Practical Analysis of Physical Separation Technology of Waste Printed Circuit Boards From the Perspective of Process Mineralogy

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Keywords: Waste printed circuit boards, crushing, dissociation granularity, physical sorting.

Abstract: This paper analyzes and evaluates the practicability of physical separation technology for waste printed circuit boards from the perspective of process mineralogy. After the waste computer circuit boards were crushed and screened twice with a multifunctional crusher and a ball mill, the particle morphology, particle size, dissociation and the influence of temperature and humidity in different particle size range were characterized and measured. On this basis, the influence of the change of each factor on the separation efficiency of physical separation technology was analyzed. Finally, from the perspective of technological progress and environmental protection, some suggestions are put forward for common physical sorting technologies, such as wet crushing or low-temperature crushing in the crushing stage, and adding vacuum devices and drying devices in the sorting process,I hope this paper can make some contributions to the disposal of waste circuit boards and the development of circular economy.

1. Introduction

Printed circuit board (PCB) is almost an essential component of electronic products and equipment, and it is the most complex, valuable and dangerous component. As people gradually increased demand for electronic product, update speed more and more frequent, amount of waste printed circuit board also increase[1], it is estimated that recycled every year is about 1.1 million tons of waste household appliances in China, in which waste printed circuit boards (WPCBs) accounted for about 30%[2], WPCBs containing glass fiber and epoxy resin and the high grade metal[3], the material composition as shown in Table 1, metal accounted for about 40%, plastic accounted for about 30% of the glass fiber and other non-metallic accounted for about 30%, recycling WPCBs metal and nonmetal can effectively relieve the shortage of natural resources bottleneck,However, attention should be paid to hazardous metals and complex flame retardant components in the recycling process.At present, the process of recycling WPCBs from the perspective of environmental protection and economic benefits has become a research focus[4,5], However, due to the diversity and complexity of PCB in materials, component types, shapes and sizes, many researchers say that it is extremely challenging to recycle WPCBs correctly[6-9].

The recycling process of WPCBs is generally as follows: pretreatment (disassembly and mechanical crushing)→physical sorting (using the difference of particle size, density and magnetoelectricity)→refining and purification (wet method, fire method and biological method). Mechanical breakage is one of the most important pretreatment[10], the process of metal and nonmetal crushing granularity and fully dissociation is an important premise of subsequent separation and physical separation is the use of WPCBs particle shape, density and electrical conductivity difference between shape separation[11,12], gravity separation[13] and electrostatic separation[14, 15] technology to separate the metal and nonmetal, but these physical separation technology of separation efficiency is limited by the metal and nonmetallic dissociation degree,hardness, particle shape and size, particle surface factors such as water content. These influence factors often result in the loss of large amounts of metal during crushing and physical separation. At present, there are few studies on the evaluation of the practicability of physical sorting technology, this study attempts to analyze the practicability of physical sorting technology from the perspective of process mineralogy.Therefore, WPCBs particles are characterized and analyzed by mineralogical processing methods such as particle size analysis, particle shape observation and dissociation degree measurement. Finally, the practicability of physical sorting technology is discussed according to the analysis results, and the research emphasis of physical sorting technology for discarded printed circuit boards in the future is pointed out.

Table 1: This caption has one line so it is centered.

Metal (about 40%）	content/%	Plastics (about 30%）	content /%	Other nonmetals (about 30%）	content /%
Cu	6.0-27.0	PE	10-16	SiO2	15-30
Fe	1.2-8.0	PP	4.8	Al2O3	6.0-10
Al	1.3-7.2	PS	4.8	Alkaline earth oxide	6.0
Zn	0.2-2.2	PVC	2.4	Titanate, mica	3.0
Pb	1.0-4.2	PTPE	2.4		
Ni	0.3-5.4	epoxy resin	4.8		
Sn	1.0-5.6	nylon	0.9		
Sb	0.1-0.4				
Au(ppm)	80-2050				
Ag(ppm)	110-4500				
Pt(ppm)	5.0-30				
Pd(ppm)	50-2200				
Co	1.0-4000				
Ti	1.0-4000				
Cr	0.2-0.4				
Mo	0.02				

2. Materials and Methods

2.1. Experimental Materials

The computer motherboard circuit board raw materials selected in the experiment are provided by Shanghai Electronic Waste Recycling Collaborative Innovation Center, which is the most widely used FR-4 epoxy resin glass fiber copper clad laminate (FR-4 epoxy resin copper clad laminate for short). The glass fiber and epoxy resin in the substrate cross-link to form an adhesive sheet, which is embedded between two layers of copper foil. The thickness of copper foil is generally 0.05-0.06mm, the thickness of epoxy resin is about 0.3mm, and bromine is also contained.

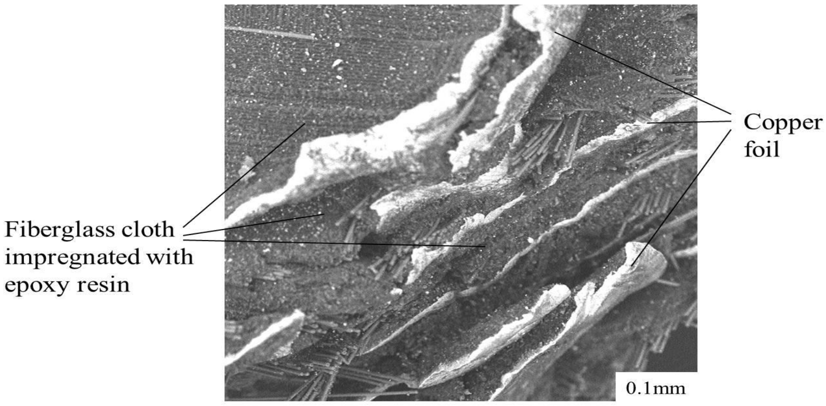


Figure 1: SEM image of cross section of circuit board.

2.2. Experimental Methods

WPCBs is characterized and separated by mineral processing methods (crushing, sieving and sorting), Fig.2 shows that WPCBs is crushed and sorted by mechanical and physical methods, and metal and nonmetal components are separated and enriched in this process.

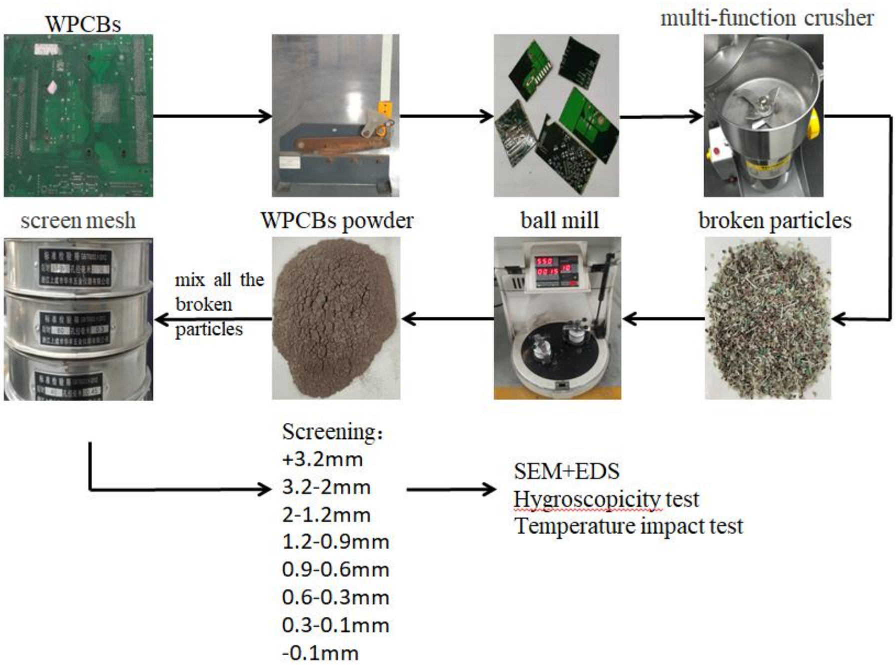


Figure 2: Flow chart of wpcbs crushing and sorting.

2.2.1. Disassembling and Crushing

Waste printed circuit boards contain many easily removable electronic components, such as capacitors, resistors, etc,In order to facilitate crushing and sorting, these components were removed with tweezers, scissors and other tools in advance, and then WPCB was crushed in two stages by using a high-speed multifunctional crusher and a ball mill, aiming at achieving complete dissociation of metal and nonmetal. WPCBs is crushed in a multifunctional crusher, and then sieved,because there are very few particles with a particle size of -0.1mm after sieving, some fragments in each particle size range after sieving are put into a ball mill for secondary crushing.

2.2.2. Screening

The crushed particles passing through the two grinding stages were manually screened by laboratory standard inspection sieve, and the waste PCB particles with eight particle sizes of +3.2mm, 3.2-2mm, 2-1.2mm, 1.2-0.9mm, 0.9-0.6mm, 0.6-0.3mm, 0.3-0.1mm and -0.1mm were obtained.

2.2.3. Analysis of Dissociation and Temperature Influence

In order to fully dissociate metal and nonmetal in WPCBs and achieve the best granularity of materials needed in the subsequent physical separation technology, it is necessary to determine the dissociation degree and select the appropriate crushing granularity and crusher type before crushing. Scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) were used to analyze the morphology of the particles in different particle sizes, and to observe and analyze the dissociation of metal and nonmetal

In the process of crushing, because the crusher works for a long time, the internal cavity of the crusher will produce higher temperature, which will soften the epoxy resin and make it harder to break, thus affecting the subsequent physical separation efficiency. In order to study the change of epoxy resin with the increase of temperature in the crushing process, the heating phenomenon in the crushing process was simulated in this study,Small pieces of WPCBs were heated to 100℃, 120℃, 140℃, 160℃, 180℃, 200℃, 220℃ and 240℃, respectively, and then put into a multifunctional crusher for crushing for 3min. After sieving, the cross-sectional morphology of epoxy resin in each particle size range was observed by SEM.

2.2.4. Determination of Moisture Absorption Characteristics

Moisture absorption characteristics is mainly to circuit boards in the determination of moisture absorption of epoxy resin, epoxy resin are susceptible to change with the hot and humid environment impact performance, the moisture absorption process including through physical diffusion, cracks and crack physical moisture absorption of moisture absorption, and through hydrogen bonding resin chemical absorption of moisture, chemical absorption of moisture is a kind of irreversible chemical reaction[16]. In this study, the physical moisture absorption phenomenon of epoxy resin in WPCBs was observed and explained. The experimental instrument is an electronic balance with an accuracy of 0.0001g.The crushed particles with different particle sizes were placed in the experimental workshop for 72 hours in the natural environment. The hygroscopicity test adopts the weighing method, and the materials are weighed after being placed for 2h, 4h, 8h, 16h, 32h, 48h and 72h respectively,After weighing, the materials are put into the experimental workshop, and the whole weighing process is completed within 2min. The water absorption rate Mt is calculated according to formula (1):

$$M_t = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

Mt: the water absorption rate of material particles at time t;
W0: the initial mass of material particles;
Wt : is the mass of material particles at time t.

3. Results and Discussion

3.1. Screening Results and Appearance and Morphology Analysis of Crushed Materials

Figure.3 show the particles of different sizes obtained by screening waste computer circuit boards. According to the particle appearance, because the circuit board contains metal and nonmetal, and the hardness is different from that of natural ore, among the particle components with the particle size of +1.2mm for computer circuit board, the metal component is similar in shape to nonmetal, which is flaky or blocky, and the metal and nonmetal are conjoined, so the dissociation effect is poor. In the particle size range of -1.2+0.9mm, the non-metallic component is flaky or needle-like, and the metallic component is blocky or bent and folded into a ball, which is because the metal has strong toughness and can be extended and deformed during crushing. In the particle sizes of -0.9+0.1mm, the needle-like nonmetal is increased, and the metal is in block or ball shape. For particles with a size of -0.1mm, the naked eye can only see that both nonmetal and metal are in powder form. It is observed by scanning electron microscope that among nonmetal components, glass fiber is in bar shape, epoxy resin is in plate shape or tile shape, and metal is in block shape or pellet shape.

In view of the above observation results, it can be considered to separate some metals from non-metallic particles by shape sorting in large-size components. In addition, some metal and nonmetal particles are in free state in the components with particle size of -0.9+0.1mm. Because the density of metal is higher than that of nonmetal such as glass fiber and epoxy resin, the first separation process of crushed metal and nonmetal components can be carried out by using gravity separation technology under appropriate crushing particle size.

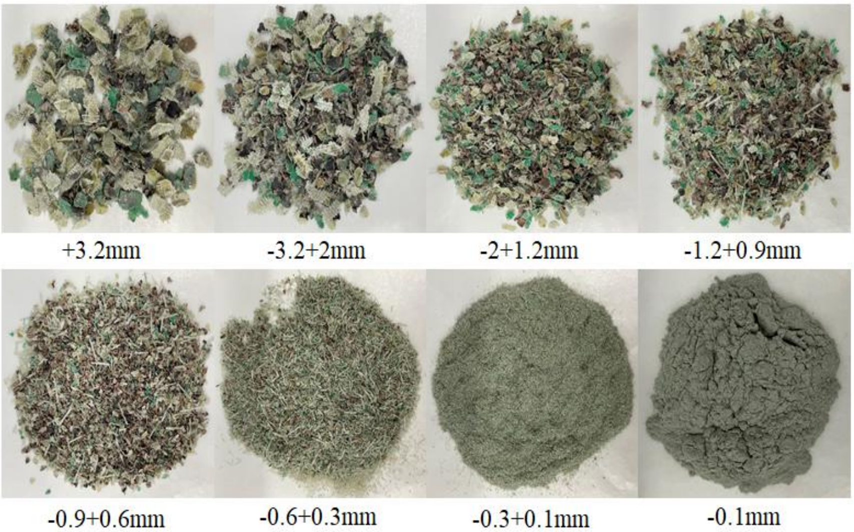


Figure 3: Waste computer circuit board scraps after screening.

3.2. Analysis of Dissociation

Figure 4 is SEM images of discarded computer circuit boards in various particle sizes, and Figure.5 and Figure.6 are SEM and EDS analysis results of particles with a particle size of -0.1mm after the computer circuit boards are crushed by a multifunctional crusher and a ball mill. The observation results show that metal particles have been basically dissociated from nonmetal at the particle size of -0.6+0.3mm, but glass fibers in nonmetal are wrapped by epoxy resin to form fiber bundle structure. Fig 5a is an SEM picture of particles with a particle size of -0.1mm obtained after crushing by a multifunctional crusher,The glass fiber and epoxy resin are not fully dissociated, but after crushing by a ball mill (Figure 5b), the glass fiber bundle is broken and the glass fiber and epoxy resin are basically separated.

The energy spectrum analysis of the selected points in Fig.5b is shown in Fig.6, and the selected points are metal and nonmetal particles which are basically dissociated into monomers. The results show that at the particle size of -0.1mm, the surface of non-metallic particles is still attached with metal, the presence of Si, Ca and Al can be determined as glass fiber, and the presence of other metallic elements such as Cu, Mg and Ag may come from the ceramic or metal oxides in the components that are not completely removed during the disassembly process [17].

Therefore, as far as crushing equipment is concerned, ball mill has better crushing effect than multifunctional crusher. The electron microscope results of WPCBs particles with different particle sizes show that when the particle size is about 0.1mm, the metal can be completely dissociated, but the glass fiber can not be completely decomposed with non-metals such as epoxy resin and flame retardant. In addition, when the grinding particle size is too fine, metal and non-metal particles may adhere to each other. The non-conductive powder on the surface of metal particles is one of the main reasons for the poor electrostatic separation effect [18].

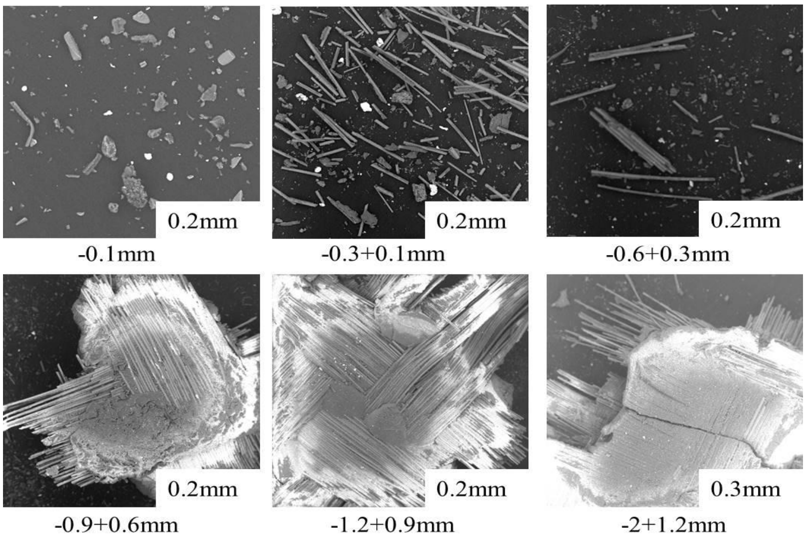


Figure 4: SEM image of discarded computer circuit board.

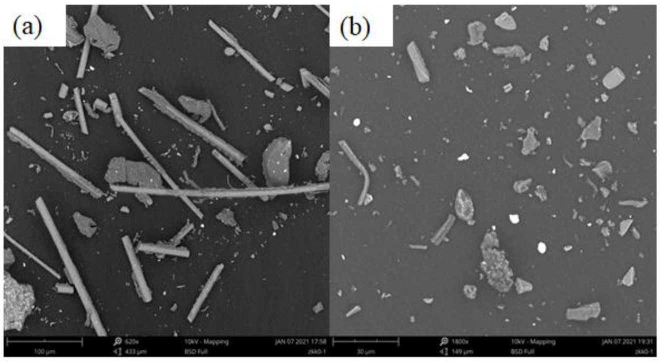
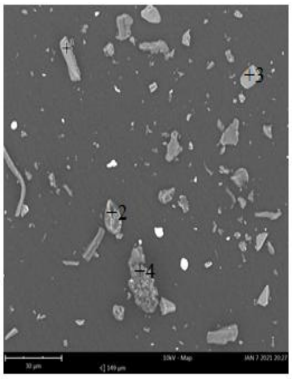


Figure 5: SEM picture of particles with a particle size of -0.1mm; (a) crushing by a multifunctional crusher (b) crushing by a ball mill.



EDS Analysis

Element (Wt%)	Point 1	Point 2	Point 3	Point 4
Si	77.56	86.83	51.66	65.87
Al	22.44	—	16.31	—
Ag	—	13.17	—	—
Ca	—	—	27.24	—
Cr	—	—	1.96	—
Mg	—	—	—	34.13

Figure 6: Energy spectrum analysis table of selected points in Fig.5b (removing elements: B, C, O).

3.3. Analysis of the Influence of Temperature on Dissociation

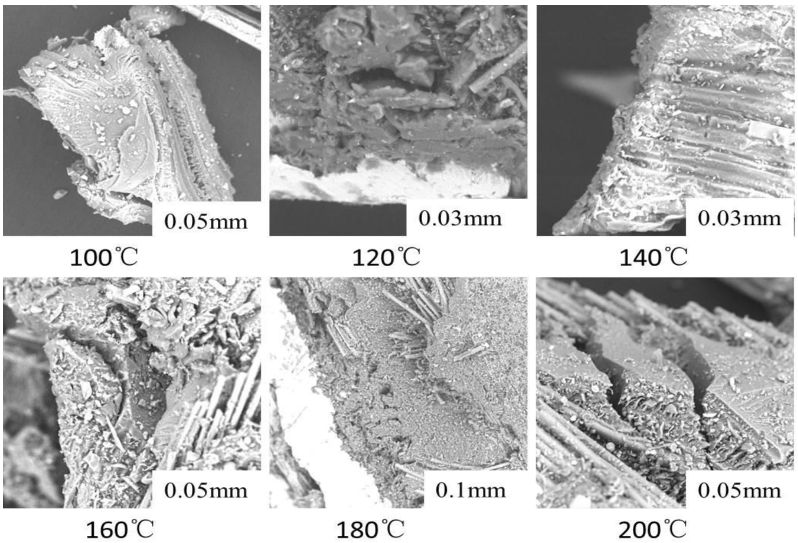


Figure 7: SEM picture of waste computer circuit board particles which are broken after simulating heating.

Figure 7 is an SEM picture of computer WPCBs particles obtained by crushing after heating to different temperatures. It can be seen from the figure that with the increase of temperature, the cross section of the broken epoxy resin becomes coarser, and the surface adhesion to some fine metals and other non-metallic particles increases, resulting in poor dissociation effect.In addition, when crushing, the higher the temperature, the more obvious the smell of poisonous gas emitted during crushing. Therefore, it is recommended to adopt wet crushing[19] or low-temperature crushing[20] in the crushing stage. If dry crushing is adopted, attention should be paid to the influence of temperature, dust removal device should be installed and air exhaust should be timely.

3.4. Hygroscopicity Results

Figure 8 is the change charts of water absorption rate of samples in winter indoor natural environment within 72 hours, respectively,It can be seen from the figures that the total water absorption rate of each particle size increases with the increase of time in natural environment, but the increase range is not obvious, which may be due to the small amount of samples used in this study and the low indoor humidity in winter. Kumagai S and Yoshimura N[21] compared and analyzed the hygroscopicity of epoxy resin at different temperatures, and found that the temperature increase would promote the hygroscopicity of epoxy resin materials, and the surface dielectric properties decreased after hygroscopicity. Therefore, the moisture content on the particle surface may be an important factor that causes the separation efficiency of electrostatic separation technology to deteriorate,To reduce the influence of moisture content on the particle surface, it is suggested to dry the WPCBs particles before adopting electrostatic separation technology to improve the separation efficiency.

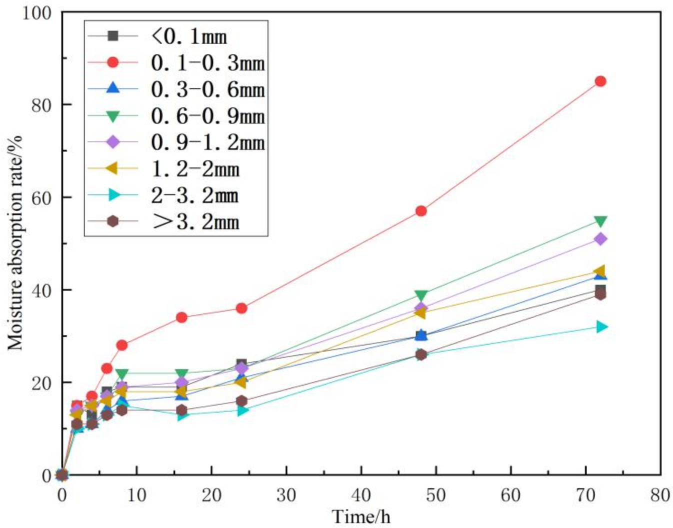


Figure 8: Moisture absorption of waste computer printed circuit board particles with time in natural environment.

4. Conclusions

The innovation of this paper is to evaluate the practicability of mechanical-physical separation technology from the point of view of process mineralogy and the influence of particle morphology, particle size, dissociation degree and other factors on physical separation methods. According to the results of this study, the following conclusions are drawn:

(1) The crushing results show that the crushing effect of ball mill is better than that of multifunctional crusher with shear force. The morphology of crushed particles after screening was observed by naked eyes. It was found that when the particle size was about 0.9mm, the non-metallic particles were flake or needle-shaped, and the metal particles were block or bent and folded into a mass. Shape sorting could be used to help separate metal and non-metallic components,When the particle size is -0.6mm, the metal and nonmetal are basically dissociated, and the density of metal components is higher than that of nonmetal,At this time, gravity separation can be selected as the preliminary separation process.

(2) Through SEM+EDS observation, it is found that metal and nonmetal are basically dissociated when the particle size is -0.6+0.3mm; at a small particle size (-0.1mm), metal and nonmetal are completely dissociated, but the dissociation between glass fiber and epoxy resin is not ideal, at this particle size, nonmetal particles adhere to metal particles and become a mixture of particles. This phenomenon will lead to the change of physical properties such as density and conductivity of nonmetal and metal particles,Ultra-fine particles are easily disturbed by air flow in the separation process, and the trajectory under the compound force field no longer meets the ideal state. Physical separation technology cannot achieve the best separation effect. Therefore, before crushing, the optimum crushing particle size should be determined according to the subsequent sorting process.

(3) The results of simulating the heating phenomenon in the machine cavity during the crushing process of WPCBs show that with the increase of temperature, the smell of toxic and harmful gases becomes more obvious, the epoxy resin gradually softens, the viscosity increases, and a large number of fine metal or other nonmetal particles adhere to its surface, which greatly reduces the separation efficiency. Therefore, it is recommended to use wet crushing or low temperature crushing to reduce the influence of temperature, fine dust and harmful gases.

(4) The moisture absorption test results of WPCBs particles show that if the particles are placed in natural environment for a long time, the quality of the particles will increase due to moisture absorption, and the moisture content on the surface of the particles will increase, which will make the electrostatic separation effect worse. It is suggested to add vacuum device and drying device in mechanical-physical separation process to reduce the influence of moisture and airflow disturbance on particle surface.

(5) The crushed materials can be divided into several components according to the size, shape, dissociation degree, etc. Different physical separation technologies are selected for different components, so that the separation effect of each physical separation technology can reach the best.

Acknowledgments

This work was supported by the National Key R&D Program of China (No.2018YFC1902303)；Gaoyuan Discipline of Shanghai -Environmental Science and Engineering (Resource Recycling Science and Engineering) , and Shanghai Second University of Technology Postgraduate Program Fund (EGD18YZ0052).

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