Behavior of $\text{SO}_2$ in the Process of Flue Gas Circulation Sintering (FGCS) for Iron Ores

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(Received on May 3, 2013; accepted on August 12, 2013)

In order to reduce $\text{SO}_2$ emission in the iron sintering process, the flue gas circulation sintering (FGCS) process has been recommended and put into practice. In this process, flue gas containing low $\text{SO}_2$ concentration is recirculated to the sintering process, achieving the concentration of $\text{SO}_2$ content in the off-gas, which is favorable for current flue gas desulphurization processes. In this study, $\text{SO}_2$ behavior in different sintering zones was investigated under the simulated experimental conditions. In the moisture condensation zone and sinter mixture zone, $\text{SO}_2$ of recirculated flue gas is absorbed by the moisture and slaked lime of sinter mixture; in the drying and preheating zone, part of $\text{SO}_2$ in circulating flue gas is absorbed by dry slaked lime in sinter mixture under low temperature conditions, and $\text{SO}_2$ is generated by oxidation of sulfides and re-released by decomposition of sulphurous acid; in the hot zone, $\text{SO}_2$ in circulated gas is partially absorbed by the molten phases, newly crystallized minerals such as calcium ferrite and dissociative CaO; in sinter zone, part of $\text{SO}_2$ is absorbed by residual CaO in sinter under the condition of humid circulated flue gas, which results in unfavorable increase of residual S in the up layer sinter.

KEY WORDS: iron ore sintering; flue gas circulation process; $\text{SO}_2$ emission; desulphurization.

1. Introduction

In the first decade of the 21st century, the global steel production has experienced the second high-speed growth period, the production of crude steel increases from about 800 million t/a in 2000 to 1 527 million t/a in 2011.1) However, the environmental issues of the iron and steel industry become increasingly serious. The most prominent ones are the off-gas emissions from the sinter strands which contain particulates such as dust, heavy metals, etc.2,3) $\text{SO}_2$ emission from iron ore sintering accounts for about 70% of the total $\text{SO}_2$ emission in the iron and steel industry.4,5)

Generally, sulfur appears in the form of sulfide and sulfate ($\text{FeS}_2$, $\text{CuFeS}_2$, $\text{CaSO}_4$, $\text{MgSO}_4$, etc.) in the raw iron ores, and in the form of elemental sulfur or organic sulfur in solid fuels. In the sintering process, more than 90% sulfur in raw materials releases and enters into flue gases in the form of $\text{SO}_2$.6,7) In the conventional sintering process, behavior of $\text{SO}_2$ during the sintering can be described as being generated, absorbed and re-released.8) $\text{SO}_2$ is mainly generated by the oxidation of element sulfur and sulfides in the drying and preheating zone and by the sulfate decomposition in the hot zone. $\text{SO}_2$ is absorbed by alkaline substances and liquid-state water of sinter mixture in the sinter mixture zone and moisture condensation zone, after that, the release of $\text{SO}_2$ occurs due to drying and preheating.9) The flue gas of iron ore sintering is characterized by large quantity (4 000–6 000 m$^3$/t-sinter), high temperature (120–180°C), high dust emission, high moisture content (about 10%), as well as low $\text{SO}_2$ content (it is generally 400–1 500 mg/Nm$^3$).10)

Primary measures for reducing $\text{SO}_2$ emission include utilization of raw materials with low sulfur content, minimizing fuel consumption (mainly coke breeze) and increasing the sulfur uptake in the sinters. Flue gas desulphurization (FGD) processes are other effective ways to reduce $\text{SO}_2$ emission and wildly used in coal fired power plants presently, such as wet FGD (lime-gypsum process, $\text{Mg(OH)}_2$ process, etc.), dry FGD (regenerative activated carbon process, etc.), and semi-dry FGD (circulating fluidized beds process, MEROS process, etc.).11–15) However, many issues still exist as current desulfurization technologies are characterized by giant investment for equipments, heavy operating cost and low desulfurization efficiency because of low $\text{SO}_2$ concentration in the conventional sintering process.

An innovative flue gas circulation sintering (FGCS) process was initially put forward to reuse sensible heat in the exhaust gases from the sintering machines. The sensible heat is transferred directly back to the sinter bed by the hot recirculated gases.16–18) It not only takes advantage of sensible heat in exhaust gas by combustion of CO at the front of flame, resulting in reducing the sintering fuel consumption, but also significantly decreases atmospheric pollutant emissions. In addition, during the FGCS process, $\text{SO}_2$ content in the flue gases obviously increases, which exerts positive effect on the subsequent flue gas desulphurization.19) However, there is lack of researches on behaviors of $\text{SO}_2$ during this process. The purpose of this study is to reveal the behavior of $\text{SO}_2$ in different zones of sintering bed for FGCS process and its effects on the production and quality to fin-
ished sinter by simulated experiments in the laboratory.

2. Results and Discussion

2.1. Absorption of SO₂ by Raw Materials

In the conventional sintering process, most of SO₂ in flue gas from upper sintering bed is absorbed by alkaline substances and moisture in the sinter mixture. After that, the absorbed SO₂ re-releases from sinter mixture by drying and preheating. During the FGCS process, SO₂ content in circulated flue gas is much higher than that of air sucked in the conventional sintering process, which results in the increase of SO₂ content in the flue gases after going through the sintering bed. The absorption of SO₂ by the sintering materials is studied by simulated experiments firstly.

The schematic diagram of main equipments in this experiment is presented in Fig. 1. The composition of inlet gas was controlled by adjusting the flowmeters of gas cylinders. SO₂ content was fixed at 1 850 ppm which is generally the highest content of the conventional sintering process, with a total inlet gas flow rate of 5.0 L/min. The inlet gas was led into a cylindric reactor with 28 mm in diameter after mixing thoroughly. The materials were charged into the reactor to a bed height of 50 mm. A metallic sieve was installed at the bottom of reactor to block fine particles and make sure inlet gas pass through evenly. Gas composition analyzer of DELTA 65-3 type and Vario Plus enhanced analyzer (MRU, Germany) were used. The off-gas was treated by Ca(OH)₂ solution to absorb the residual SO₂ before emission into the air.

Firstly, variation of SO₂ content is recorded when SO₂ goes directly through reactor without materials as a reference. Absorption content of SO₂ is expressed as the difference of SO₂ content between the reference and those with materials filled in the reactor. Thus, absorption content of SO₂ can be calculated as follows:

\[ C_a = C_0 - C_1 \]

Where: \( C_a \) is absorption content of SO₂ by materials filled in the reactor, ppm; \( C_0 \) is the content of SO₂ in the reference experiment, ppm; \( C_1 \) is the instant content of SO₂ in off-gas after absorption by raw materials, ppm. The total absorption amount of SO₂ within the absorption time is obtained by integrating the curve of instant SO₂ absorption content versus absorption time.

2.1.1. Absorption of SO₂ by Individual Dry Raw Material

In the sintering process, sinter mixture will be dried by hot flue gas coming from the upper sinter bed at all time and the flue gas containing SO₂ always passes through the dried sinter mixture. In this section, absorption of SO₂ by individual dry sinter material including iron ore, fluxes, fuel, etc. was studied initially. Raw materials were dried in the oven at 105°C for 4 h before being filled into the reactor. The results of SO₂ content absorbed by different dry raw materials are presented in Fig. 2.

It can be seen that SO₂ is slightly absorbed by iron ore, dolomite, limestone, coke breeze and burnt lime respectively and the total absorption contents of SO₂ for 10 min are less than 200 ppm. However, when the reactor was filled with dry slaked lime, the absorption content of SO₂ increases dramatically in the first 2 min, and then decreases, its total absorption content of SO₂ for 10 min is as high as 2 269 ppm. Therefore, it can be concluded that dry slaked lime is capable of absorbing a larger number of SO₂ than other dry materials, the reason may be mainly attributed to the reaction between Ca(OH)₂ and SO₂.

2.1.2. Absorption of SO₂ by the Wet Raw Materials

Moisture plays an important role in the granulation of the sinter mixture and heat conducting during the sintering process. The moisture content of the original sinter mixture is generally about 8.0%, while in the moisture condensation zone, the moisture content of the sinter mixture increases significantly, even exceeds 12%.16)

2.1.2.1. Absorption of SO₂ by the Wet Iron Ore

Absorption content of SO₂ by the iron ore with different moisture content in the absence of burnt lime was studied and the results are shown in Fig. 3. Moisture content of iron ore mixture was 0%, 6%, 8%, 10% and 12%, respectively. The results indicate that the absorption content of SO₂ by humid iron ore increases with the increase of moisture in iron ore mixture. The total absorption content of SO₂ reaches 640 ppm and 1 720 ppm when the moisture varies from 6% to 12% respectively. The reason is that SO₂ easily dissolves in moisture and reacts with water to form sulfurous acid.

2.1.2.2. Absorption of SO₂ by the Wet Slaked Lime

Experimental results mentioned above reveal that the dry slaked lime and moisture in the mixture are two major factors affecting the absorption of SO₂. The effect of slaked
lime with a certain moisture on the absorption of SO2 was further studied. The absorption tests were carried out by varying the moisture content from 0% to 12% and the results were shown in Fig. 4.

As observed from Fig. 4, the absorption content of SO2 increases with increasing the moisture content of the slaked lime. And the total absorption contents of SO2 achieving 2269 ppm, 4203 ppm, 4588 ppm, 5234 ppm and 5577 ppm are obtained, respectively. Compared with the absorption content of SO2 for the dry slaked lime, absorption contents of SO2 in the presence of moisture increase obviously. It indicates that humid slaked lime significantly enhances the SO2 absorption by the mixture. This is mainly attributed to the formation of H2SO3 and CaSO3/CaSO4 in accordance with the following reactions.

\[ \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_3 \] \hspace{1cm} (1)

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \] \hspace{1cm} (2)

\[ \text{Ca(OH)}_2 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O} \] \hspace{1cm} (3)

\[ \text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3 \] \hspace{1cm} (4)

\[ \text{CaO} + \text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4 \] \hspace{1cm} (5)

\[ \text{Ca(OH)}_2 + \text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4 \cdot \text{H}_2\text{O} \] \hspace{1cm} (6)

2.1.2.3. Absorption of SO2 by the Sinter Mixture

In this study, sinter mixture with basicity (R=CaO/SiO2) of 2.2 was consist of iron ores, 5.5% basic fluxes and 4.5% coke breeze. Extra water was added eliminating theoretical requirement for slaking burnt lime when adjusting the moisture of sinter mixture. And sinter mixture was obtained by mixing these raw materials manually.

The absorption contents of SO2 by the sinter mixture with different moistures are given in Fig. 5. Moisture of the sinter mixture varied in the range of 0% and 12%. As can be seen from Fig. 5, the absorption of SO2 is slight when moisture content of sinter mixture is 0%, but it increases gradually with the increase of moisture content in the sinter mixture. The total absorption contents of SO2 are changed from 258 ppm to 1211 ppm when the moisture varies from 0% to 12% respectively.

Thus, it can be concluded that the absorption of SO2 mainly depends on slaked lime when the moisture of the sinter mixture is 0%, resulting in slight absorption content as slaked lime has the best SO2 absorption ability than other dry raw materials. Increasing the moisture content of the sinter mixture, burnt lime will firstly be slaked which brings about high SO2 absorption content because slaked lime absorbs SO2 dramatically. Moreover, SO2 easily dissolves in free water of sinter mixture forming sulfurous acid and the interaction between water and slaked lime enhance SO2 absorption tremendously. As a result, the absorption content of SO2 increases obviously with the increase of moisture content in the sinter mixture.

From the results discussed above, it can be concluded that SO2 exists in circulated flue-gas can be absorbed by certain materials in the sinter mixture, especially slaked lime and moisture. Therefore, part of SO2 during the FGCS process will be absorbed, enriched and re-released when low SO2 content flue-gas is recirculated to the sinter bed, which is beneficial for the concentrative emission of SO2.

2.2. Absorption of SO2 in the Hot Zone

In the conventional sintering process, the hot zone (temperature between 1100°C and 1400°C) can be divided into two stages. The first stage is the generation of SO2 and molten phases due to coke breeze high-intensity combustion accompanying with rapid increase of temperature. The second stage is the cooling process with crystallization of molten phase and formation of some new minerals as temperature decreases due to sucked fresh air. In the FGCS process, the
former stage is the same even though the recirculated gas contains SO₂. But the latter one is obviously different as SO₂ in the recirculated gas may be absorbed during the cooling process by the molten phases, newly crystallized minerals such as calcium ferrite and dissociative CaO.

In this section, to simulate the absorption of SO₂ in the cooling process, micro-sintering method was adopted using hematite ore as raw material. The chemical composition of hematite ore is given in Table 1. First, hematite ore and pure calcium oxide (CaO) were ground to 100% passing through 0.074 mm. Then, the ground iron ores and CaO were dried in an air-oven at 120°C for 8 h and mixed thoroughly with a certain proportion. About 2.0 g mixture with the basicity (CaO/SiO₂) of 2.5 and 10% of moisture was agglomerated to be a cylindric briquette with 10 mm in diameter under the pressure of 10 MPa. The briquette was dried in air and put in a corundum boat, then roasted in a horizontal electric tube furnace which is electrically heated. The schematic diagram of micro-sintering equipment is shown in Fig. 6. The boat carrying the briquettes was pushed into the electrically heated pipe furnace from the pipe orifice to the sintering zone after reaching certain temperature. O₂ content in the inlet gas was fixed at 18%, gas flow rate was 5.0 L/min, and roasting time was 5 min. The mixed gas containing SO₂ was only let into the tube during the 5 min. After being roasted at given temperature for certain period, the briquettes were cooled to room temperature for 10 min under N₂ atmosphere, then discharged from the furnace. SO₂ contents of the inlet gas were 0 ppm, 500 ppm, 6000 ppm, respectively. The effects of roasting temperature representing the temperature of molten phases in the hot zone on residual sulfur content were studied. The residual sulfur content in the cooled briquettes was analyzed after roasting.

Roasting temperature has a significant impact on the residual sulfur contents in the roasted briquettes. The results in Fig. 7 indicate that the sulfur content increases with the decrease of temperature from 1325°C down to 1200°C. When SO₂ content in the inlet gas is 500 ppm, the residual sulfur content of briquette is about 0.05%. Increasing the SO₂ content to 6000 ppm, the residual sulfur content remarkably increases up to 0.42% at 1200°C. Therefore, the sulfur content of roasted briquettes would be enriched with higher SO₂ content in the inlet gas. And SO₂ will be absorbed by newly crystallized minerals or dissociative CaO along with the temperature decreases in the practical FGCS process.

### 2.3. Characterization of SO₂ in Simulated FGCS Process by the Sintering Pot

The experiments and discussion above mainly reveal the behavior of SO₂ during FGCS process. To verify the results obtained from above simulated tests, sintering experiment was carried out by using the sintering pot in laboratory with different contents of SO₂ in circulating flue gas, and the residual sulfur content in the finished sinter and the emission of SO₂ in the off-gas in FGCS process were analyzed.

#### 2.3.1. Raw Materials

Raw materials used in the sintering tests include iron-bearing materials (iron ore fine and return fine) and basic fluxes (limestone, dolomite and burnt lime). The chemical compositions of raw materials are shown in Table 2. The proximate analysis of coke breeze is shown in Table 3. And the theoretical chemical composition of finished sinter is shown in Table 4.

#### 2.3.2. Method

Sinter mixture consists of the raw materials above under...
certain proportion with basicity fixed at 2.2. Circulating flue gas was composed by mixing O\textsubscript{2}, CO, SO\textsubscript{2} and N\textsubscript{2} obtained from compressed cylinders according to the volume percentage in the flue gas. SO\textsubscript{2} content in the inlet gas was increased from 0 ppm to 3,000 ppm and O\textsubscript{2} content of inlet gas was fixed at 18%. Water vapor in circulating flue gas was 5% generated by heating water in shaft furnace. The proportion of O\textsubscript{2} content and water vapor was chosen according to a former research which suggested that sintering process carried out under these conditions possessed good sintering indexes. The inlet gas was taken into sintering pot after heated by a vertical resistance furnace to appropriate temperature. The schematic diagram of sintering apparatus is shown in Fig. 8. It can be seen that the sintering pot is divided into different zones including sinter mixture zone, moisture condensation zone, drying and preheating zone, hot zone and sinter zone, as discussed above. After the stimulated FGCS experiments finished, the up layer (100–150 mm), the middle layer (250–300 mm) and the bottom layer (350–400 mm) of sinter were discharged from sintering pot, crushed and sampled carefully. Then the residual sulfur contents in different layer samples were analyzed, respectively.

2.3.3. Experimental Results

The residual sulfur contents obtained in different layers of finished sinters are given in Fig. 9. Compared with that obtained from the conventional sintering process (SO\textsubscript{2} content in the inlet gas is 0), the residual sulfur contents in the sinter obtained by the FGCS process remain constant when there was only 500 ppm of SO\textsubscript{2} in the inlet gas. While increasing SO\textsubscript{2} content of inlet gas to 1,000 ppm, residual sulfur contents in different layers increase in various degrees with the largest extent in the up layer. Residual sulfur content in sinter presents an increasing trend with the SO\textsubscript{2} concentration increases from 1,000 ppm to 3,000 ppm. It can also be observed that the residual sulfur content in the up layer increases greater than the other two layers. The reason is that SO\textsubscript{2} is partly absorbed by the finished sinters because of the existence of water vapor in the recirculated flue gas and dissociative CaO in the finished sinter. At the same time, residual sulfur content in sinter is partly derived from the absorption of SO\textsubscript{2} in the hot zone.

During the simulated FGCS experiments, the contents of SO\textsubscript{2} in off-gas are also detected and shown in Fig. 10. It can be observed that the maximum SO\textsubscript{2} content is only 1,256 ppm in the conventional sintering process. When the flue gas containing SO\textsubscript{2} varying from 500 ppm to 2,000 ppm is recirculated, the peak values of SO\textsubscript{2} content in the off-gas correspondingly increase from 1,882 ppm to 2,599 ppm, which is much higher than that in the conventional sintering process. It indicates that SO\textsubscript{2} content in the off-gas is enriched finally during the FGCS process which is beneficial for flue gas desulphuration (FGD).

In addition, it can be seen from Fig. 10 that SO\textsubscript{2} contents in off-gas remain constant at first as SO\textsubscript{2} in inlet gas is absorbed by raw materials in sinter bed, such as water and humid slake. But when the moisture condensation zone and sinter mixture zone disappear, the SO\textsubscript{2} absorption ability of sinter bed reduces sharply leading to the SO\textsubscript{2} contents in off-gas increase obviously. At the end of the sintering process, coke breeze combustion finishes gradually, which results in the decrease of SO\textsubscript{2} contents after the peak value. It is worthwhile to note that SO\textsubscript{2} contents in off-gas decrease continuously even less than that in inlet gas. The reason is SO\textsubscript{2} will be absorbed by newly crystallized minerals such as calcium ferrite and dissociative CaO in the hot zone and by residual CaO in finished sinter under the condition of humid circulating flue gas goes through sintering bed. However, SO\textsubscript{2} contents increase again as the SO\textsubscript{2} absorption ability of

### Table 4. Theoretical chemical composition of finished sinter/mass%.

<table>
<thead>
<tr>
<th>Sinter</th>
<th>TFe</th>
<th>SiO\textsubscript{2}</th>
<th>CaO</th>
<th>MgO</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>56.80</td>
<td>4.50</td>
<td>9.91</td>
<td>2.02</td>
<td>2.78</td>
</tr>
</tbody>
</table>

![Fig. 8. Schematic diagram of sintering apparatuses for FGCS.](image)

![Fig. 9. Residual sulfur content of finished sinters in different layers.](image)

![Fig. 10. Effects of SO\textsubscript{2} content in the circulated gases on SO\textsubscript{2} content in the off-gas.](image)
finished sinter is limited. As a result, it can be concluded that the variation rule of SO$_2$ in off-gas is in accordance with the behaviors of SO$_2$ discussed above during the FGCS process.

3. Conclusions

In the FGCS process, flue gas containing SO$_2$ is circulated through all sintering zones from top to bottom through sinter bed. Experimental results indicate that moisture, CaO (slaked lime) and newly crystallized minerals are main factors leading to SO$_2$ adsorption in whole sintering process. Behaviors of SO$_2$ in different zones of FGCS process can be summarized as follows:

1. In the moisture condensation zone and sinter mixture zone, there are large amount of moisture and humid slaked lime in sinter mixture which have strong SO$_2$ absorption ability. SO$_2$ in circulated flue gas and newly generated SO$_2$ are mostly absorbed by wet raw material in this zone and fixed in the form of sulphurous acid and CaSO$_4$ and CaSO$_3$.

2. When circulated flue gas containing SO$_2$ goes through the drying and preheating zone, a small part of SO$_2$ will be absorbed by dry slaked lime. Simultaneously, SO$_2$ is generated by oxidization of sulfides and re-released by decomposing sulphuric acid.

3. In the hot zone, it is where large amount of SO$_2$ is generated because of coke breeze combustion and decomposition of sulfate at high temperature. But during the cooling process, SO$_2$ in circulating flue gas will be absorbed by newly crystallized minerals such as calcium ferrite and dissociative CaO.

4. In sinter zone, part of SO$_2$ is absorbed by residual CaO in sinter under the condition of humid circulating flue gas, which will result in unfavorable increase of residual S in the up layer sinter.

Overall, during the FGCS process, SO$_2$ content enriches obviously in off-gas after circulating. Additionally, it need to note that the residual sulfur content in finished sinter is higher than that in the conventional process if SO$_2$ content in the inlet gas exceeds 2000 ppm.

Acknowledgements

The authors wish to express their thanks to Program for New Century Excellent Talents in University (NCET-11-0515) and the fundamental research funds for the Central Universities for financial support of this research.

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