Discovery of Potassium Chloride in the Sintering Dust by Chemical and Physical Characterization

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Sintering plant dust arrested by electrostatic precipitator (ESP dust) in an integrated iron and steel company is perceived as a precious secondary material to steelmaking process, due to the presence of important elements to the industry such as, Fe and C with an attractive concentration. However, some hazardous elements such as, K, Na, Zn, Pb, seriously destroying normal working of the blast furnace, are enriched meanwhile. Therefore, it becomes very important to know how to separate these elements from Fe and C before reusing the dust. The aim of this work is to carry out a chemical, physical, structural and morphological characterization of the sintering dust. The dust was subjected to granulometry analysis, chemical analysis, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy via SEM (EDS), X-ray mapping analysis via SEM and X-ray diffraction. With the help of these analysis ways and some comparison made between characterization of the dust before and after water leaching, an encouraging conclusion was drawn: KCl was identified in the sintering dust with a content percentage up to 30%. Considering serious lack of potassium fertilizer in China, it is necessary to recover KCl from the sintering dust. In addition, endanger of K to the steelmaking process is restricted at the same time.

KEY WORDS: sintering dust; electrostatic precipitator; phase analysis; potassium chloride.

1. Introduction

Sintering dust is a solid waste generated during the sintering process collected by electrostatic precipitator. It is considered as a kind of dangerous dust because of its complicated components such as heavy metals and hazardous organics. Due to the great amount generated, 4 kg of dust per ton of steel, an evaluation of the steel recycling alternatives is necessary.

Elements Fe and C cannot be fully used in the sintering process due to its small size and strong air blowing. Thus they are left in the dusts by electrostatic precipitator. A usual way to treat the sintering dust is returning it to the sintering furnace to reuse Fe and C. However, a great amount of other elements such as, K, Na, Zn, Pb are also reused in the recycle, which is harmful for normal operation of blast furnace. Even early in the 1960s, researchers discovered serious destruction of alkali metals to the blast furnace. Many years’ practice as well proves that volatility and bunching of alkali metals, due to its low boiling point, always affect convulsion ability of sintering machine, decrease production capability of the machine and increase its load. Thus it is necessary to study new technologies for its processing.

It is well known that limited potassium resource cannot satisfy requirements of prosperous agriculture in China. Take the year of 2006 as example, consumption of the potassium resource is about 11 million ton, with 8 million ton imported, approximately 80% of the foreign dependency degree. Generally, KCl is the major material of non-chlorine potassium fertilizer. As to China, production of KCl depends on saline lake in Qinghai. However, enough KCl resource is not available due to limitation in techniques and economy.

In recent years, some researchers did some work on extracting potassium from limestone kiln ashes and cement kiln ashes. In general, and especially in developed countries, the treatment processes of the steelmaking dusts commonly used aim mainly the recovering of Zn, Pb, Fe, C. Two typical examples are Rotary kiln and Rotary hearth furnace direct reduction techniques. However, seldom literature reports about recovering potassium from sintering dust of iron and steel making. In this paper, a chemical, physical, structural and morphological characterization of the sintering dust has been done, with an aim to verify presence of KCl in the dust. In addition, content of KCl in the dust is up to 30%, a considerable number for Chinese agriculture. If KCl can be recovered from the sintering dust with a recovery rate of 90%, considering the great amount of sintering dusts, it is promising to produce 500 000 ton of KCl every year, which is equivalent to 600 000 ton of K2SO4. This means another 1/3 potassium fertilizer of the gross output in 2006 can be obtained by reusing potassium in the sintering dust. In one word, it is meaningful to recover KCl from the sintering dust, not only developing new potassium resource, but avoiding the destruction of potas-
sium to blast furnace.

2. Experimental

Particles samples of all sizes were obtained from an integrated iron and steel plant located in Laiwu, Shandong province of China, sampling was done every 2 h to obtain enough particles for analysis. The method selects the proper stack position and then puts the sampling probe into the stack sampling point. Raw materials for the sintering process include blended ore, coke breeze, limestone, and returned fine particles from the sintering plant.

2.1. Granulometry Analysis

The ESP dust (Sintering plant dust arrested by electrostatic precipitator) granulometric distribution and the medium size of its particles were evaluated. A Laser Granulometer model SEISHIN LMS-30 from Japan was used.

2.2. Determination of Elemental Constituents

One-fourth of the particle sample was mixed with a 20 mL acid mixture (HNO₃ : HClO₄ : HF = 5 : 3 : 2, v/v) in a Teflon lined closed vessel and placed in a high-pressure digestion oven at 170°C for 5 h. The digested acid mixture was analyzed to determine the trace elements. A Perkin-Elmer OPTIMA 3000 ICP-AES was used to determine the Al, Ca, Fe, K, Mg, Na, Pb, Cu, Ni and Zn concentrations.

2.3. Determination of PAHs

2.3.1. Chemicals

The 16 USEPA PAH (Polycyclic Aromatic Hydrocarbons) standards (purity of >99%) including Naphthalene (NaP), Acenaphthylene (AcPy), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno[1,2,3-cd]pyrene (IND), Dibenzo(a,h)anthracene (DBA), and Benzo(g,h,i)pyrene (BghiP) were purchased from Supelco Inc. (USA). In general, the higher the molecular weight of PAHs, the more serious the carcinogenic risk they pose. They are classified by the numbers of aromatic rings as follows: 2-ring including NaP; 3-ring including AcPy, Acp, Flu, PA and Ant; 4-ring including FL, Pyr, BaA and CHR; 5-ring including BbF, BkF, and BaP; and 6-ring including IND, DBA, and BghiP. Dichloromethane, hexane, silica gel (0.098–0.154 mm, activated at 130°C for 16 h prior to use), anhydrous sodium sulfate (baked at 500°C for 4 h prior to use) and other reagents were pesticide grade and/or residue analysis grade.

2.3.2. Sample Extraction and Cleanup

10.00 g samples with 5.00 g anhydrous sodium sulfate were extracted using Soxhlet extraction procedure. The samples were extracted for 18 h with 80 mL of mixed solvent (hexane : acetone = 1:1, v/v). The extract was concentrated on a rotary evaporator equipped with a water bath held at 65°C, and the solution volume was reduced to 2 mL.

In the cleanup process, the residual solution was introduced into a silica column (1 cm i.d. and 30 cm length), and the column was eluted with 25 mL of mixed solvent (dichloromethane : hexane = 2:3, v/v) after elution of 25 mL n-hexane. About 2 cm anhydrous sodium sulfate was packed at the fore-end of the cleanup column for the purpose of excluding water. The effluent containing PAHs was collected and concentrated again as above, then quantified to 10 mL (adding acetonitrile). The final solution was analyzed with the liquid chromatograph LC-10Avp.

2.4. X-ray Diffraction

The structural characterization of both ESP dust and its filter residue obtained after water leaching were performed through X-ray diffraction analysis in an appliance model M21 from MAC Co. Ltd. of Japan. X-ray patterns of samples powdered to 300 mesh were obtained in the 2θ-range from 10° to 90° with a scan step of 0.05°/2θ, and fixed counting time of 1 s for each step. The pattern was analyzed by using the Search-match software.

2.5. Scanning Electron Microscopy and Micro-analysis

Scanning electron microscopy (SEM) with X-ray energy dispersive spectrometry (EDS) was performed to gain further knowledge of the ESP dust particles structure, morphology and their chemical composition before and after water leaching. The samples were pressed in an organic resin by cold cure, grounded with silicon carbide paper and polished with diamond suspension. The samples were carbon coated for imaging and EDS analysis. The same samples were also subjected to the element distribution analysis (Cl and K) through X-ray mapping analysis via SEM.

3. Results and Discussion

3.1. Granulometric Analysis

The granulometric distribution analysis of the ESP dust is shown in Fig. 1.

The mean particle size of ESP dust determined by laser granulometer was 8.297 μm. It can be seen from Fig. 1 that the ESP dust has a heterogeneous distribution of particle size, where about half have size below 10 μm, and the other half between 10 and 54.64 μm. Such an irregular granulo-

Fig. 1. Granulometric distribution of ESP dust.
metric distribution is probably due to the agglomerated state of the particles, which is well known to have fine granulometry.

N. Menad and H. Tayibi pointed out that the dust particles generated from sinter plants are finer than some other dust sources, such as blast furnace and basic oxygen furnace emissions.\(^{12}\) The ESP dust tend to exist as aggregates consisting of very fine individual particles. Most of the individual particles were lower than 10 µm.

### 3.2. Chemical Characterization

#### 3.2.1. Elemental Composition of the ESP Dust

The results of the chemical analysis of ESP dust are presented in Table 1. Results indicate that Fe, K, Ca, Al, and C are the major elements in the sintering process. It is worthy to be noted that the contribution of K is high in the dust. According to the elemental composition of particles in particulate emissions from an integrated iron and steel facility in Tsai Jiu-Horng’s investigation,\(^{13}\) the contribution of K and Pb is higher in the sintering process than in the other processes, especially the K contribution, which is about 11.5 mass% of the particle mass in the sintering process.

Potassium is more easily volatilized than other metal elements except mercury in this study. Therefore, potassium compounds volatilized in the sintering process and then condensed into particles. In addition, there were many raw materials containing K\(_2\)O, i.e., BF slag and slurry.

#### 3.2.2. Ionic Compound Concentration

Table 2 shows the ionic compound concentration of the ESP dust after water leaching. Results indicate that the chloride concentration is the highest of all the ionic compounds tested, with concentration of 154.88 mg/g. Sulfate is the second highest, which is largely lower than Cl\(^-\) concentration. The chloride compounds may be attributed to materials like polyvinyl chloride contained in the iron and steel scrap, as reported by Tsai Jiu-Horng.\(^{13}\)

#### 3.2.3. PAHs Concentration

Sixteen PAHs were analyzed in this study. All of them were detected in the sintering dust except Acenaphthylene. Table 3 shows the PAHs concentrations and Fig. 2 gives the ring distribution of the PAHs. The percentage of the mass contribution of the 16 PAHs was 5-ring (37.5%) > 4-ring (32.6%) > 6-ring (26.4%) > 3-ring (3.4%) > 2-ring (0.05%). Apparently, four, five and six ring PAHs were the dominant ones in the dusts. In addition, BaP is acknowledged as a higher potential carcinogen compound than the other PAHs and is detectable in the dusts (5 574 ng/g). Correct disposal of the sintering dusts is essential in view of the potential hazard.

The mechanism of formation of PAHs, which is well investigated in the incineration process, is poorly understood in the electric precipitating process. There are two possible reasons:\(^{13,14}\)

1. The raw materials contain these molecules, and they are incompletely destroyed during sintering.
2. These molecules are formed from chlorinated precursors such as PCBs, chlorinated phenols and chlorinated benzene in the process of static electric precipitation, or via reactions with fly ash.

#### 3.3. X-ray Diffraction

Figures 3 and 4 show the X-ray diffraction pattern of the ESP dust sample before and after water leaching.

As it can be seen, KCl, NaCl, Fe\(_2\)O\(_3\), and PbO\(_2\) are present in the ESP dust sample. It is thus easy to be understood that there is almost no KCl and NaCl observed in the ESP dust after water leaching. And Fe\(_2\)O\(_3\) is the major phase presented in Fig. 4. However, the signals from most of the phases exhibit overlapping in some extent, and the presence of these phases cannot be unequivocally assured.\(^{15,16}\) As it will be shown, to improve the phase identification in samples it is necessary to use other techniques, such as scan-
3.4. Scanning Electron Microscopy and Microanalysis

Figure 5 shows a general distribution of ESP dust particles, where most particles aggregate drastically. It is easy to understand the aggregation with resort to particle size analysis results of the dust. In another word, the SEM analysis further prove the analysis results of granulometric distribution.

Figures 6 and 7 show scanning electron micrographs of the ESP dust particles before and after water leaching respectively, with magnification 1000 X. And Tables 4 and 5 show the results of EDS analysis of areas identified in the figures.

It can be seen that comparing with Table 4, except elements Cl and K, contents of the other elements in the Table 5 increase to some extent, especially for element Fe. This phenomenon is in a good agreement with the analysis result of XRD. Furthermore, it is observed that almost all the elements cannot be dissolved except for Cl and K. This is no doubt an advantage to separate KCl from the other elements by water leaching.

To further verify presence of KCl phase in the ESP dust,
Table 5. Energy dispersive spectrometry (EDS) of areas 1 to 4 in Fig. 7 (mol%).

| Element | Area 1(%) | Area 2(%) | Area 3(%) | Area 4(%) |
|---------|-----------|-----------|-----------|-----------|
| Al      | 8.922     | 6.932     | 3.670     | 6.034     |
| Si      | 12.58     | 10.77     | 4.804     | 9.642     |
| S       | 1.871     | 3.538     | 2.865     | 4.165     |
| Cl      | 1.675     | 7.711     | 0.540     | 10.25     |
| K       | 0.175     | 1.067     | 0.000     | 3.416     |
| Ca      | 28.37     | 17.25     | 13.46     | 22.79     |
| Fe      | 42.34     | 34.88     | 73.15     | 30.39     |
| Cu      | 2.039     | 1.321     | 0.427     | 1.927     |
| Pb      | 2.006     | 16.52     | 1.089     | 11.39     |

Fig. 8. SEM EDS mapping of Cl and K for an ESP dust particle (magnification ×20 000).

Fig. 9. SEM EDS mapping of Cl and K for an ESP dust region (magnification ×200).

Fig. 10. SEM EDS mapping of Cl and K for a region of ESP dust after water leaching (magnification ×200).

Fig. 8 shows secondary electron image of a KCl particle in the sintering emission (magnification ×20 000). Furthermore, Figs. 9 and 10 show secondary electron images of two ESP dust regions (magnification ×200) and the X-ray mapping for the elements of Cl and K before and after water leaching respectively.

It is necessary to be noted that there could be some error due to operation noise of the machine. That is to say, some signals in the two figures may be produced by machine noises. However, it is clear to see that potassium in the sintering dust is mainly combined with chloride. So distribution of Cl and K is always the same, with a drastic content...
decrease after water leaching because of its water-solubility. In addition, there is still some KCl left in the leaching residual. A possible reason is the insufficient washing in the filtering process.

4. Conclusions

(1) The mean particle size of ESP dust is 8.297 μm. The ESP dust has a heterogeneous distribution of particles, where the size ranges from 1.09 to 54.64 μm;

(2) K contribution is the second high in the sintering dust next to Fe, which is 11.50%;

(3) Fifteen PAHs were detected in the sintering emissions, and the total mass contribution is 611 20.8 ng/g. BaP, a higher potential carcinogen compound than the other PAHs, is detectable in the dusts (5 574 ng/g);

(4) XRD technique detected the following phases in the ESP dust: KCl, NaCl, Fe₂O₃ and Pb₃O₄, and Fe₂O₃, CaMg(CO₃)₂, MgFe₂O₄, CaCO₃ and Pb₃O₄ in the ESP dust after water leaching;

(5) It is proved that K in the ESP dust is mostly presented in the phase of KCl, which is easy to be separated from other elements such as Fe, C and so on. This feasibility is verified by using SEM EDS and mapping technique;

(6) It is expected to recover KCl from the ESP dust, not only contributing to lessen endanger of K to blast furnace, but to ease the lack of K contained fertilizer in China.

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