Speciation of PM$_{2.5}$ Released from Iron Ore Sintering Process and Calculation of Elemental Equilibrium

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The aim of this study was to elucidate the speciation of PM$_{2.5}$ and proportion of each typical speciation via calculation of chemical mass balance. The results from elemental and morphological analyses showed that PM$_{2.5}$ consisted of diverse components mainly including O, Fe, Ca, Al, Si, and trace elements K, Na, Pb, S, and Cl. These components mainly existed in spherical, cubic, polyhedral, flake-like and bulk-like particles. Through examining the chemical composition and distribution property of main components in typical particles, Fe, Ca and O were determined to present in the speciation of Fe$_2$O$_3$–CaO from melting process, while Al, Si and O existed in the speciation of $x$Al$_2$O$_3$–$y$SiO$_2$ from fuel fly ash. K, Na, Pb and Cl could exist in the speciation of KCl, NaCl and PbCl$_2$ respectively from chlorination reactions. Moreover, Ca, K, Pb, O and S could form sulfates of CaSO$_4$, K$_2$SO$_4$ and PbSO$_4$, respectively. Calculation of O, S and Cl equilibrium in PM$_{2.5}$ indicated that Fe$_2$O$_3$–CaO accounted for about 30.63%, $x$Al$_2$O$_3$–$y$SiO$_2$ accounted for about 7.02%, K(Pb/Na)Cl accounted for about 41.29%–49.77%, and K$_2$(Ca/Pb)SO$_4$ accounted for about 21.05%–12.57%.

KEY WORDS: iron ore sintering; PM$_{2.5}$; speciation; chemical mass balance.

1. Introduction

Atmospheric contamination caused by PM$_{2.5}$ (aerosol particulate matter with aerodynamic diameter ≤ 2.5 μm) has become the worldwide focused issue. Emitted PM$_{2.5}$ is regarded as the important health hazard, and it has a direct influence on health through respiration since it can even go directly to the alveoli of the lungs.1–4) As PM$_{2.5}$ characterizing tiny size and huge specific surface area, heavy metals and persistent organic pollutants were enriched in PM$_{2.5}$, which may interfered with biochemical mechanisms.5–7)

Iron and steel industry is a prevailing stationary emitter of atmospheric particles, which even serves as the main source of PM$_{2.5}$ in some areas as determined by source apportionment method.8–11) Throughout the whole steelmaking chain, sintering process is an important high-temperature stage, which also characterizes energy-intensive and pollution-intensive. It is the main emitter of both gaseous pollutants like SOx, NOx, COx, etc., and aerosol particulate matters.12–14) Practically, the particulate matters (PM) emitted from sintering process account for about 45% of the total amount in steelworks.15) However, due to its high specific resistance, electrostatic precipitators are difficult to realize efficient capture for PM$_{2.5}$, which takes up more than 80% of the total escaped PM in flue gas.15,16) Therefore, sintering process is actually an important emission source of PM$_{2.5}$ in integrated steelworks. Controlling the emission of PM$_{2.5}$ in this process is of great significance to decrease its emission of the whole iron and steel industry.

However, achieving a well-rounded profile about the characteristics of PM$_{2.5}$ is the prerequisite to develop effective measures for PM$_{2.5}$ emission reduction in sintering process. Previous research mainly focused on the PM$_{2.5}$-containing dusts emitted from sintering stacks. The finding results showed that K, Cl were the main components in the dust, and also discovered the presence of Fe, NH$_4^+$, Ca, Na, Pb, Cd, etc. Possible speciation of these elements in the dusts included KCl, PbCO$_3$, CdCl$_2$, CaCO$_3$, etc.17–19) Unfortunately, there is little direct information about the properties of PM$_{2.5}$ released from the sintering process with the exception of our recent reports.20,21) According to our research,20) the emission property, main chemical compositions, morphological properties of PM$_{2.5}$ released during the whole sintering process were revealed. Also, we found out how operation parameters and raw mixtures influenced the emissions of PM$_{2.5}$.21) However, in the past research, we mentioned little about the speciation of main components existed in PM$_{2.5}$, which was an important property to reveal its formation mechanism in sintering process. In this investigation, XRF, SEM-EDS techniques were applied to elucidate the speciation of PM$_{2.5}$, and chemical mass balance approach was adopted to calculate the proportion of each typical speciation existed in PM$_{2.5}$. 

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2. Materials and Methods

2.1. Materials

In this research, sintering raw materials were provided by a large-scale integrated steelwork in China. Table 1 gives the chemical compositions of each material. During sinter making process, the mass proportions of mixed iron ores, limestone, quicklime, dolomite, coke breeze and return fines were 66.63%, 3.22%, 3.87%, 5.28%, and 4.0%, 20% respectively. Based on their proportions, the final sinter product characterized Fe content of 56.24%, SiO$_2$ content of 4.98%, MgO content of 2.00%, and basicity (CaO/SiO$_2$, mass%) of 1.73. Table 1 shows that the coke breeze ash mainly consisted of Al$_2$O$_3$ and SiO$_2$, and the raw materials all contained a small amount of trace elements: K, Na, Pb, Zn, Cl, S.

2.2. Experimental Methods

The equipment used for sintering trials was a laboratory-scale sinter pot with depth of 700 mm and diameter of 180 mm. Raw materials were blended according to their proportions in section 2.1, during which adding water to meet the prescribed level of 8.0%. After blending, charging the mixtures into a drum granulator with length of 1400 mm and diameter of 600 mm to granulate fine ores into granules. The granules were then fed into the sinter pot. After feeding, an burner fuelled by natural gas ignited the coke breeze distributed in the surface layer. Combustion front then moved downwards sustained by an induced draught fan. The whole sintering process started from the ignition point to the burning through point at which the flue gas had reached its maximum temperature that recorded by a K-type thermocouple. For each individual sampling case, a low-pressure cascade impactor (Model WY-1, China) was used to collect PM from flue gas, as shown in Fig. 1.

During sampling process, PM samples were collected by Whatman QMA Quartz fiber filters with the help of the low-pressure cascade impactor, which was able to segregate PM into ≤2.5 μm and > 2.5 μm according to their aerodynamic diameter. The portion of PM ≤2.5 μm was examined to display the properties of PM$_{2.5}$. For guaranteeing the representativeness of PM samples, isokinetic sampling is the prerequisite, and detailed information is found elsewhere.\(^{20,21}\)

After sampling, the upper part of particles ≤2.5 μm was removed from the filter using a scalpel for further analysis. The elemental composition of PM$_{2.5}$ was analyzed by energy dispersive XRF (X-Ray Fluorescence: EAGLE III, America). Field emission scanning electronic microscopy (FESEM: HeliosNanolab600i) with energy dispersive X-ray (EDX) was used to analyze particle morphology and major chemical distribution in typical particles. For guaranteeing the accuracy of chemical composition, each individual case was repeated at least 3 times.

Moreover, contents of K, Na, Pb, Zn, and S, in raw mixtures and sinter were examined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES Optima 30, Jobin Yvon, France). Detailed analytical steps could be described as ground samples with size range of −0.074 μm were dissolved by acid digestion with aqua regia added to fluorhydric acid (4 mL HCl, 4 mL HNO$_3$ and 2 mL HF). After that, solutions were heated at 120°C for 9 h, and then made up to 25 mL with 2 mL boric acid and 13 mL pure water.

| Ore types         | Mixed iron ores | Limestone | Quicklime | Dolomite | Coke breeze | Return fines | Mixed raw materials |
|-------------------|-----------------|-----------|-----------|----------|-------------|--------------|---------------------|
| TFe               | 58.88           | 0.60      | 0.20      | 0.40     | 2.32        | 56.24        | 50.31               |
| CaO               | 0.95            | 53.90     | 79.62     | 34.29    | 0.91        | 8.60         | 7.69                |
| SiO$_2$           | 4.57            | 0.83      | 3.90      | 0.70     | 6.20        | 4.98         | 4.46                |
| MgO               | 0.55            | 1.57      | 1.28      | 18.80    | 0.20        | 2.03         | 1.82                |
| Al$_2$O$_3$       | 2.14            | 0.52      | 0.99      | 0.34     | 4.34        | 2.38         | 2.12                |
| S                 | 0.059           | 0.013     | 0.051     | 0.005    | 0.960       | 0.100        | 0.100               |
| K                 | 0.062           | 0.051     | 0.008     | 0.020    | 0.119       | 0.051        | 0.058               |
| Na                | 0.029           | 0.006     | 0.009     | 0.017    | 0.102       | 0.024        | 0.029               |
| Pb                | 0.012           | 0.000     | 0.000     | 0.000    | 0.001       | 0.008        | 0.010               |
| Zn                | 0.035           | 0.004     | 0.002     | 0.002    | 0.004       | 0.024        | 0.028               |
| Cl                | 0.027           | 0.003     | 0.003     | 0.012    | 0.058       | 0.004        | 0.022               |

\(^a\)LOI: loss on ignition at 950°C in air

\(^b\)TFe: Total iron content

Fig. 1. Schematic diagram for PM sampling from sintering flue gas.
water. Finally, ICP-AES was used to analyze targeted trace elements. The contents of Cl in raw materials and sinter were determined using a Dionex model 120 ion chromatograph.\(^{22,23}\) Equations (1) and (2) were used to calculate the removal rates and recovery rates of trace elements, respectively.

\[
\eta = \left(1 - \frac{c_r m_r}{c_p m_p}\right) \times 100\% \quad \text{Eq. (1)}
\]

\[
R = \frac{c_r m_r}{c_p m_p} \times 100\% \quad \text{Eq. (2)}
\]

Where \(\eta\) and \(R\) are the removal rates and recovery rates of trace elements, respectively, mass\%; \(c_r\), \(c_p\) and \(c_v\) are the proportions of trace elements in sinter, PM\(_{2.5}\) and raw mixtures (include LOI) respectively, mass\%; \(m_s\), \(m_p\) and \(m_r\) are the total mass of sinter, emitted PM\(_{2.5}\) and raw mixture for each case, kg.

3. Results and Discussion

3.1. Chemical Composition and Morphology of PM\(_{2.5}\)

Figure 2(a) outlines the chemical composition of PM\(_{2.5}\) released from the whole sintering process. It was found that PM\(_{2.5}\) mainly consisted of O, Fe, K, and Cl, which accounted for about 16%, 15%, 20% and 26% respectively. Moreover, the contents of Ca, Si, and Al in PM\(_{2.5}\) reached about 5%, 2% and 2%, while other trace elements Na, Pb and S reached about 2%, 7% and 2% respectively. Clearly, the contents of trace elements achieved a considerable enrichment in PM\(_{2.5}\) compared with their levels in mixed raw materials (Table 1). Additionally, the total content of these tracers in PM\(_{2.5}\) account for about 59%. Figure 2(b) gives the removal and recovery rates of the trace elements, showing that Cl and S were easily removed from the raw materials as the removal rates reached around 90%. Compared with K, Na, and Zn, Pb characterized higher removal rate reaching about 44%. The low removal rate of Zn well agreed to its lower content in PM\(_{2.5}\) shown in Fig. 2(a). By contrast, the value of recovery rates of the trace elements showed well consistency to their removal rates with the exception of S. S shows a peculiar manner of the trace elements such that the content of S in mixed raw materials and its removal rate was highest, while its content in PM\(_{2.5}\) was merely 2.36%. This implied that only a small amount of S was transformed into PM\(_{2.5}\).

Figure 3 demonstrates the morphological property of PM\(_{2.5}\) obtained by SEM. The body of PM\(_{2.5}\) formed by the major and minor components mainly appearing as polyhedron-like (particle-a), sphere-like (particle-b), square-like (particle-c), flake-like (particle-d) and bulk-like (particle-e) particles. Such diversity of PM\(_{2.5}\) in components and morphologies involves the linkage between typical particles and main chemical components to determine the speciation of PM\(_{2.5}\).
3.2. Speciation Analysis of PM$_{2.5}$

3.2.1. Fe–Ca–Al–Si–O-Related Particles

Figure 4(a) gives the morphology and main elements distribution in typical spherical particles (particle-b) obtained by SEM-EDS mapping analysis. Clearly, Fe, Ca and O showed well over-lapped distribution in these particles. According to the chemical compositions obtained by EDS analysis (Table 2), Particle-b mainly comprised Fe, Ca, and O, which respectively took up about 28%, 39% and 12% of the total mass. Relevant molar ratio was around 2:1:6. According to the research finds elucidated in coal combustion process, the spherical particles were convinced to form from mineral melting process under high temperatures.$^{24,25}$

During sintering process, the mineral melting was also an important process happened in the sinter bed with initially started at the surface of granules. The airflow would blow the liquid droplets into flue gas while moving downwards, and they would be transformed into spherical particles due to surface tension and cooling. $xFe_2O_3$-$yCaO$ was the major melting phase formed in this process. Taking the molar ratio of Fe to Ca into account, the coefficients $x$ and $y$ were both 1, while the unbalanced O was probably combined with Al, Si and Mg. As for sintering process, these spherical particles were formed from the melting process of $Fe_2O_3$–CaO derived from solid-phase reaction between $Fe_2O_3$ and CaO.$^{26}$

Figure 4(b) displays the morphology of typical flake-like particles (particle-d). In accordance with their chemical compositions shown in Table 2, Al, Si and O accounted for about 18%, 20% and 43% in the particle-1, while they accounted for about 13%, 27% and 43% in particle-2. Relevant molar ratio of Al, Si and O was 1:1.4, 1:2:5.6 respectively. Since Al and Si were existed in the form of oxides, the two flake-like particles were $Al_2O_3$-$2SiO_2$ and $Al_2O_3$–$SiO_2$ respectively. As shown in Table 1, the coke breeze ash mainly consisted of $Al_2O_3$ and $SiO_2$, which was an important source of Al-Si-O-related particles. Our previous research also indicated that coke breeze ash contained about 6% particles with size range <2.5 μm.$^{20}$

Figure 4(c) gives the morphology and distribution of main components in the polyhedral particle (particle-a). The distribution area of Ca, S and O were overlapped in this particle, and the chemical composition observed in Table 2 indicated that this particle mainly consisted of Ca,
Fig. 4 (continued). SEM images and mapping of typical Pb–Cl–S–O-related particles. (f) Pb–Cl-related particles; (g) Pb–S–O-related particles.
Table 2. Chemical compositions of typical Fe–Ca–Al–Si–O-related particles (mass%).

| Elements | Spherical particle-1 | Spherical particle-2 | Flake-like particle-1 | Flake-like particle-2 | Polyhedral particle |
|----------|----------------------|----------------------|-----------------------|-----------------------|---------------------|
| O        | 28.54                | 27.46                | 42.57                 | 42.56                 | 39.57               |
| Fe       | 38.44                | 39.80                | 2.42                  | 3.05                  | 1.75                |
| Ca       | 12.25                | 11.98                | 1.31                  | 1.90                  | 23.07               |
| Al       | 2.49                 | 2.13                 | 18.81                 | 12.79                 | 0.79                |
| Si       | 3.23                 | 2.74                 | 20.28                 | 27.19                 | 2.18                |
| Mg       | 1.24                 | 0.69                 | 1.15                  | 1.34                  | 0.06                |
| K        | 5.03                 | 4.73                 | 3.44                  | 3.28                  | 3.50                |
| Na       | 0.35                 | 0.24                 | 0.78                  | 0.43                  | 0.40                |
| Pb       | 1.81                 | 1.74                 | 1.27                  | 1.38                  | 1.89                |
| Zn       | 0.11                 | 0.36                 | 0.15                  | 0.22                  | 0.14                |
| S        | 0.32                 | 0.33                 | 0.72                  | 0.85                  | 18.21               |
| Cl       | 6.12                 | 7.35                 | 5.13                  | 4.99                  | 5.92                |

Table 2 (continued). Chemical compositions of typical K–Na–Cl–S-related particles (mass%).

| Elements | Cubic particle-1 | Cubic particle-2 | Flake-like particle-1 | Flake-like particle-2 | Flake-like particle-3 |
|----------|-----------------|-----------------|-----------------------|-----------------------|-----------------------|
| O        | 2.43            | 3.23            | 31.98                 | 32.20                 | 32.00                 |
| Fe       | 0.00            | 0.00            | 2.37                  | 2.17                  | 0.00                  |
| Ca       | 0.00            | 0.22            | 2.85                  | 2.65                  | 0.00                  |
| Al       | 0.48            | 0.00            | 0.34                  | 0.55                  | 0.26                  |
| Si       | 0.60            | 0.00            | 0.75                  | 1.50                  | 1.25                  |
| Mg       | 0.00            | 0.00            | 0.16                  | 0.12                  | 0.00                  |
| K        | 48.74           | 2.19            | 34.33                 | 32.34                 | 35.03                 |
| Na       | 0.95            | 39.92           | 3.20                  | 3.42                  | 4.66                  |
| Pb       | 1.47            | 1.14            | 2.68                  | 2.33                  | 2.90                  |
| Zn       | 0.00            | 0.08            | 0.47                  | 0.71                  | 0.67                  |
| S        | 0.22            | 0.12            | 14.40                 | 14.13                 | 15.21                 |
| Cl       | 42.56           | 51.96           | 5.86                  | 5.32                  | 7.73                  |

Table 2 (continued). Chemical compositions of typical Pb–Cl–S-related particles (mass%).

| Elements | Polyhedral particle-1 | Polyhedral particle-2 |
|----------|-----------------------|-----------------------|
| O        | 1.61                  | 18.01                 |
| Fe       | 0.30                  | 3.44                  |
| Ca       | 0.10                  | 1.76                  |
| Al       | 0.54                  | 3.28                  |
| Si       | 0.67                  | 1.53                  |
| Mg       | 0.10                  | 0.44                  |
| K        | 5.97                  | 3.41                  |
| Na       | 0.10                  | 1.36                  |
| Pb       | 65.59                 | 53.32                 |
| Zn       | 0.15                  | 0.10                  |
| S        | 0.30                  | 8.42                  |
| Cl       | 24.59                 | 4.94                  |

S and O, with molar ratio about 1:1:4 according to their mass proportions. Therefore, this particle was CaSO₄, and similar particles were verified to be CaSO₄ as well by other researchers.²⁷ For further revealing the formation mechanism of CaSO₄, the size distribution of lime stone, dolomite and slaked lime less than 0.5 mm were analyzed using a Malvern Mastersizer 3000, and it was found that the particles ≤ 2.5 μm accounted for about 9.88%, 2.15% and 15.99% respectively. Since the fined-grained materials served as the adhesive fines during granulation process, it was convenient for the particles ≤ 2.5 μm to contact with SO₂-containing flue gas directly. This phenomenon indicated that the formation of CaSO₄ could happen in sinter bed between fined-grained fluxes and captured SO₂ by wet mixture layer. The flue gas would also be the source of power for CaSO₄ particles to transform into flue gas. However, the escaped fluxes particles reacting with SO₂(g) in flue gas to form CaSO₄ particles was also possible. More detailed research would be done to reveal this process. The related chemical reactions (1) to (3) between fine-grained Ca-based fluxes and SO₂ has been proved to be the source of CaSO₄ in sintering process.²⁸,²⁹

\[ \text{CaO(s)} + \text{SO}_2(g) \rightarrow \text{CaSO}_4(s) \]  

\[ \text{CaO(s)} + \text{SO}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{CaSO}_4(s) \]  

\[ \text{CaSO}_4(s) + 1/2\text{O}_2(g) \rightarrow \text{CaSO}_4(s) \]  

3.2.2. K–Na–Pb–Cl–S-Related Particles

Figure 4(d) outlines the morphology of typical square-like and bulk-like particles (particle-c and particle-e) f. These particles were main K–Cl–related particles, while also contained Na–Cl-related particle. The abundant K–Cl-related particles showed well agreement to their higher contents in PM₂.₅. From the chemical compositions (Table 2) of square-like particle-1, it was found that K and Cl existed in this particle in the speciation of KCl, while Na and Cl were also determined as NaCl. Figure 4(e) gives the morphology and the distribution property of the main elements in the smooth flake-like particles (particle-d). Apparently, they were K–O-related particles. The chemical compositions of three similar particles showed that the contents of K, S and O were all around 32%, 14% and 32% (Table 2). Their molar ratio was close to 2:1:4:6, which indicated that K, S, and O existed in these particles in the speciation of K₂SO₄, and the rest O was mainly derived from the oxides of Fe, Si and Al. Like the formation of the chlorides of K/Na, their vapors could also react with SO₂ due to their great chemical reactivity. It was not hard to comprehend that the sulfates of K/Na formed in flue gas and also moving downwards with flue gas. Therefore, K-related particles in PM₂.₅ showed two types of speciation. During the sintering process, K’s removal rate reached 24%. It was also verified that chlorination reaction played an important role in the volatile of alkali metals, while sulphides in raw materials had an effect to restrain their volatilization to form a minor portion of sulfate.

Figure 4(f) shows typical SEM image and distribution of major elements in the polyhedral particle (particle-a), and it was found that Pb and Cl showed well overlapped

\[ \text{CaO(s)} + \text{SO}_2(g) \rightarrow \text{CaSO}_4(s) \]  

\[ \text{CaO(s)} + \text{SO}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{CaSO}_4(s) \]  

\[ \text{CaSO}_4(s) + 1/2\text{O}_2(g) \rightarrow \text{CaSO}_4(s) \]
property. The chemical composition shown in Table 2 also indicated that this particle consisted of Cl of 24.79% and Pb of 65.59%, which presented a molar ratio about 2.3:1. This information implied that Pb and Cl existed in this polyhedral particle in the speciation of PbCl₂, and the rest Cl was combined with K due to its content also reached about 6%. Figure 4(g) gives the morphology and major element distributions of another type of polyhedral particle (particle-a). Apparently, Pb, S and O exhibited high overlapping degree. The chemical composition of this particle (Table 2) also showed that Pb, S and O existed in this particle as the main components accounting for about 53.32%, 8.42% and 18.01% respectively. Their molar ratio reached 1:1:4.4, which indicated that Pb, S and O existed in this particle in the speciation of PbSO₄, and the rest O coming from the oxides of Fe, Ca, Al, Si, etc. Figure 2(b) has revealed the easy removal property of Pb in sintering process. Forming chlorides and sulfates were the two important paths for Pb to transform into PM₂.₅.

3.3. Calculation of Chemical Mass Balance

According to the analysis mentioned above, the components of PM₂.₅ existed mainly in the speciation of Fe₂O₃–CaO, xAl₂O₃·ySiO₂, K(Pb/Na)Clₓ, and K₂(Ca/Pb)SO₄. As summarized in Fig. 5, the main transformation paths for these speciations included minerals melting, escaped fine fuel fly ash, chlorination reactions and forming sulfate. However, each element differed greatly from each other in terms of mass proportions in PM₂.₅, which determined the contribution degree of each transformation paths. For deeply elucidating this difference and determining the proportions of each typical speciation in PM₂.₅, the content of each speciation obtained by X-ray fluorescence analyzer (XRF) in PM₂.₅ was calculated on the basis of chemical mass balance. As shown in Table 3, the principle for calculating the proportion of each speciation was to reach mass balance of O, S, and Cl in PM₂.₅. Specific calculation process follows in four main items: (1) Taking the molar quantity of Fe and its presence in Fe₂O₃–CaO into account, figuring out the molar number of oxygen consumed by Fe. (2) Taking the total molar number of Ca and the part existed in Fe₂O₃–CaO into account, figuring out the part of oxygen combined in the form of CaO and CaSO₄ respectively, and also figuring out the part of S consumed. (3) Firstly figuring out the molar quantity of Cl consumed by K, Na and Pb with hypothesis all of them existed in the speciation of chlorides, which was 0.599 mol, 0.111 mol and 0.069 mol respectively (Table 3). The total amount 0.779 mol that surpassed the practical molar quantity of 0.647 mol, and then figuring out the molar quantity of S needed to compensate the difference, which indicated that 0.066 mol S would be combined with K and Pb; (4) Figuring out the molar quantity of oxygen consumed by Al, Si in the form of their oxides and by S in the speciation of sulfate. According to the mass balance of O, S, and Cl, the proportions of each speciation in PM₂.₅ were calculated, and the results are shown in Fig. 6(b). Since it was difficult to determine the specific proportion of K and Pb existed in the speciation of chlorides or sulfates, the change intervals of K(Na/Pb)Clₓ and K₂(Ca/Pb)SO₄ were given based on the hypothesis that only K forming 0.66 mol of K₂SO₄ or all of the Pb transforming into PbSO₄. In PM₂.₅, Fe₂O₃–CaO accounted for about 30.63%, xAl₂O₃·ySiO₂ accounted for about 7.02%, K(Pb/Na)Clₓ accounted for about 7.02%, K₂(Ca/Pb)SO₄ accounted for about 41.29%–49.77%, and K₂(Ca/Pb)SO₄ accounted for about 21.05%–12.57%.

Figure 6(a) shows that the calculated total amount of O, S, and Cl was successfully close to the practical one found in Table 3, which verified the main existed speciation of the main components to a great extent. More work will be done to precisely quantify the proportion of chlorides and sulfates in future investigation.

| Elements | Proportion (mass%) | Molar quantity (mol) | O-consumption (mol.) | Cl-consumption (mol.) | S-consumption (mol.) |
|----------|--------------------|----------------------|----------------------|----------------------|----------------------|
| O        | 16.99              | 1.062                |                      |                      |                      |
| Fe       | 15.88              | 0.284                | 0.425                | 0                    | 0                    |
| Ca       | 6.01               | 0.150                | 0.142a               | 0.033b               | 0                    |
| Al       | 1.93               | 0.072                | 0.011                |                      |                      |
| Si       | 2.30               | 0.082                | 0.164                |                      |                      |
| K        | 21.28              | 0.599                |                      |                      | 0.599                |
| Na       | 2.55               | 0.111                | 0.111                |                      | 0.066                |
| Pb       | 7.13               | 0.034                |                      |                      | 0.069                |
| Cl       | 22.98              | 0.647                |                      |                      |                      |
| S        | 2.45               | 0.077                | 0.306                |                      |                      |

0.142a: Refers to the oxygen consumed when Ca existed in Fe₂O₃–CaO; 0.033b: Refers to the oxygen consumed when Ca existed in CaSO₄.
4. Conclusions

(1) PM$_{2.5}$ released from sintering process mainly comprised O, Fe, Ca, Al, Si, and trace elements K, Na, Pb, S, and Cl. These components primarily presented in spherical, cubic, polyhedral, flake-like and bulk-like particles.

(2) In PM$_{2.5}$, Fe, and Ca existed in the speciation of Fe$_2$O$_3$–CaO from melting process, while Al, and Si existed in the speciation of xAl$_2$O$_3$–ySiO$_2$ from fuel fly ash. K, Na, Pb and Cl could exist in the speciation of KCl, NaCl and PbCl$_2$ respectively from chlorination reactions. Moreover, Ca, K, Pb and S could form sulfates of CaSO$_4$, K$_2$SO$_4$ and PbSO$_4$ respectively.

(3) In PM$_{2.5}$, Fe$_2$O$_3$–CaO accounted for about 30.63%, xAl$_2$O$_3$–ySiO$_2$ accounted for about 7.02%, K(Pb/Na)Cl accounted for about 41.29%–49.77%, and K$_2$(Ca/Pb)SO$_4$ accounted for about 21.05%–12.57% through the calculation of O, S and Cl mass balance.

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