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# Spent Lead-Acid Batteries Crushing Mechanical Properties and Impact Crushing Effect

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**Abstract:** The spent lead-acid battery contains a large amount of lead metal and waste acid. If not treated or simply treated, it will cause serious environmental pollution and even endanger human health. The paper focuses on the recovery of valuable resources such as lead paste and plastic by replacing chemical methods with physical ones, which the bending performance was tested with electronic universal testing machine and the impact performance measured with plastic pendulum impact testing machine. At the same time, a self-designed crusher is also used for impact crushing. The test results showed that the plastic shell is hard and brittle and has strong resistance to bending, but its impact resistance is weak. The spent lead-acid batteries were crushed by self-designed impact crusher. In the broken products, the grids and fiber separators were distributed between 2.2-0.5 mm in diameter, while plastics mainly over 10 mm and lead paste mainly below 0.1 mm. The XRD results show that the lead in each particle size has different forms and contents of lead. Different comminution experiments show that the appropriate process parameters can achieve the existence of valuable resources such as plastics, grids, and lead pastes in spent lead-acid batteries according to their shape and size, which helps the subsequent sorting and recovery of valuable materials.

**Keyword:** Spent Lead-Acid Batteries, Mechanical Properties, Impact Crushing, Granular Distribution, Resource Recovery

## 1. Introduction

Lead-acid battery is a mature power equipment and energy storage system [1-2]. It has been widely used in automobiles, electric bicycles, small dynamic energy storage systems and stationary applications due to its low manufacturing cost, high operational safety, and relative ease of carrying [3]. In China, the lead-acid battery industry has expanded into an industry with more than 400 factories [4]. The production of lead-acid batteries has grown steadily during the past 10 years, and the production capacity reached 221 GWh in 2014, accounting for more than 40% of global output of lead-acid batteries [5]. On the other hand, lead-acid batteries have a certain useful life, such as car batteries are generally 3-5 years. It has been estimated that the number of spent lead-acid batteries about 7 million tons in China's annual report [6]. If large amounts of discarded lead-acid batteries are left outdoors or simply disposed of in landfills, heavy metals and waste acids will cause environmental pollution and threaten human health.

The main resources available for spent lead-acid batteries are polymer containers (usually plastic), lead alloy grids, waste acids and pastes. Lead paste is an important secondary lead production raw material, including lead oxide (9%), lead dioxide (28%), lead sulfate (60%) and a small amount of lead (3%) [7]. In the coming years, the total lead production will increase, while the level of primary lead production in the first ten years will remain unchanged, In other words, all the growth will be supported by the secondary output. Therefore, secondary lead production will play a crucial role in the sustainable development of the lead industry [8-9]. The process of hydrometallurgy [10-11] and pyrometallurgy [12] are common use to recover lead from spent lead-acid batteries, which recycling technology is relatively mature and essentially chemical. However, prior to metallurgical and chemical processing, pretreated spent lead-acid batteries are usually crushed, crushed, and physically separated. In this process, lead-acid batteries are divided into many groups including lead paste, sulfuric acid, fiber separators, and plastics [13].

The physical sorting of foreign waste lead-acid batteries is commonly used by the CX crushing and sorting system of Italian Engitec, the M. A crushing and sorting system of M. A, and the Russian heavy medium sorting system [14-16] However, the clean production level of China's regenerative lead enterprises is not high, about 75% are scattered small workshops or small enterprises to manually disassemble waste lead-acid batteries, which is still a big gap compared with foreign countries [17]. It is noted that metallurgical and chemical processing of waste lead-acid batteries will cause secondary environmental pollution. Therefore, based on purely physical methods, how to recover the valuable resources of lead paste, plastics and grids from spent lead-acid batteries was discussed in this paper.

## 2. Materials and Methods

### *2.1. Materials and Dismantling Test*

Test battery is an electric bicycle special lead-acid battery (Chaowei 6-DZM-20). Its rated voltage is 12V, rated capacity 20Ah, and the average mass 6.925kg. It is 181, 77 and 170 mm in length, width and height, respectively. Using a small hacksaw, screwdriver, wire pliers and other tools to separate the battery from the slot cover (Figure 1a), it can be seen that each battery has 6 mutually uncomplicated cells, and each cell has an electrode group (Figure 1b). The composition and quality of each part of the material after dismantling are shown in Table 1.

After disassembling one of electrode group and peeling the plastic case (Figure 1c), it was found that the positive and negative electrodes of cell were separated by a fiber separator (Figure 1d). When this layer of white fiber separator was opened carefully, positive lead paste (Figure 1e) and negative lead paste (Figure 1f) were exposed, coated on the surface of the grid (Figure 1g). Table 2 is shown the composition and quality of each part after dismantling an electrode group.

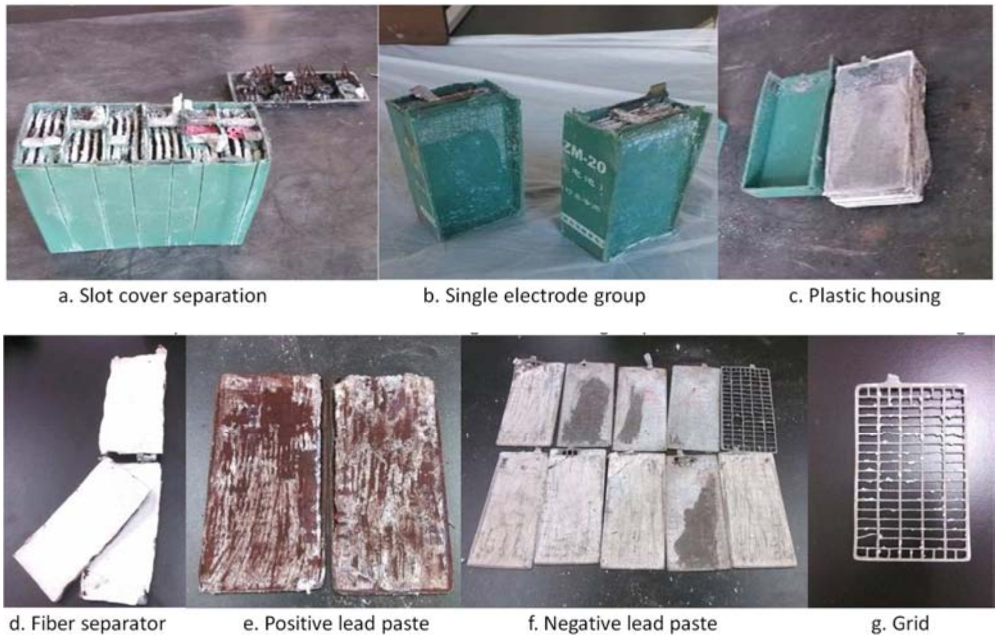



***Figure 1.*** *spent lead-acid battery and its components after dismantling.*

***Table 1.*** *The product composition of spent lead-acid battery after dismantling*

| Composition | Quality /kg | Quality percentage /% |
|---|---|---|
| Plate group | 6.251 | 90.27 |
| Plastic shell | 0.510 | 7.36 |
| Bus conductor | 0.164 | 2.37 |
| Total | 6.925 | 100.00 |

***Table 2.*** *The product composition of an electrode group after dismantling.*

| Composition | Quality /g | Quality percentage /% |
|---|---|---|
| Positive lead paste | 802.5 | 42.13 |
| Negative lead paste | 646.4 | 33.90 |
| Grid | 390.6 | 20.48 |
| Fiber separator | 66.6 | 3.49 |
| Total | 1806.1 | 100.00 |

It can be seen from Table 1 and Table 2 that after dismantling one spent lead-acid battery, the main valuable components are lead paste, grid, and plastic, accounting for 91.86% of the total weight of the lead-acid battery. If the three products are efficiently recovered, the recycling of spent lead-acid batteries will be realized.

Dismantling product shows that the negative electrode paste is mainly Pb and the reaction resultant $PbSO_4$, the positive electrode paste is $PbO_2$ and the reduced PbO. The working principle diagram of the electrode group is shown in Figure 2.

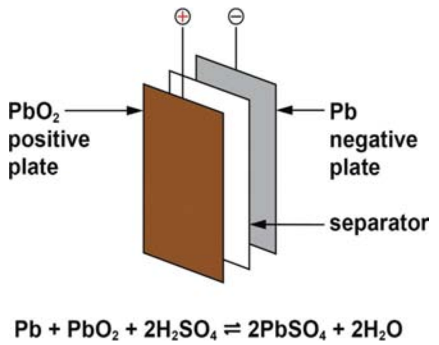



***Figure 2.*** *The working principle of electrode group in lead-acid battery.*

### 2.2. Mechanical Properties Testing Standards and Equipment

Via manually dismantling the spent lead-acid battery, it was found that the internal plate group of the battery is composed of soft lead paste and grid while the outer shell of high-strength acrylonitrile-butadiene-styrene plastic (ABS plastic) to resistant to acid, heat and shock. So, it is must break the plastic shell before shredding the spent battery. And the determination of crushing mechanical properties of spent lead-acid battery is basically equivalent to that's of the plastic housings.

The mechanical performance standards referenced are: National Standards for the determination of plastics-bending properties (GB/T 9341-2008) and Standards for the determination of impact properties of plastics-simple beams (GB/T 1043.1-2008). The bending performance was measured using a CMT4000 series microcomputer controlled electronic universal testing machine, while the impact performance measured with a ZBC-25A plastic pendulum impact testing machine.

### 2.3. Bending Performance Test

Since the sample thickness was 2.5mm which less than that of the National Standard of 4.0mm, its recommended test size cannot be used according to the National Standard GB/T9341-2008. Based of GB/T9341-2008, the ratio of sample length (L) to thickness (h) should be 20:1, with the length 50mm and the thickness 2.5mm. The bending strain rate was set to 1mm/min. The bearing and indenter radius were 2.0mm and 5.0mm, respectively. The results are shown in Table 3 and Figure 3 is shown the stress-strain curve of sample W4.

***Table 3.*** *Spent lead-acid battery bending performance.*

| Specimen | Length (mm) | Width (mm) | thickness (mm) | Span (mm) | Bending Strength (MPa) |
|---|---|---|---|---|---|
| W1 | 48.5 | 28.2 | 2.5 | 30 | 6.955 |
| W2 | 49.4 | 27.1 | 2.6 | 30 | 6.425 |
| W3 | 49.3 | 26.1 | 2.7 | 30 | 5.919 |
| W4 | 48.2 | 25.0 | 2.7 | 30 | 7.450 |
| W5 | 48.2 | 25.9 | 2.5 | 30 | 7.987 |
| W6 | 50.6 | 26.7 | 2.5 | 30 | 6.650 |
| Average value | 49.0 | 26.5 | 2.58 | 30 | 6.898 |

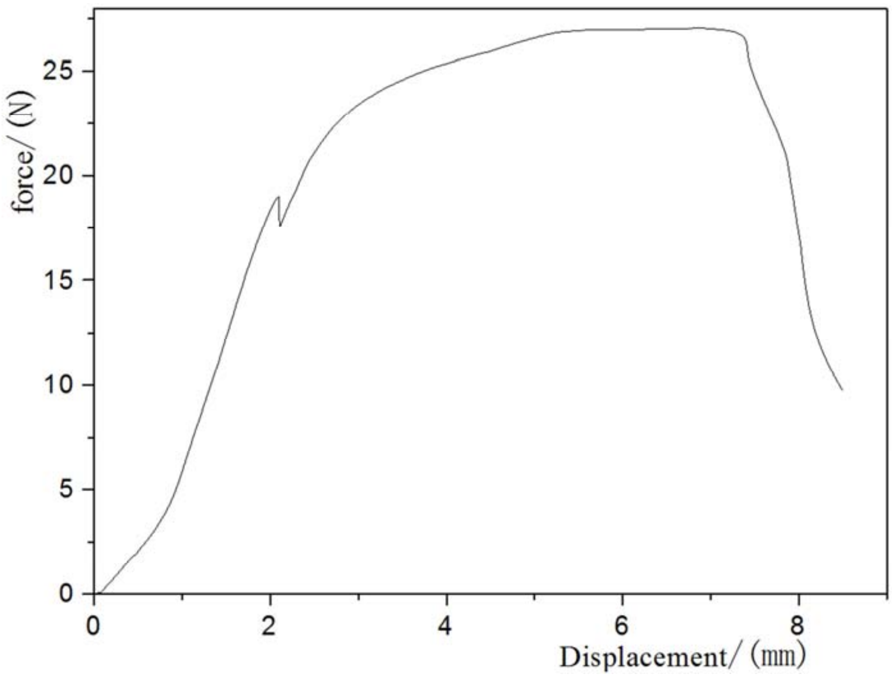



***Figure 3.*** *Force-bending displacement curve of plastic sample W4.*

### *2.4. Impact Mechanical Performance Test*

Refer to the National Standard GB/T1043.1-2008, a simple beam impact crushing performance test of the two plates of Figure. 1c was carried out. The results are shown in Table 4 and Figure 4.

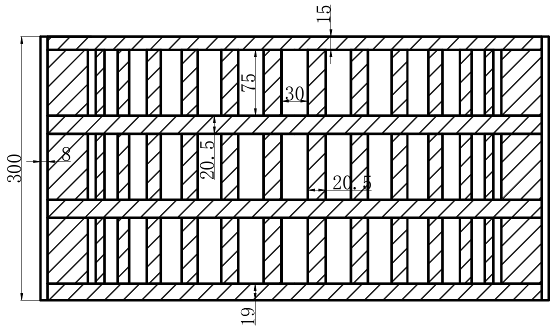
***Table 4.*** *Spent Lead Acid Battery Impact Crushing Performance.*

| Specimen | Length (mm) | Width (mm) | thickness (mm) | Cross-sectional area ($cm^2$) | Impact energy (J) | Impact strength ($J/cm^2$) |
|---|---|---|---|---|---|---|
| D1 | 116.5 | 101.6 | 30.6 | 118.36 | 69.70 | 87.10 |
| D2 | 157.3 | 84.3 | 32.7 | 132.60 | 46.60 | 58.20 |
| Average value | | | | 125.48 | 58.15 | 72.65 |

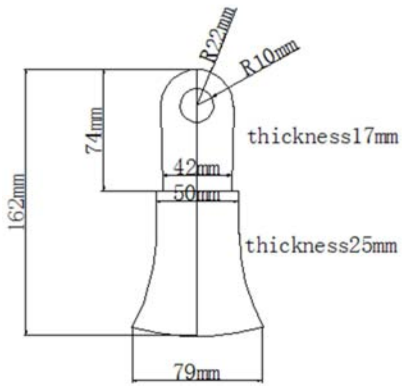
***Figure 4.*** *The Impact Crushing Effect of Plates of Spent Lead-Acid Batteries.*

### *2.5. Impact Crusher Design*

According to the experimental results of the mechanical properties of spent lead-acid batteries, the impact crusher was designed with model MX-320*620mm, the speed of the hammerhead in the crushing chamber 1680r/min, the motor drive power 11KW, the processing capacity about 0.5t/ h, which dry and wet crushing can all be achieved. The core parts such as impact hammerhead and screen were manufactured by Jiangxi Mingxin Metallurgical Equipment Co., Ltd. The mesh size is 75*30mm, as the main parameters shown in Figure 5a, and the hammer head shape parameters shown in Figure 5b.




a. Screen design




b. Broken hammer head

***Figure 5.*** *Impact crusher screen and hammer main parameters.*

### *2.6. Impact Crusher Crushing Effect*

#### *2.6.1. Battery Broken*

***Table 5.*** *Spent lead-acid battery composed of different particle size broken products.*

| Particle size /mm | >10.0 | 10-2.2 | 2.2-0.5 | 0.5-0.1 | <0.1 |
|---|---|---|---|---|---|
| Composition | Plastic<br>Grid | Plastic,<br>Grid<br>Fiber separator | Grid<br>Fiber separators<br>Lead paste | Fiber separators<br>Lead paste | Lead paste |

Controlling the influent flow rate of $0.25m^3/h$, the whole cell body was crushed under the hammerheads of groups 2 and 4, respectively. The broken products of the 4 groups of hammerheads were sieved with 10/5/2.2/1.1/0.5/0.3/0.2/0.1 standard sieves. The main composition of breakdown product with different particle size is shown in Table 5. The particle size and mass of each broken product are shown in Figure 6.

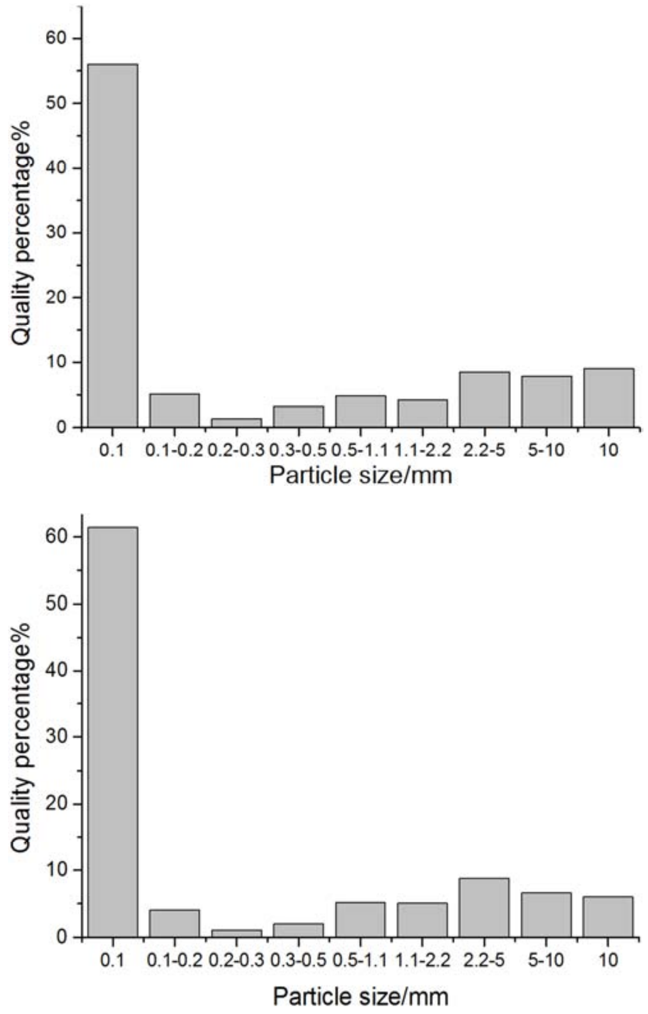



*Figure 6. Different hammers crushing effect comparison.*

### *2.6.2. Plastic Shell Crushing*

The plastic shell was crushed with the influent flow rate $0.25m^3/h$ and 4 groups of hammerheads, which result shown in Figure 7.

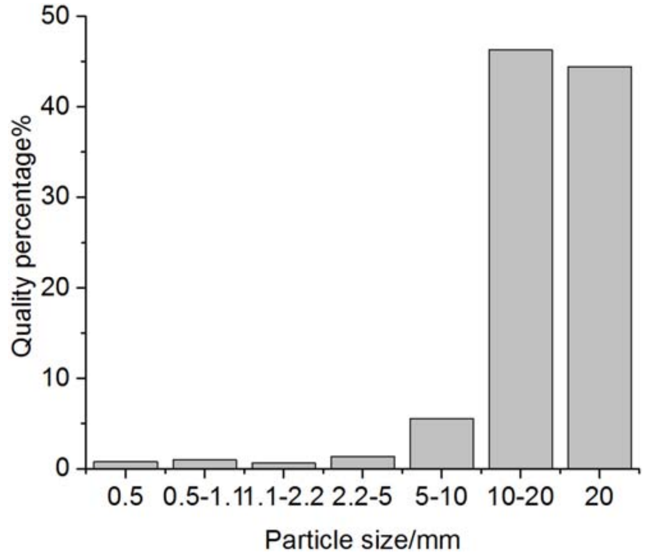



***Figure.7.** Plastic shell crushing product each particle size quality ratio.*

### *2.6.3. Single Cell Battery Breaking*

Manually split single-cell battery was wet crushing over 4 groups of hammerhead and the water flow rate $0.25m^3/h$. The percentage of broken product with different particle size was shown in Figure 8.

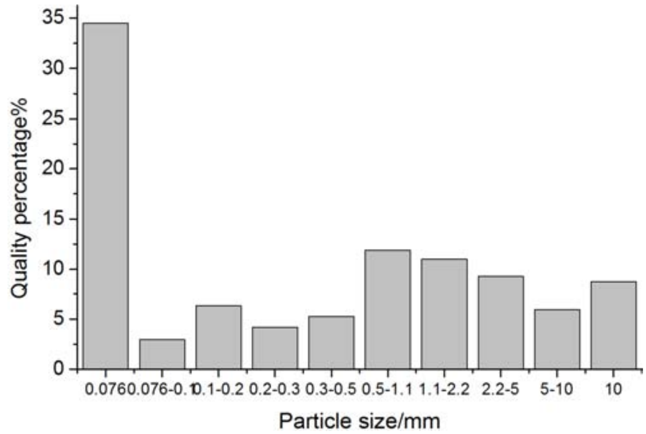
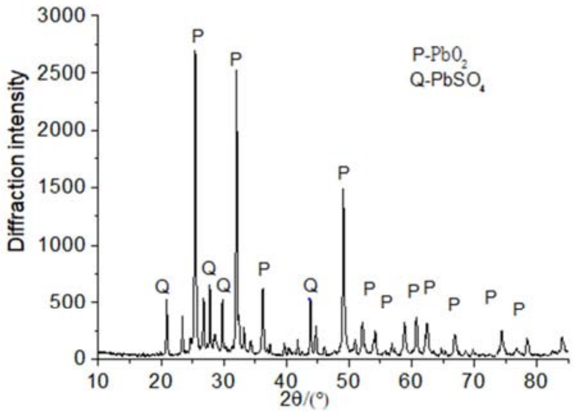
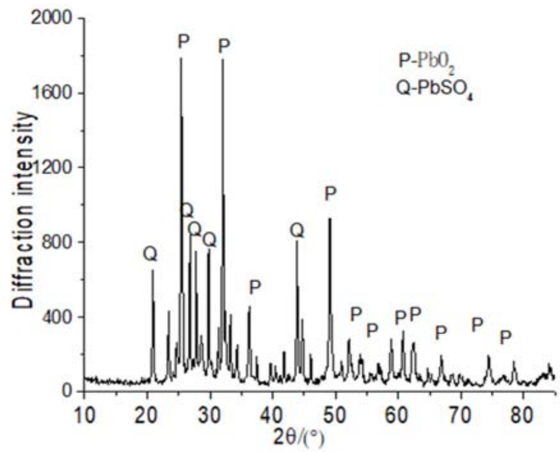



***Figure 8.** The percentage of broken product with different particle size for single-cell battery.*

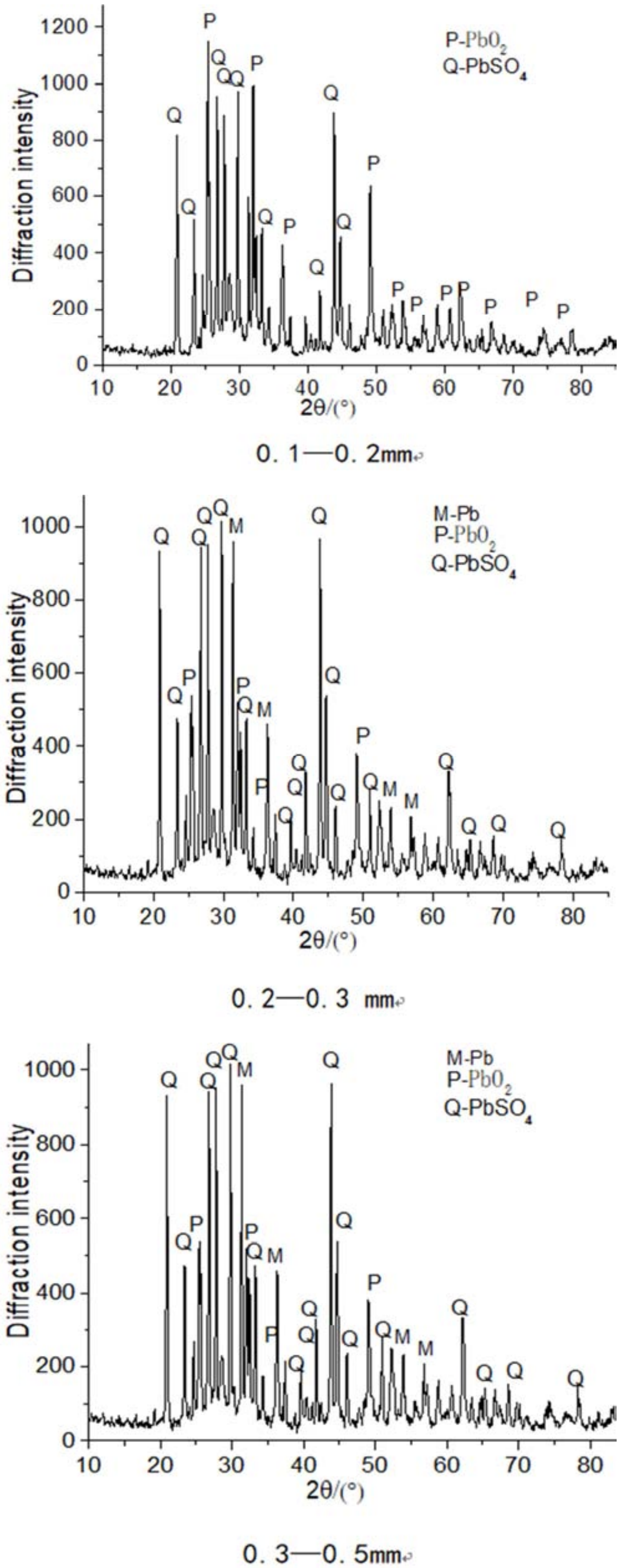
### *2.6.4. XRD Determination of Lead Paste with Different Particle Sizes*




−0. 076mm




0. 076—0. 1mm



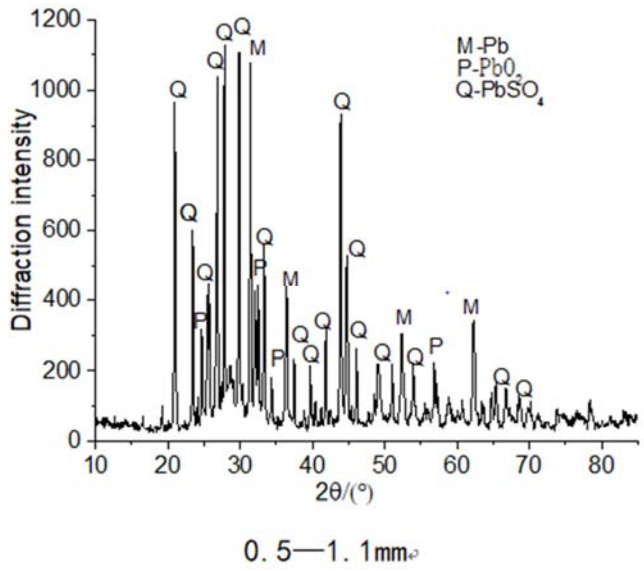




*Figure 9. XRD of lead paste with different particle sizes.*

After scrapping the spent lead-acid battery plates, the products were sieved with standard sieves. XRD tests were performed on the sieved-size lead pastes to analysis their composition. The test results are shown in Figure 9.

## 3. Results and Discussion

From the bending stress-displacement curve in Figure 3, it can be seen that as the stress increases, the deformation amplitude gradually increases. There is a yield point with less changed in the stress and large variation in the deformation. From Table 3, it is clearly that the average bending strength is 6.898 MPa. High strength indicates good rigidity for the material.

Table 4 showed that the average impact strength of the spent lead-acid battery was 72.65 J/cm$^2$. It can be seen from Figure 4 that the plastic is broken into several pieces with brittle fracture characteristics after impact crushing, which is also a key basis to select the crusher.

Figure 6 showed that the product with particle size below 0.1mm accounted for more than 56% of the total battery, which have the largest proportion. Table 5 indicated that almost all materials with particle size below 0.1mm are lead pastes. The yield of product under 0.1mm with 4 hammerheads is 5.4% higher than that of the 2 hammerheads. It may be due to the increased probability of contact between the hammerheads and the spent batteries under the 4 hammerheads. And the yields of other particle size were less changed. Considering the subsequent effective separation of the fine particle size products, 4 hammerheads are better for crushing.

It can be known from Figure 7 that the crushing of the plastic crust has a coarser particle size, with 98.2% of products above 1.1 mm and only 1.8% below 1.1 mm, relating to the hard and brittle nature of the plastic shell. It facilitates separation from subsequent fine particle size products, especially lead paste.

Figure 8 indicated that the product mass below 0.1 mm accounts for 37.47%. According to the particle size and material composition distribution in Table 5, lead paste occupies more than 1/3 of the total mass of broken products. The particle size of grid and the fiber separator was between 0.5-2.2mm and account for 22.88%. Above 10mm, it is composed of mainly plastic shell and little grids. Due to different product with different particle size after crushing, screening can be used to separate and enrich the broken products. This will facilitate the separation and recovery of valuable lead metal.

From Figure 9 it is clearly that lead oxide is the main component of lead paste below 0.1 mm particle size. With the particle size decreasing, the lead oxide content increased. Lead component appears in the lead paste with 0.2mm, which is mainly the fine part of the positive electrode grid corrosion. With the increase of the grain size, the lead oxide content in the lead paste decreased but the lead sulfate gradually increased. While the lead oxide was not substantially visible above 0.5 mm, this also verifies that the positive lead paste was in the form of a powder and the negative electrode was bulk. According to the difference in the shape and content of lead in different particle sizes of lead paste, it can be separated. This will be described in the next article.

# 4. Conclusions

(1) The major components of waste lead-acid batteries are lead paste, grids and plastics, which accounting for 91.86% weight of the total battery. Its shell and plate group are all wrapped in plastic. To efficiently dispose of lead-acid battery, the plastic housing must be broken first. Therefore, the determination of the mechanical properties of the plastic housing represents the determination of the crushing mechanical properties of the spent lead-acid battery.

(2) Mechanical tests show that the plastic shell is hard and brittle and has strong resistance to bending, but its impact resistance is weak. The self-designed impact crusher can be used to crush the spent lead-acid batteries. The plastics in the broken products were mainly distributed in large particles over 10 mm. The grids and fiber separators were distributed between 2.2-0.5 mm in diameter. The lead paste was mainly distributed below 0.1mm in particle size.

(3) Spent lead-acid battery achieved a pre-separation after the impact broken according to different shapes (plastic sheet, grid columnar, lead paste was granular or powder), which create the conditions for the next hydraulic separation.

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# References


[1] Chang Y, Mao X, Zhao Y, et al. Lead-acid battery use in the development of renewable energy systems in China [J]. Journal of Power Sources, 2009, 191 (1):176-183.

[2] Treptow R S. The Lead-Acid Battery: Its Voltage in Theory and in Practice [J]. Journal of Chemical Education, 2002, 79 (3):334-338.

[3] Ambrose H, Gershenson D, Gershenson A, et al. Driving rural energy access: a second-life application for electric-vehicle batteries [J]. Environmental Research Letters, 2014, 9 (9):094004.

[4] Zhao, J., Cao, G. Extended Producer Responsibilities in the Lead-Acid Battery Industry. China Battery Industry Association, Beijing, 2015, pp. 1–50.

[5] Tian X, Wu Y, Gong Y, et al. The lead-acid battery industry in China: outlook for production and recycling [J]. Waste Manage. Res.2015, 33 (11):986-994.

[6] Li Xinzhan. Policy boosting the recovery of waste lead-acid batteries for a new era [J]. China Nonferrous Metals, 2018 (08):46-47.

[7] Zhu X, Li L, Sun X, et al. Preparation of basic lead oxide from spent lead acid battery paste via chemical conversion [J]. Hydrometallurgy, 2012, 117-118:24-31.

[8] Kuijp, T., Huang, L., Cherry et al. Health hazards of China's lead-acid battery industry: a review of its market drivers, production processes, and health impacts [J]. Environmental Health, 2013, 12 (1):61.

[9] Chen L, Xu Z, Liu M, et al. Lead exposure assessment from study near a lead-acid battery factory in China [J]. Science of the Total Environment, 2012, 429 (429):191-198.

[10] Zhu X, He X, Yang J, et al. Leaching of spent lead acid battery paste components by sodium citrate and acetic acid [J]. Journal of Hazardous Materials, 2013, 250-251 (8):387-396.

[11] Cheng Ma, Yuehong Shu, Hongyu Chen. Recycling lead from spent lead pastes using oxalate and sodium oxalate and preparation of novel lead oxide for lead-acid batteries [J]. RSC Advances, 2015, 5 (115):94895-94902.

[12] Gomes G M F, Mendes T F, Wada K. Reduction in toxicity and generation of slag in secondary lead process [J]. Journal of Cleaner Production, 2011, 19 (9):1096-1103.

[13] Sun Z, Cao H, Zhang X, et al. Spent lead-acid battery recycling in China – A review and sustainable analyses on mass flow of lead [J]. Waste Management, 2017, 64:190.

[14] Hu Hongyun, Zhu Xinfeng, Yang Jiakuan. Research progress in wet recycling of spent lead-acid batteries [J]. Chemical Progress, 2009, 28 (9):1662-1667.

[15] RAMUS K, HAWKINS P. Lead/acid battery recycling and the new Isamelt process [J]. Journal of Power Sources1993 (42):299-313.

[16] Gao Qian, Zhu Longguan, Shu Yuehong, et al. Research and discussion on crushing and sorting of spent lead-acid batteries [J]. Battery, 2013, 50 (1): 3-7.

[17] Chen Wenjian. Spent batteries Pollution Status and Prevention Suggestions [J]. Environmental Science, 2014 (9):31-33.