied. Coke 100%, that was, all sintering fuel using coke. Coke 0%, that was, all sintering fuel using pulverized coal. SO$_2$ and NO$_x$ recorded data from the first 4 seconds of oxygen content in the experiment as a starting point, followed by 40 minutes as the finish line. the amount of coke and pulverized coal in different experimental groups were shown in table 2. The total dry weight of the sinter cup was 80 kg.

Table 2. The proportions of coke and pulverized coal in sintering fuel.

| Experience group | Name            | The mass percentage of sintering raw materials (%) | Dosage (kg) | Total weight (kg) | Carbon content of mixed material (%) |
|------------------|-----------------|-----------------------------------------------|-------------|------------------|-------------------------------------|
| Coke 100%        | Coke            | 4.50                                          | 2.79        | 2.79             | 3.668                               |
|                  | Pulverized coal | 0.00                                          | 0.00        |                  |                                     |
| Coke 75%         | Coke            | 3.38                                          | 2.10        | 2.84             | 3.650                               |
|                  | Pulverized coal | 1.14                                          | 0.74        |                  |                                     |
| Coke 50%         | Coke            | 2.25                                          | 1.40        | 2.89             | 3.639                               |
|                  | Pulverized coal | 2.30                                          | 1.49        |                  |                                     |
| Coke 25%         | Coke            | 1.13                                          | 0.70        | 2.93             | 3.629                               |
|                  | Pulverized coal | 3.45                                          | 2.23        |                  |                                     |
| Coke 0%          | Coke            | 0.00                                          | 0.00        | 3.00             | 3.650                               |
|                  | Pulverized coal | 4.65                                          | 3.00        |                  |                                     |

As the unit of the data collected by Testo350 flue gas analyzer was ppm, the total volume of SO$_2$ and NO$_x$ that was collected during sampling period according to the equipment pump flow and sampling time, could be calculated by the following formula:

$$m_{SO_2\text{or}NO_x} = \int c_i \times M_{SO_2\text{or}NO_x} \times Q \times 1000 \times \frac{22.4 \text{ mol} / L}{dt}$$

In the formula, $m_{SO_2\text{or}NO_x}$ was the SO$_2$ or NO$_x$ collection in the experiment, mg; $c_i$ was the SO$_2$ or NO$_x$ concentration in the collected flue gas, ppm; $M_{SO_2\text{or}NO_x}$ was SO$_2$ or NO$_x$ of the molar mass, g/mol; $Q$ was the equipment pump flow, L/s; $t$ was the time, s.

3. Results and discussion

3.1. The influence of coke ratio upon SO$_2$ emission
As the ratio of coke was changed, the content of S in the fuel would be changed. The specific change was shown in table 3.

Table 3. The S content in sintering fuels and total SO$_2$ emissions.

| Experience group | S content in fuel (g) | Compare with coke 100% total S content | Amount of SO$_2$ (mg) | Compare with coke 100% total SO$_2$ emissions | Flue gas temperature (°C) |
|------------------|-----------------------|----------------------------------------|-----------------------|---------------------------------------------|--------------------------|
| Coke 100%        | 20.65                 | 1.00                                   | 20.36                 | 1.00                                        | 351                      |
| Coke 75%         | 17.76                 | 0.86                                   | 13.69                 | 0.67                                        | 375                      |
| Coke 50%         | 14.83                 | 0.71                                   | 13.84                 | 0.67                                        | 314                      |
| Coke 25%         | 11.87                 | 0.57                                   | 11.42                 | 0.56                                        | 306                      |
| Coke 0%          | 9.00                  | 0.43                                   | 10.82                 | 0.53                                        | 340                      |
As seen from table 3, the SO$_2$ in the flue gas emissions increased with the increased coke ratio, which was consistent with the fact that the S content in the fuel grew with the improvement of coke ratio in the fuel.

![Figure 2](image-url)  

**Figure 2.** The emission concentration of SO$_2$ in each experimental group.

In the sintering cup experiment, the emission rate of SO$_2$ had two peaks, and the maximum discharge occurred in the second peaks in figure 2. After the initial ignition, the first peak of SO$_2$ emission would appear, which was mainly because the over wet zone had not been fully formed, and the absorption of SO$_2$ was weak. SO$_2$ was produced by the oxidation and decomposition of sulfides at the upper part of the sinter cup, resulting in a lower peak in this stage. In the subsequent sintering process, the SO$_2$ in the flue gas was basically maintained at a relatively steady content. At the end of the sintering process, the second peaks appeared. It was due to the disappearance of the wet band and the release of all the SO$_2$ absorbed by the wet band. The sintering desulfurization process was basically an oxidation reaction, which meant the process of sulfide oxidation decomposition and SO$_2$ desorption and diffusion. The change of coke ratio changed the S content in the sinter so that the SO$_2$ emission in the sintering process was also affected.

The relationships of O$_2$ content, flue gas temperature and SO$_2$ emission concentration were shown in figure 3. The oxygen content dropped sharply from the ignition and maintained a low content level during the ignition stage (Stage I). At the end of the ignition stage, the sintering material began to make self combustion and the sintering reaction occurred. At this time, the oxygen content was lifted and maintained at a certain level. At this stage, the flue gas temperature increased slowly (Stage II). At the end of the material combustion, the oxygen content grows significantly, the flue gas temperature also went up rapidly, and the maximum peak value of SO$_2$ emission occurred (Stage III). At the end of the sintering process, the oxygen content was restored to the air level, the flue gas temperature dropped slowly after the peak, and the SO$_2$ emission declined sharply after the peak value. When oxygen content and gas temperature reached peak value, SO$_2$ emission would disappear (Stage IV). With the increase of the proportion of coke, the combustion performance of the sintered material was improved, and the second peak of the SO$_2$ emission came earlier. It accorded with the change between oxygen content and flue gas temperature.

**3.2. The influence of coke ratio upon NOx emission**

If the ratio of coke changed, the content of N in the fuel would change too. The detailed information about the change was shown in table 4.
Figure 3. The relationship of O$_2$ content, flue gas temperature and SO$_2$ emission concentration.

Table 4. The N content in sintering fuel and total NO$_x$ emissions.

| Experience group | N content in fuel (g) | Compare with coke 100% total N content | Amount of NO$_x$ (mg) | Compare with coke 100% total NO$_x$ emissions | Flue gas temperature (℃) |
|------------------|-----------------------|---------------------------------------|-----------------------|-----------------------------------------------|----------------------------|
| Coke 100%        | 30.13                 | 1.00                                  | 6.16                  | 1.00                                          | 351                        |
| Coke 75%         | 25.49                 | 0.84                                  | 4.31                  | 0.70                                          | 375                        |
| Coke 50%         | 20.78                 | 0.68                                  | 4.44                  | 0.72                                          | 314                        |
| Coke 25%         | 16.03                 | 0.53                                  | 3.39                  | 0.55                                          | 306                        |
| Coke 0%          | 11.40                 | 0.37                                  | 3.11                  | 0.50                                          | 340                        |
Figure 4. The emission concentration of NO\textsubscript{x} in each experimental group.

As shown in table 4, as the NO\textsubscript{x} in sintering flue gas was mainly fuel type NO\textsubscript{x} (mainly based on NO\textsubscript{a}, accounting for about 90%), the change trend of total NO\textsubscript{x} emission in flue gas was the same as that of SO\textsubscript{2}. The NO\textsubscript{x} in the flue gas emissions would increase when the coke ratio was improved, which was consistent with the increase in N content in the fuel.

At the initial stage of ignition, the N elements in the fuel were burnt and oxidized to produce NO\textsubscript{x}. The NO\textsubscript{x} content in the flue gas increased rapidly, which made the NO\textsubscript{x} emission reach the first peak value in figure 4. At the end of the ignition, the self-combustion of sintering material began and the sintering reaction took shape. In the initial stage, the surface temperature of the material layer was relatively low, the combustion efficiency declined, and the suction pressure of the exhaust fan was reinforced. In a given unit time, the air concentration through the material layer is increased so that the concentration of NO\textsubscript{x} was reduced. As the sintering reaction continued, the temperature of the material layer was raised rapidly, and the combustion band became dramatically wide, resulting in a dramatic increase in the amount of NO\textsubscript{x}. Therefore, the concentration of NO\textsubscript{x} had a significant increase in a short time, and the second peak came into being. Afterwards, the concentration of NO\textsubscript{x} decreased and fluctuated in a steady range. As the sintering process approached the end, the width of the combustion zone reached its maximum and then narrowed rapidly until the end of sintering. During such process, the third peak value of the NO\textsubscript{x} emission occurred and then dropped sharply until its disappearance.

The relationships of O\textsubscript{2} content, flue gas temperature and NO\textsubscript{x} emission concentration were shown in figure 5. In the sintering cup experiment, the emission rule of NO\textsubscript{x} was closely related to that of oxygen content. At the end of the ignition stage, the sintering material began to make self combustion and the sintering reaction happened. When the oxygen content was improved, the second peak value of NO\textsubscript{x} appeared (Stage II). Afterwards, the oxygen content maintains at a certain level. At this stage, though NO\textsubscript{x} emission decreased sharply, it indeed stayed within a certain range (Stage III). After the combustion of raw materials, the oxygen content was increased significantly, the flue gas temperature went up rapidly, and the maximum peak value of NO\textsubscript{x} emissions appeared (Stage IV). At the end of the sintering process, the oxygen content was restored to the air level. Moreover, the flue gas temperature dropped slowly and the NO\textsubscript{x} emission was reduced sharply after the peak value. When oxygen content and gas temperature reached peak value, NO\textsubscript{x} emission almost came to its end (Stage V). With the increase of the coke proportion, the third peak (the maximum emission) of NO\textsubscript{x} appeared earlier than before. Such phenomenon was the same as that of SO\textsubscript{2}. 
4. Conclusions
(1) The total emission of SO$_2$ increased with the increase of the coke proportion, which was consistent with the increase of S content in the fuel. Since the over humid zone had a strong absorption effect on SO$_2$, the concentration of SO$_2$ showed a typical bimodal state, and the maximum emission began in the second peaks. With the increase of the coke proportion, the combustion performance of sintered material was improved, and the second peak value of SO$_2$ emission came earlier.
(2) In sintering flue gas, NO\textsubscript{x} was the mainly fuel type NO\textsubscript{x}. The total emission of NO\textsubscript{x} increased with the increase of the coke proportion, which was consistent with the increase of N content in the fuel. NO\textsubscript{x} concentration showed three peaks. With the increase of the proportion of coke, the third peak of NO\textsubscript{x} came earlier, which was the same as that of SO\textsubscript{2}.

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