

CHEMICAL, PHYSICAL AND MORPHOLOGICAL CHANGES OF SINTERING DUST BY MECHANICAL ACTIVATION

Feng Chang¹, Shengli Wu^{1,2}, Jianliang Zhang¹, Mingyin Kou¹, Hua Lu¹, Laixin Wang¹

¹School of Metallurgical and Ecological Engineering, University of Science and Technology
Beijing; 30 Xueyuan Road; Haidian District, Beijing, 100083, P. R. China

²School of Metallurgy and Chemical Engineering, Jiangxi University of Science and
Technology; No.156, Kejia Ave.; Ganzhou, Jiangxi, 341000, P. R. China

Keywords: Mechanical activation; Sintering dust; Characterization

Abstract

Sintering dust has been regarded as an important secondary resource in a modern steel plant. Sintering dust was mechanically treated using different milling machines and experimental conditions in air atmosphere. The changes in phase constitution, particle size, specific surface area, particle morphology, and lattice parameters of activated sintering dust were determined. It was found that the agglomeration of the particles take place during extended dry milling with accessible pores for Nitrogen gas. The maximum specific BET surface area in the stirring wet grinding and planetary wet grinding increases to 43.06 and 46.45 m²/g after activated 360 min respectively. With the increasing of energy input, the intensity of diffraction peaks of dolomite and hematite gradually decreased. Furthermore, the previous phase almost disappeared eventually under any experimental conditions. In addition, Fourier transform infrared spectroscopy indicates that organic matter and carbonate decompose easier than other phases, especially under stirring wet milling.

Introduction

The sintering of iron ore is an agglomeration process in which blends of iron ore, fluxes, fuel in the form of coke and reverted materials from steel works are mixed together to produce a feed suitable for the blast furnace. 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. According to statistics, 4 kg of sintering dust was produced per ton of steel, that is, about 3.291 million tons of sintering dust was generated in 2014 in China. The comprehensive utilization rate of sintering dust is less than 20%, and most of the sintering dust is stored at the plant. Not only does the large amount of sintering dust take up much land including farmland, it also causes environmental pollution to different degrees. The sintering dust contains a high content of SiO₂, CaO and MgO, which can cause a high incidence of silicosis to the workers, especially in the sintering of high basicity sinter. Therefore, the sintering dust must be dealt with by some kind of treatment.

The existing treatment processes for sintering dust can be roughly divided into the following four categories: sintering process, pellet process, direct reduction process and hydrometallurgical process. [1][2][3][4] With the enrichment circulation of harmful elements, it is difficult for the sinter process to totally digest the dust produced by itself. Research has shown that, the pelletability of sintering dust is much worse than the blast furnace dust or basic oxygen furnace dust. The direct reduction process is suitable for handling dust with high content of zinc. The hydrometallurgical process is mainly adopted to extract potassium in the sintering dust, however,

it needs enough water and it would cause new pollution. In addition, the recovery rate of value elements in sintering dust by pyrometallurgical or hydrometallurgical process is finite.

Mechanical activation (MA), a narrow field of the Mechanochemistry (MC) applied for the activation of chemical reaction by mechanical energy, has been used in mineral processing to produce finely ground particles, increased surface area and improved chemical reactivity of milled materials. To promote the pelletability, direct reduction kinetic conditions, and leaching kinetic conditions of sintering dust, pretreatment by mechanical activation have been investigated.

The goal of this paper is to study the chemical, physical and morphological changes of mechanically activated sintering dust by means of granulometry analysis, specific surface area analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

Experimental

Raw material

The sintering dust used in this study was kindly supplied by Baosteel in China. The main chemical composition of the initial sample is given in Table I. The Total iron and calcium oxide content in sintering dust is about 45% and 11%, respectively. The total content of fluxes is around 17%. In addition, the content of potassium, sodium, zinc and lead elements are relatively low. The XRD pattern of the initial dust sample can be seen in Figure 1. It showed mainly hematite, dolomite and Potassium chloride, while small amount of limestone and Sodium chloride reflection peaks. The BET specific surface area of the starting sintering dust sample was 9.18 m²/g. Sintering dust appear to relatively loosely agglomerated, and some of them was bright under SEM.

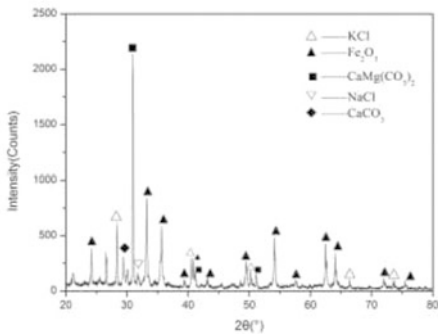


Figure 1. The XRD patterns of initial sintering dust

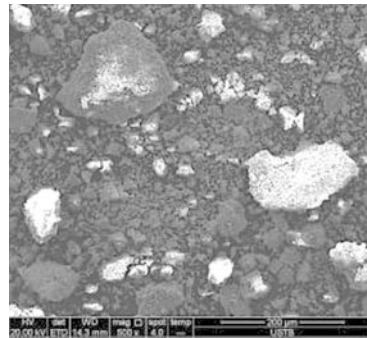


Figure 2. The particles morphology of initial sintering dust

Table I. The main chemical composition of the initial sample (wt. %)

TFe	FeO	CaO	SiO ₂	Al ₂ O ₃	MgO	K	Na	Zn	Pb	Cl	C
44.66	2.49	11.14	1.80	1.92	2.47	2.82	0.93	0.07	0.30	4.58	4.20

Mechanical activation and characterization

The changes brought about by different milling devices during the mechanical activation of sintering dust were investigated using two types of ball mills; planetary and stirring mills. The milling was carried out by different sizes of steel media from 3 mm to 20 mm. A statistical design for two levels of grinding methods and six levels of milling time (10, 30, 60, 120, 180, 360 min) was used. All experiments were performed in air and deionized water atmosphere. Each experiment was carried out independently and in closed condition. The experimental milling conditions are displayed in Table II. The material of mill tank and mill media is stainless steel. As milling media, the diameters of stainless steel ball used in planetary mill are 6, 10, and 20 mm. However, it is only 3 mm in stirring mill. The mass ratio of deionized water to sintering dust is 1.5 to 1 when wet grinding is conducted.

The particle size distribution of the mechanical activated samples was measured by laser diffraction (LMS-30) with anhydrous ethanol as dispersing medium. The mean particle diameter and granulometric surface area were obtained from the particle size distribution. The specific surface area of the samples was determined by the BET method with AUTOSORB-1C (Quantachrome, USA). Samples were degassed by heating at 150 °C for 120 min immediately prior to measurements. Multi-point measurements were made to give a more accurate value. The X-ray diffraction (XRD) patterns were collected by a Rigaku TTRIII at a scanning speed of 2°/min using Cu K α radiation ($\lambda=0.15418$). The XRD patterns of the samples were recorded in the range $2\theta=20^{\circ}$ – 80° , using a step size of 0.02°. The surface structure was studied by scanning electron microscope with MLA 250 system. FTIR spectra were collected on an Infrared spectroscopy (NEXUS 670-FTIR, Nicolet, America) between 4000 and 400 cm^{-1} with a 4 cm^{-1} resolution and 32 scans. The samples were prepared as KBr pellets.

Table II. Experimental milling conditions

Milling conditions	Stirring milling	Planetary milling
Atmosphere	Air, Deionized water	Air, Deionized water
Milling time (min)	10, 30, 60, 120, 180, 360	10, 30, 60, 120, 180, 360
Ball to powder weight ratio	5:1	5:1
Speed (rpm)	400	400
Media diameter (mm)	3	20, 10, 6
L(mm) \times Φ (mm)	224 \times 168	100 \times 117

Results and discussion

Particle size

The effects of the milling on the particle size distributions are summarized in Figure 3. The initial sintering dust has relatively wide distribution in comparison to the milled samples. The gap differences between the curves imply that the rate of breakage in the earlier stages of milling is higher than the later stages of grinding. As the milling progresses, the breakage rate decreases whatever methods and experimental condition are applied.

However, there are some differences among the particle size distributions resulted in different grinding methods and operational conditions. From the perspective of short time mechanical activation, planetary wet milling and stirring dry milling tend to produce finer particles faster. In terms of prolonged mechanical activation, the stirring grinding is better than the planetary grinding; and the wet grinding is more effective. In the case of stirring wet milling, prolonged grinding tends to produce finer particles. This indicates that further size reduction in such mills at

the given circumstances is possible. In the planetary dry mill, the further size reduction is impossible if the milling time exceeds 1 h in planetary dry mill. But, intriguingly, when the dry milling time reaches to 180min, the sintering dust goes through a significant agglomeration process. For planetary wet milling, the agglomeration phenomenon lags behind the dry counterpart. In a word, dry grinding is liable to agglomerate, and planetary dry grinding tends to reunion particles earlier than planetary wet grinding. The agglomeration could be expected to decompose again with the extended milling, in particularly in dry mills. Stirring wet milling can prevent the reunion from happening. The agglomeration of particles were reported previously by many authors for various minerals in the prolonged milling and intensive milling conditions, confirming that this is a feature of extended intensive dry milling. [5] [6]

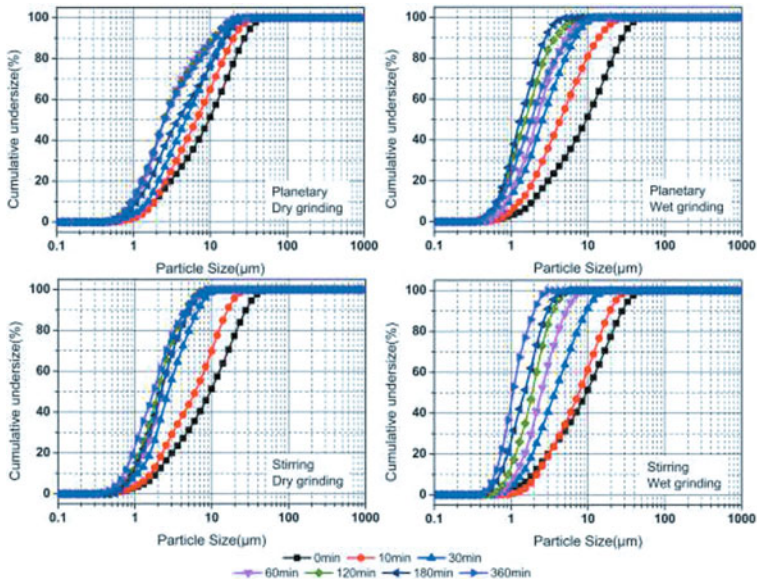


Figure 3. Particle size distributions of activated sintering dust using different milling devices and operational conditions along with the size distribution of initial sintering dust

BET specific surface area

The BET specific surface area of the planetary wet milling and stirring wet milling samples after different milling times is illustrated in Figure 4. According to P. Pourghahramani et al., the BET specific surface area of activated high-purity hematite concentrates in the initial stages of grinding increases rather sharply and continues to rise gradually. [7] Whereas, different from hematite concentrates, one most obvious feature for activated sintering dust is that the BET specific surface area decreasing a little in the initial stage whatever milling methods were applied. This is simply because that large number of fine particles of potassium chloride and sodium chloride dissolve in the water. Then, as the decomposition of hematite and dolomite particles, the BET specific surface area increased. The maximum specific surface areas in the milling with planetary wet mill and stirring wet mill are 43.06 and 46.45 m²/g, respectively. The effect by planetary wet milling was better for short time milling, whereas, the contrary result was achieved

for long time milling. Even though the agglomeration phenomenon aroused during the final stages of planetary wet milling, the specific surface areas of sintering dust continued increasing. It indicated that the agglomeration of the particles take place during extended dry milling with accessible pores for Nitrogen gas.

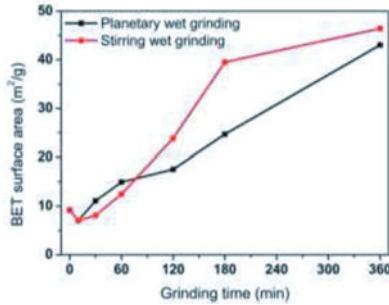
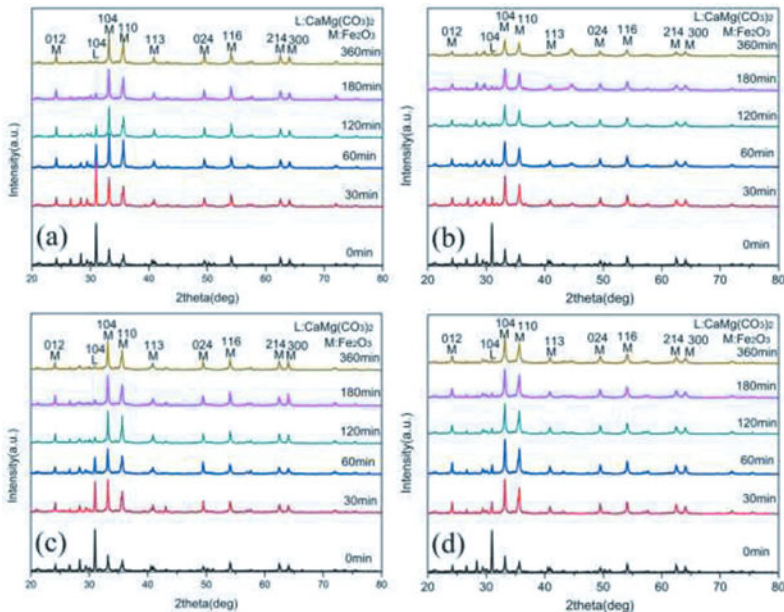


Figure 4. Changes in the BET specific surface area of sintering dust ground in planetary wet milling and stirring wet milling.

X-ray diffraction



(a) Planetary dry grinding; (b) Planetary wet grinding; (c) Stirring dry grinding; (d) Stirring wet grinding. Figure 5. The X-ray diffraction patterns of activated sintering dust as function of the grinding time using different milling devices and operational conditions.

The collected XRD patterns of the sintering dust are summarized in Figure 5 for different milling devices and operational conditions. XRD patterns show that with the grinding prolonged, the reflection peaks of potassium chloride, dolomite and hematite gradually become broad and low even disappeared, indicating that initial sintering dust did not undergo significant reactions during the milling. But the disappearance of diffraction peak at the position of 28.35 deg indicated that potassium chloride had promptly dissolved in water when stirring wet grinding was conducted. The XRD method studies do not show phases below 2 wt. %. This agrees with the observations of Kaczmarek and Ninham [8] and Stewart et al. [9]. However, our observations disagree with the findings of Kosmac and Courtney [10]. They reported a transformation of α - Fe_2O_3 to Fe_3O_4 during ball milling in a planetary mill. It is evident that our milling conditions could not change the stability of hematite.

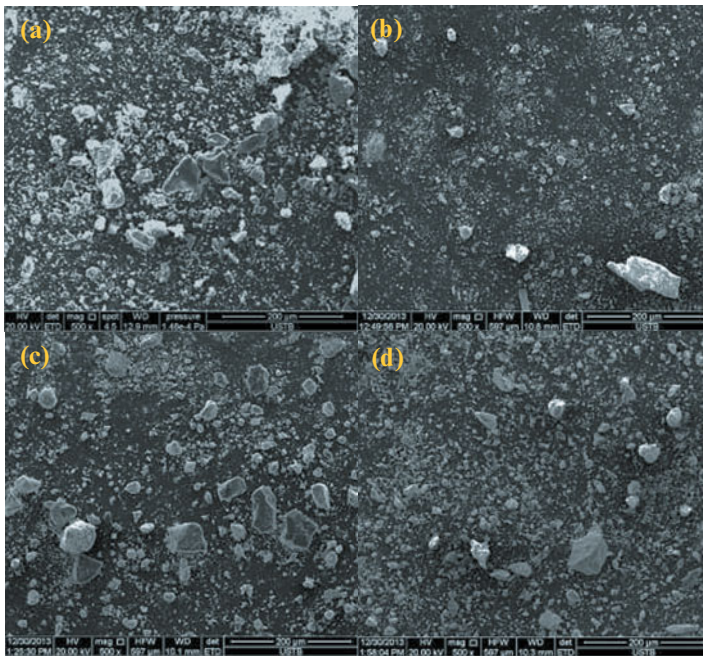


Figure 6. SEM photographs of sintering dust: (a) planetary dry grinding 30 min, (b) planetary wet grinding 30 min, (c) stirring dry grinding 30 min, (d), stirring wet grinding 30 min.

Table III. The grain size and lattice distortion of hematite under different milling conditions

Grinding type	Grinding time (min)	Air		Deionized water	
		Grain size (nm)	Lattice distortion (%)	Grain size (nm)	Lattice distortion (%)
Planetary grinding	30	107.1	0.02	65.8	0.012
	180	105.2	0.026	48.5	0.071
	360	97	0.033	25.5	0.103
Stirring grinding	30	103.6	0.014	80.7	0.035
	180	100.1	0.021	51.1	0.042
	360	87.3	0.037	50.3	0.077

In terms of the hematite phase, its grain size gradually decreased and lattice distortion gradually increased with the grinding time prolonged, as shown in Table III. The grain size and lattice distortion of hematite in the original sample were 109.5 nm and 0.009%, respectively. The effect by wet grinding was obviously better than dry grinding. The minimum grain size reached 25.5 nm after 6 hours planetary wet milling, and the corresponding maximum lattice distortion was 0.103%.

Morphological changes

The SEM micrographs of the planetary milling and stirring milling samples after milling 30 min are illustrated in Figure 6. The large agglomerated particles were basically separated and some hard bulk particles appeared as scattered distribution. As received by particle size analysis, the particle size decreases whatever methods and experimental condition are applied. Compared to dry milling, wet milling tends to produce much finer particles.

FTIR spectra

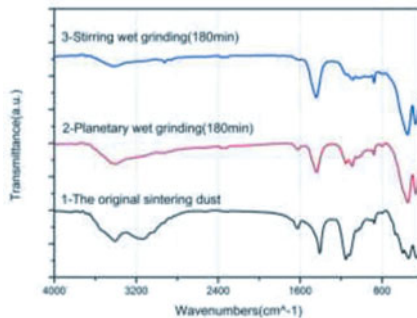


Figure 7. FTIR spectra of sintering dust

Due to high surface sensitivity, FTIR measurements were conducted to monitor the changes of the surface properties of the ground particles in both mills. The FTIR spectra of nonactivated and activated sintering dust after 180min planetary wet grinding or stirring wet grinding are presented in Figure 7. According to Figure 7, there are important changes in the relative

intensities, broadening and shifting of peak positions, which confirm once again the strong structural distortion as explained by XRD analysis. The disappearance of the bands around 3138 cm^{-1} correspond to C-H stretching vibration absorption peak indicates that unsaturated polycyclic aromatic hydrocarbons decomposes easier than other phases. The disappearance of the bands around 673 cm^{-1} and 598 cm^{-1} correspond to CO_3^{2-} bending vibration absorption peak and Al-OH key respectively. The almost disappearance of the bands around 1153 cm^{-1} correspond to C-O stretching vibration absorption peak indicates that dioxin twists easier than other phases, especially under stirring wet milling. Further surface sensitive measurements will be conducted in forthcoming works to gain a better insight about the mechanochemical characteristics in high energy grinding experiments.

Conclusions

- (1) Dry grinding is liable to agglomerate, and planetary dry grinding tends to reunion particles earlier than planetary wet grinding. Stirring wet milling can prevent the reunion from happening.
- (2) The BET specific surface areas of sintering dust decreased first by the disappearance of fine potassium chloride, however, it increased with prolonged grinding whether the sintering dust particles reunited or not.
- (3) With the grinding prolonged, the grain size of hematite gradually decreased, while the lattice distortion gradually increased. The change ratio by wet grinding was greater than dry grinding.
- (4) The potassium chloride phase, unsaturated polycyclic aromatic hydrocarbons and CO_3^{2-} in sintering dust disappeared by stirring wet grinding.

Acknowledgements

The financial support of the National Natural Science Foundation of China (U1260202) is gratefully acknowledged.

References

- [1] D.L. Zeng et al., "Research Advancement of Comprehensive Utilization of Iron-bearing Dust in Iron and Steel Plants," *Sintering and Pelletizing*, 36 (6) (2011), 45-49.
- [2] X. Liu et al., "Removal of Potassium and Preparation of Potassium Sulfate from Sintering EAF Dust," *Metal Materials and Metallurgy Engineering*, 39 (3) (2011), 40-45.
- [3] C. Peng et al., "Separation and Recovery of Potassium Chloride from Sintering Dust of Ironmaking Works," *ISIJ International*, 49 (5) (2009), 735-742.
- [4] X.F. She et al., "Study on Basic Properties of Typical Industrial Dust from Iron and Steel Plant and Analysis of Its Utilization," *The Chinese Journal of Process Engineering*, 9 (S1) (2009), 7-12.
- [5] P. Balaz et al., "Thiourea Leaching of Silver from Mechanically Activated Tetrahedrite," *Hydrometallurgy*, 43 (1-3) (1996), 367-377.
- [6] Q.W. Zhang et al., "Mechanochemical Changes in Gypsum When Dry Ground with Hydrated Minerals," *Powder Technology*, 87 (1) (1996), 67-71.

- [7] P. Pourghahramani et al., "Microstructural Characterization of Hematite During Wet and Dry Millings Using Rietveld and XRD Line Profile Analyses," *Powder Technology*, 186 (1) (2008), 9-21.
- [8] W.A. Kaczmarek et al., "Preparation of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ Powders by Magnetomechanical Activation of Hematite," *IEEE Transactions on Magnetics*, 30 (2) (1994), 732-734.
- [9] S.J. Stewart et al., "Effects of Milling-induced Disorder on the Lattice Parameters and Magnetic Properties of Hematite," *Journal of Magnetism and Magnetic Materials*, 260 (3) (2003), 447-454.
- [10] T. Kosmaca et al., "Milling and Mechanical Alloying of Inorganic Nonmetallics," *Journal of Materials Research*, 7 (6) (1992), 1519-1525.