Emission Behavior and Physicochemical Properties of Aerosol Particulate Matter (PM$_{10/2.5}$) from Iron Ore Sintering Process

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Iron ore sintering process is the major emission source of PM$_{10/2.5}$ (aerosol particulate matters less than 10 μm/2.5 μm in aerodynamic diameter) in integrated steelworks. The aim of this investigation is to obtain the emission behavior and major inorganic characteristics of PM$_{10/2.5}$ from typical sintering stages. Particulate matters were collected and classified into different size fractions with a cascade impactor, and the properties of PM$_{10/2.5}$ were analyzed by XRF, SEM-EDS techniques. The results show that sintering stages initiated from the gradual disappearing process of over-wetted layer to the burning through point are the main emitting area of PM$_{10}$, and sintering bed has potential ability to scrub PM$_{10}$ from flue gas. The main chemical composition of PM$_{2.5}$ emitted from the beginning of an integrated sintering process to the point where flue gas temperature began to rise characterizes high contents of Fe and low contents of volatile trace elements; PM$_{2.5}$ emitted from the flue gas temperature rising process characterizes high contents of K, Pb, Cl and S, and low content of Fe for the first half, while characterizes high contents of Al, Si, and low content of Fe for the second half. Such information can be helpful in exploiting controllable technologies on disposing PM-related pollutants in practice.

KEY WORDS: iron ore sintering; aerosol particulate matter; emission properties; chemical composition.

1. Introduction

Atmospheric problem caused by aerosol particulate matter (PM) has become a world-widely concerned topic. Emitted particles have been proved to be one of the major health hazards that could give rise to heavy or even deadly diseases after being inhaled through respiratory system. Indeed, the PM emitted from the stack of sintering process accounted for about 45% of the total PM emissions and it was also a major emitter for heavy metals. Previous research with regard to the properties of PM during sintering process unanimously showed that combustion layer and preheating & drying layer were the main source of dusts. Unfortunately, their research favored to elucidate the chemical composition or emitting properties of coarser-grained dust with size range exceeding 10 μm, while current de-dust equipment easily enables to remove this part of dust from flue gas. None of them afforded any information about the properties of PM$_{10/2.5}$ (particulate matters less than 10 μm/2.5 μm in aerodynamic diameter), which are generally more hazardous and has a high penetration to de-dust devices. Others that provided the chemical profile and morphological features of PM$_{10/2.5}$ mainly focused on the particles sampled from the stack, while the information about the properties of PM$_{10/2.5}$ generated throughout an integrated sintering process was still not found.

In this investigation, particulate matters generated from sintering process were sampled and divided into different size ranges by a low-pressure cascade impactor, and the properties of PM$_{2.5}$ were examined by XRF, SEM-EDS. This study will provide the information with regard to the
properties of particulate matters of an integrated sintering process, which can be helpful for sintering plants to exploit controllable technologies for reducing particulate matters.

2. Material and Methods

2.1. Raw Materials

The sintering process is a pretreatment-step where iron ores, fluxes (limestone, dolomite and quick-lime), return fines (sinter less than 5 mm) and solid fuel (coke breeze with size range 0.5–3 mm) are necessary raw materials for agglomeration. Table 1 gives the basic chemical composition and proportions of raw materials, based on which the final sinter product characterized Fe content of 56.38%, SiO₂ content of 4.92%, MgO content of 2.00%, and basicity (CaO/SiO₂, mass%) of 2.00.

Figure 1 describes the size distribution of −0.5 mm fraction in mixed raw material, and that of ash of coke breeze examined by laser diffraction using a Malvern Mastersizer 3000. Among them, the ash of coke breeze was obtained via the methodology described as about 5 g coke breeze sample with size range of 0.5–3 mm was charged into a corundum porcelain boat of 80 mm(length)×20 mm(width)×30 mm(height), and then heating the sample at 815±10°C (GB/T2001-1991) for 1 h using an electrically-heated horizontal furnace with airflow of 10 L/min. From the size distribution shown in Fig. 1(a), it is found that both mixed raw material (−0.5 mm) and ash of coke breeze contained a part of particles under 10 μm, and even under 2.5 μm. As shown in Fig. 1(b), particles under 10 μm and 2.5 μm contained in raw mixed material (−0.5 mm) are 14.75%, 5.43% respectively, while that contained in the ash of coke breeze was 21.80%, 5.71% respectively. Therefore, the ash of coke breeze contained relatively high fraction of particles under 10 μm.

2.2. Experimental Methods

2.2.1. Sinter Pot Experiments

Compared with coal combustion process, sinter-making process were probably of greater complexity. A laboratory-scale sinter pot used to agglomerate fine-grained iron ores into sinter cake was applied to simulate industrial sinter-

Table 1. Chemical composition and proportion of raw materials in mixture (mass%).

| Raw materials | Mixed iron ores | Dolomite | Limestone | Quick-lime | Return fines | Coke breeze |
|---------------|-----------------|----------|-----------|------------|--------------|-------------|
| Fe            | 60.74           | 0.21     | 0.14      | 0.40       | 56.38        | 0.74        |
| SiO₂          | 4.65            | 0.87     | 1.31      | 2.85       | 4.92         | 6.20        |
| CaO           | 1.90            | 31.57    | 50.19     | 77.92      | 9.36         | 0.89        |
| MgO           | 1.54            | 19.68    | 3.30      | 3.64       | 2.00         | 0.17        |
| Al₂O₃         | 1.92            | 0.22     | 0.32      | 0.75       | 2.07         | 4.12        |
| P             | 0.0650          | 0.0045   | 0.0067    | 0.0010     | 0.0510       | 0.0063      |
| S             | 0.016           | 0.015    | 0.015     | 0.070      | 0.009        | 0.205       |
| K₂O           | 0.026           | 0.036    | 0.082     | 0.027      | 0.008        | 0.041       |
| Na₂O          | 0.038           | 0.032    | 0.021     | 0.023      | 0.015        | 0.058       |
| Pb            | 0.0062          | 0.0062   | 0.0062    | 0.0025     | 0.0055       | 0.0062      |
| Cl            | 0.0152          | 0.0152   | 0.0137    | 0.0107     | 0.0068       | 0.0149      |

LOI* = loss on ignition at 950°C in air.

Fig. 1. Size distribution of mixed raw material (−0.5 mm) and ash of coke breeze.
making process, which is schematically described in **Fig. 2**. During the process, materials given in Table 1 were mixed according to their proportions, with prescribed proportion of water added. The mixture was then charged into an electrically powered drum of length 1 400 mm and diameter 600 mm for granulating fine-grained materials into green pellets, which was conducted at 15 rev min$^{-1}$ for 4 min. After that, the green pellets were fed into the sinter pot. After feeding, the solid fuel in the surface layer was initially ignited by a natural-gas-fuelled ignition hood, and the sintering process was sustained with the support of a downdraught system. The whole sintering process started from the ignition to the burning through point at which the sinter waste gas had reached its maximum temperature, during which a K-type thermocouple was used to record the changing of flue gas temperature (FGT). For each individual sampling case, a low-pressure cascade impactor (Model WY-1, China) was used to collect particulate matter from flue, as shown in **Fig. 2**.

### 2.2.2. PM Sampling and Analytical Techniques

PM$_{102.5}$ sampling in this investigation is different from the general method. It is easy to find that general measuring method for PM$_{102.5}$ mainly focuses on the sampling of PM$_{102.5}$ in the atmosphere. During this case, restrict sampling conditions are needed to be met, such as environmental temperature 5–35°C, relative humidity 0–85%, and atmosphere pressure 80–106 kPa (JIS Z8851). However, iron ore sintering process characterizes high water vapor content of about 10 vol-%, changed temperature from environmental temperature to about 400°C. The sampler used in this report can subject higher flue gas temperature to about 500°C. Besides, a heating belt is equipped to prevent the condensation of water vapor inside the sampler, which means that the sampler used in this report shows better adaptability. Apart from that, general PM$_{102.5}$ sampler is able to capture all of the particulate matters less than 10 μm or 2.5 μm in aerodynamic diameter in one filter, which contributes to reflecting the global property of PM$_{102.5}$. However, according to the property of the impactor used in this report, which can precisely separate the PM$_{2.5}$ into 6 parts 0.7–1.4 μm, 1.4–2.5 μm, 2.5–3.6 μm, 3.6–5.0 μm, 5.0–6.9 μm and 6.9–10 μm automatically according to their aerodynamic diameter rather than collect them as a whole. Therefore, the PM$_{2.5/10}$ measured in this report practically reflects the particles within 0.7–2.5 μm and 0.7–10 μm.

To elucidate the PM emission properties during an integrated sintering process, 6 typical sintering stages have been divided according to the FGT curve (**Fig. 3**). Among them, stage-1 indicated the ignition period, stage-2 showed the gradually stabilizing process of FGT, stage-3 indicated the stable process of FGT, stage-4 was the short period before the rise of FGT, stage-5 and stage-6 comprised the first half and the second half of FGT rising process. During the sampling process, PM samples were collected by Whatman QMA Quartz fiber filters with the help of the low-pressure cascade impactor. For guaranteeing the accuracy of PM quantitative analysis, isokinetic sampling is the prerequisite. To achieve this goal, the real-time linear velocity of flue gas is calculated on the basis of real-time flue gas flow and the dimension of the flue. This information serves as the guidance to adjust the linear velocity of sampling, thereby making linear velocity of gas flue and sampling equal. Besides, the sampling time was properly set so that the mass of PM collected in each stage was less than 10 mg to avoid particles bounce off from the substrates. The PM sampling was repeated at least three times for each test case to ensure satisfactory reproducibility and accuracy. The mass of PM collected in each case was determined by weighing the substrates before and after the
sampling with a Sartorius BT125D microbalance (accuracy: 0.01 mg). Relevant equation for calculating the mass concentration of PM is given in Eq. (1).

\[ C = \frac{m_1 - m_0}{S \int_0^t v_s \, dt} \]  \hfill (1)

Where \( C \) indicates the mass concentration of PM\(_{2.5/10}\) of each sintering stage (mg/m\(^3\)); \( m_1 \) and \( m_0 \) indicate the mass of filter after and before sampling (mg); \( t \) indicates the sampling time (s); \( S \) indicates the cross-sectional area of the sampling probe (m\(^2\)); \( v_s \) indicates the real-time linear velocity of the flue gas (m/s).

After sampling, the upper part of particles was removed from the filter using a scalpel for further characterization. The PM elemental composition was analyzed by energy dispersive XRF (X-Ray Fluorescence: EAGLE III, America). Scanning electronic microscopy (SEM: JEOL JSM-5600) with energy dispersive X-ray (Oxford instruments) is used to analyze particle morphology and chemical composition of typical particles collected from each sintering stage.

3. Results and Discussion

3.1. Emission Properties of Particulate Matters

PM collected from stage-1 to stage-6 was mainly divided into two parts, PM\(_{10}\) and PM\(_{2.5}\), respectively, which was the accumulation of PM with size range 0.7–10 \( \mu \)m and 0.7–2.5 \( \mu \)m. Figure 4 gives the mass concentration of PM\(_{10}\) PM\(_{2.5}\) emitted from each stage. The concentration of PM\(_{10}\) emitted from stage-4 to stage-6 is clearly higher than that of stage-2 to stage-3. Especially for stage-2 and stage-3, the concentration of PM\(_{10}\) from these stages is even lower. Therefore, stage-4 to stage-6 is the main emitting stages of PM\(_{10}\) during an integrated sintering process. PM\(_{2.5}\) emitting properties show marginal difference to that of PM\(_{10}\). Stage-4 and stage-5 are the dominant stages in terms of PM\(_{2.5}\) emis-

![Fig. 4](image_url)  
**Fig. 4.** Emission properties of PM in different sintering stages.

![Fig. 5](image_url)  
**Fig. 5.** SEM images of PM\(_{2.5}\) from different sintering stages. (a) Stage-1; (b) Stage-2; (c) Stage-3; (d) Stage-4; (e) Stage-5; (f) Stage-6.
sion, while stage-6 just emits a small part of PM$_{2.5}$, which is much lower than the concentration of PM$_{10}$. From stage-1 to stage-3, the emitting concentration of PM$_{2.5}$ drops gradually, and only 0.24 mg/Nm$^3$ of PM$_{2.5}$ is achieved in stage-3. Consequently, though major part of PM$_{10}$ emits in stage-4, stage-5 and stage-6, the emitting properties of PM$_{2.5}$ are dissimilar. Only stage-4 and stage-5 serve as the stages where major part of PM$_{2.5}$ emits into flue gas.

3.2. Morphological Properties of PM$_{2.5}$

Morphological properties of PM$_{2.5}$ collected from different sintering stages are described in Fig. 5. As can be observed from Figs. 5(a), 5(b) and 5(c), most of the particulates are characterized by discrete spheres, with a diameter under 1 $\mu$m, while only contains a small part of flake-like particles, and other irregular particles. However, the morphology of particles from stage-4 starts to change. Spherical particles ($< 1\mu m$) from this stage only take up a small proportion of the total particles, and more coarser particulates appeared, which are characterized by flake-like shapes and angular shapes with smooth surface can be observed in Fig. 5(d). Particulates emitted from stage-5 and stage-6 exhibited greater shape-related irregularities from other stages (Figs. 5(e) and 5(f)). Less spherical particles can be observed, but the surface of the particles tends to be sticky. Large number of fine particles sticks to the surface of coarser particles or several fine particles aggregated to form a coarser particle.

3.3. Chemical Profile of PM$_{2.5}$

Figure 6 gives the chemical compositions of PM$_{2.5}$ collected from different sintering stages. PM$_{2.5}$ of stage-1, stage-2, stage-3 and stage-4 mainly comprises Fe, Ca, Al and Si, among which the content of Fe are considerably higher than other components. Therefore, it can be speculated that the particles sampled from these stages mainly come from iron ores, while just a small part of them derives from fluxes and fuel ashes. Besides, particles also contain a small part of other elements, which were generally tracers in raw materials, like Na, K, S, F, Cl, Pb, Ti etc. (Table 1). As a consequence, trace elements get enriched in fine particles.

Remarkable chemical difference between particles from stage-5 and that from stage-1 to stage-4 is observed. Fe content in PM from stage-5 is much lower than that from stage-1 to stage-4, while the contents of S, K, Cl and Pb are considerably higher. As for the particles collected from stage-6, their chemical composition is characterized by higher contents of Al, Si, while its Fe content is also much lower than the particles from stage-1 to stage-4. Trace elements like Pb, S, and K in particles are considerably lower than that in particles from stage-5. Therefore, during the whole sintering process, the major fraction of hazardous elements such as S, K, Cl and Pb are released into flue gas in stage-5.

3.4. Further Discussion and Practical Implication

As stated above, the emission of PM$_{10/2.5}$ throughout the sintering process concentrated on stage-4 to stage-6, while the emission concentration of PM$_{10/2.5}$ is especially lower in stage-2 and stage-3. This interesting phenomenon shows close relationship to the changing and moving characteristics of sintering layers.

(1) Emission mechanism of PM$_{10/2.5}$ from stage-1 to stage-3

Figure 7(a) shows that a high-temperature layer including
combustion layer, drying & preheating layer formed during the ignition process, from which therefore PM started to form and entrain the downward flue gas; Figs. 7(b)–7(c) mainly indicates the gradual forming process of over-wetted layer, which has been proved to be a wet scrubber to capture particles from flue gas.\(^{15}\) Consequently, it is not hard to comprehend that the lower emission concentration of PM in stage-2 and stage-3. Indeed, potential interceptive mechanism of over-wetted layer and raw mixture layer has been given in Fig. 8. When PM-bearing flue gas flows through over-wetted layer and raw mixture layer, gas flow is easy to change its previous moving direction along with the channel formed in sintering bed. However, particles, especially the coarser ones have greater potential to crash into granules when gas flow direction changes suddenly. This is also the reason that PM sampled from stage-1 to stage-3 mainly comprises small-grained spherical particles (Figs. 5(a)–5(c)). Specifically in the over-wetted layer, some channels get blocked or narrowed by condensed water from flue gas, which enables to accelerate the gas flow velocity. Therefore, not only the coarser particles, but more fine particles are captured by sinter layers due to inertia effect.

The chemical composition of particulate group closely links to that of typical particles from each stage. As indicated in Fig. 9, spherical and flake-like particles (Figs. 9(a) and 9(b)) from stage-1 to stage-3 are Fe-rich, and also have a relatively higher proportion of Ca, Al and Si. However, volatile components like K, Pb etc. only take up a small proportion. The chemical composition of these particles well serves as an explanation to the chemical composition of particulates from these stages.

(2) Emission mechanism of PM\(_{10/2.5}\) from stage-4 to stage-6

When sintering process moves to stage-4, over-wetted layer gradually disappeared (Fig. 10(a)), which weakened the interceptive behavior of sintering layer. The concentration of PM in this stage increases significantly compared with that of stage-2 and stage-3 (Fig. 4). Figures 10(b) and 10(c) correspond to the rise of FGT process, during which over-wetted layer and raw mixture layer no more existed. Large amount of particles generated are able to entrain into the gas stream without the inceptive effect of sintering layer. The major chemical composition of PM from stage-5 and stage-6 exhibited marked difference to that of stage-2 to stage-3 (Fig. 6). Typical particle from stage-5 (Fig. 11(a)) is K-Cl-rich, and also contains a part of other volatile elements like S, Pb etc. Nevertheless, the Fe content is much lower than that of particles from stage-1 to stage-4. Large amount of volatile matters entering into the flue gas and
then transforming into fine particles contributes to the special chemical composition of particles from stage-5. The special morphology of particles from stage-5 (Fig. 5(e)) may also due to the volatile matters adhering to the surface of particles. Chemical composition of particle from stage-6 (Fig. 11(b)) characterizes Al-Si-rich, while contains lower content of Fe. Abundant Si and Al contents probably come from the ash of coke breeze, of which SiO2 and Al2O3 are the dominant components (Table 1). Besides, coke breeze is able to form PM10_{2.5} during the combustion process (Fig. 1), which has the potential to enter flue gas since particles formed in stage-6 can directly enter flue gas.

In addition, the characteristics of particulate matters in laboratory-scale sintering process, including absolute particle concentration and specific chemical composition, may differ from those in practice. Nevertheless, this investigation reveals the major emission area of particulates and partial hazardous elements, and the results are still helpful for exploiting controllable techniques for disposing PM-related pollutants, like intensifying the interceptive effect of sintering bed, thereby directionally migrating PM to the ending area (stage-5 to stage-6) of sintering process for centralized reduction. Besides, taking the interceptive effect of over-wetted layer and raw mixture layer into consideration, recycling the part of flue gas emitted from stage-4 to stage-6 into the sintering process is also an effectively potential approach to reduce PM emission.

4. Conclusions

For the purpose of affording guidance for developing emission reduction technologies to dispose PM-related pollutants in practice, emission behavior and chemical profile of PM10_{2.5} emitted from different sintering stages have been researched, and conclusions can be drawn as:

(1) During the whole sintering process, sintering stages initiated from the gradual disappearing of over-wetted layer to the burning through point are the main area for PM10 emission.

(2) PM2.5 sampled from ignition period to the stable process of FGT is mainly in the form of small-grained spherical particles, while the morphology of PM2.5 from the rise of FGT process is considerably irregular and sticky with fine particles adhered.

(3) The main chemical composition of PM2.5 emitted from the ignition period to the rising point of FGT characterizes high contents of Fe and low contents of trace elements; PM from the rise of FGT process characterizes high contents of K, Pb, Cl and S, and low content of Fe for the first half, while characterizes high contents of Al, Si, and low content of Fe for the second half.

(4) Over-wetted layer and raw mixture layer enable to scrub PM10 from flue gas, the existing state of which determines the emission concentration of PM10 during the whole sintering process.

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