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# Characterization of Discarded Lead–Zinc Sulfide Ore Tailings Based on Mineral Fragments

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**Abstract:** The lead–zinc ore is a typical low-grade complex polymetallic sulphide ore. Its typical mineralogy is characterized by a high content of cryptocrystalline graphite, low content of lead, zinc, and copper, and fine grain size. However, the aggregation size of sulfide mineral aggregations is coarse, and the symbiotic relationship is relatively simple. Conventional process treatment requires the fine grinding of ore into mineral monomer dissociations followed by preferential flotation, but this method has a poor sorting index and high production cost. In this paper, the grain size of the sulfide mineral aggregates determined by mineralogical studies is used to determine the fineness of the grinding, so that the liberation degree of the sulfide ore in the coarse grinding product reaches 70%, and each flotation process is used to collect rough concentrate. In the first step of flotation, the carbon in lead–zinc sulfide ore was removed by adding #2 oil to the flotation tank at a dosage of 40 g/t. In the second flotation process, the pH was adjusted to 7.2, the dosage of isopropyl xanthate was 20 g/t, the dosage of #2 oil was 30 g/t; the flotation reagent in the third step was isopropyl xanthate, and the dosage was 7.5 g/t, with a #2 oil of 15 g/t. Each flotation process concentrate is collected. Finally, the grades of lead and zinc in the final concentrate were 1.6% and 5.71%, respectively. In addition, the recoveries of lead and zinc were 91.78% and 92.07%, respectively. The yield of tailings was 50.6%. By the flotation of sulfide aggregates, a large number of gangues are avoided to participate in fine grinding, which helps to reduce the energy consumption of the mill.

**Keywords:** mineral fragment characteristics; carbon removal; flotation; sulfide aggregates

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## 1. Introduction

As we all know, lead and zinc play an important role in people's lives and are widely used in lead–acid batteries, rolled and extruded products, galvanization, radio-active shielding, alloy, pigments, brass and bronze, and chemicals for zinc [1–3]. Today, they are mainly obtained from lead–zinc sulphide ores [4]. Demand for lead and zinc is growing every year, and the total supply of lead and zinc is expected to reach the maximum of 13 Mt in 2030–2050 and 34 Mt in 2025–2030, respectively [5]. In recent years, no new lead–zinc deposits have been found, and the depletion trend of lead–zinc resources has begun to emerge. With the gradual reduction of easy-to-dress ore, complex multi-metal difficult-to-dress ore will be a major problem in the future [6–8]. Lead and zinc exist in nature mostly as sulphide and are often associated with other minerals, and they are often selected by flotation [9]. However, due to the finer grain size of the lead–zinc minerals embedded in the gangue, the grain size of the gangue is very coarse, most of the energy in grinding is used to reduce the grain size of the gangue, and a lot of energy is wasted. On the other hand, grinding is a very energy-intensive process, which occupies 75% of the energy in the mineral processing process. At the same time, the energy utilization efficiency is very low, most of the energy is consumed by the machine itself, and only a small part of the energy is used for ore comminution [10]. Lead-zinc ore contains carbon at the same time. Due to the good floatability of carbon, the grade of the concentrate will decrease, and the dosage of reagents will increase at the same time. Pan et al. [11] explored the influence mechanism of carbon-containing materials in the flotation separation of lead–zinc ore. Through closed-circuit flotation tests, it was found that amorphous carbon accounted for a very high proportion of the total carbon, accounting for 99.7% of the total carbon in the concentrate, and had rich aromatic rings, carbonyl groups, and alkyl groups. In addition, the pore structure of amorphous carbon is rich, the specific surface area is 16.18 $m^2/g$, and the average pore size is 12.94 nm. After carbon pre-flotation, the grade and recovery of lead increased by 50.99% and 47.95%, respectively. Godirilwe et al. [12] found that the presence of organic or inorganic carbon in the ore during flotation can have a negative impact on the product index, and they recovered a carbonaceous sulphide ore of 2.08 wt% copper, recovering only about 60% of the copper. Therefore, it is necessary to remove the carbon before flotation. Many studies have been carried out on the flotation of lead–zinc ore. Nowadays, the following methods are mainly used to effect the separation of lead–zinc sulfide: Wei [13] used the new reagent to sort Pb–Zn minerals from low-grade complex sulfide ores, new reagent YZN as a zinc depressant, and new reagent BPB as a lead collector; the products had high recoveries and grades, and they also found that $Na_2S$ could precipitate $Pb^{2+}$ and have a sulfide effect on oxidized $Pb^{2+}$. Oyelola et al. [14] used gravity separation and froth flotation to separate low-grade zinc ore. Sahu et al. [15] planed the comminution process according to the mineralogical characteristics of ore to avoid over-griding. Onal et al. [16] added a gravity separation method before flotation, and used a gravity cyclone and rocker to pre-enrich the coarse particle size of the ore in advance. After that, the residual lead in the tailings was selected by flotation, and a high recovery rate of lead was obtained. In order to reveal the hydrothermal sulfidation mechanism of sulfur-bearing cerussite, Zheng et al. [17] explored the interfacial exchange process between sulfur and carbonate ion disproportionation products by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Electron Probe Micro-Analysis-Energy Dispersive Spectroscopy (EPMA-EDS), providing guidance for the recovery of lead and other non-ferrous metals. He et al. [18] studied the effect of hydration on the adsorption mechanism of benzohydroxamic acid (BHA) on the surface of cassiterite pre-adsorbed by lead ions ($Pb^{2+}$). When there is no lead ion ($Pb^{2+}$) adsorption on the surface of cassiterite, water molecules can be combined with the surface, and BHA cannot be adsorbed on the surface of the cassiterite; when the cassiterite surface is activated, BHA has a very low energy barrier and a very negative reaction energy difference with the lead ion ($Pb^{2+}$) on the cassiterite surface, indicating that BHA can be adsorbed on the cassiterite surface. Lan et al. [19] studied the flotation performance of magnesite in the absence and presence of sulfur on the surface. Through XRD, XPS, and EPMA analysis, after thermochemical modification of magnesite in the presence of sulfur, ZnS and $ZnS_2$ were produced on the surface of zinc ore, and the flotation recovery of magnesium ore increased by about 65%. Kursun [20] investigated the effects of the flotation column number and ultrasonic pretreatment on zinc recovery in three groups: firstly, the first group was subjected to only using single-stage column flotation without ultrasound, and the recovery rate of zinc was 29.41%; the second group differed from the first in that the ore was ultrasonically pretreated to obtain a recovery rate of 39.97% zinc; the third group used three stages of cleaning and three stages of scavenging flotation by column; and the final zinc recovery was 76.44%. Increased recovery means an increased contact angle and adhesion between the ore and the bubbles during flotation, which can be attributed to the dispersion of ultrasonic waves, increased collectors, and cavitation of bubbles. After a complex flotation process, the lead–zinc recovery index can reach about 80%–90%, but it is not suitable for large-scale industrial production because of its excessive number of reagents and complex processes. Bioleaching has been used to treat Pb–Zn ores, and although it has the advantage of high extraction rates, the leaching period is up to

24 d [21]. In order to extract useful elements from low-grade lead–zinc ore, Lan et al. [22] proposed a new roasting–dressing–leaching process. Although the recovery rates of zinc and lead are 86.04% and 69.08%, respectively, roasting will produce pollutants and consume fuel, which is not suitable for future environmental and resource policies. Enrichment of lead and zinc ores remains a challenge today, and many separation mechanisms have not been proposed. Information on the composition, embedding characteristics, crystal size, and crystal structure of minerals from a microscopic perspective is needed to reveal the flotation characteristics of different minerals during flotation. New theories are also needed to break through the technical limitations of Pb–Zn ore concentration. In general, the separation and enrichment of lead–zinc sulfide ore still poses great challenges, and many separation mechanisms have not yet been revealed. From the perspective of flotation, in order to achieve the separation of the target mineral and gangue, it is important to study the composition of the ore from a microscopic point of view, the characteristics of the distribution, the crystal size, and the crystal structure. At the same time, to break through the difficult problem of sorting lead–zinc ore, new theoretical support is needed.

Due to the complex structure of lead–zinc sulfide ore and the distribution of fine-grained minerals, the beneficiation of lead–zinc sulfide ore is difficult. To achieve efficient separation, it is critical to design the separation process based on the characteristics of the ore. Micro-grain lead and zinc minerals coexist closely in the ore with the minerals. A suitable grinding fineness is not only related to the liberation of useful minerals, but also affects the separation efficiency of useful minerals in the flotation process [23]. According to the ore's mineralogical characteristics, researchers have made many explorations in enrichment and separation. Jian et al. [24] found that the crush size clearly affected the heavy liquid separation process, and using a biconical dense medium cyclone (BDMC) to remove gangue from a low-grade Pb–Zn sulfide ore, it was finally determined that the gangue removal effect was the best when the particle size was in the range of $-13 + 1 \sim -20 + 1$ mm. After optimizing the BDMC operation process, the recovery rates of lead and zinc were 7.92% and 12.50%, respectively. In order to minimize the production and utilization of tailings, Souza [25] analyzed the properties of the tailings through physical, chemical, and mineralogical characterization, focusing on quantitative electron microscopy (QEM), and found that its main phases were hematite and quartz, followed by goethite, bauxite trihydrate, and kaolinite, and obtained the degree of dissociation, which provided an important basis for the utilization of tailings. Yong et al. [26] selected six typical common magnetic iron concentrates in China, studied the mineralogical characteristics of iron concentrates, revealed the intrinsic connection between the mineralogical characteristics of raw materials and sorting indexes, and established an evaluation system for the preparation of super iron concentrates based on the mineralogical characteristics of raw materials. However, the relationship between the mineralogical characteristics of Pb–Zn ores and roughing has not been developed, so it is necessary to establish a beneficiation method for Pb–Zn ores.

Lead-zinc ore is difficult to separate because of its polymetallic fractionation, fine dissemination, low grade, and low degree of liberation. Conventional lead–zinc ore beneficiation methods often liberate useful mineral monomers from the ore, a process that consumes a lot of energy; then, a series of corresponding flotation processes are designed, using a large variety of reagents and high dosages, which has the disadvantage that different lead–zinc sulfide ores require different types of reagents, and the effect is not significantly enhanced. Therefore, a Mineral Liberation Analyzer (MLA) is introduced in this paper to observe the degree of liberation of particles or aggregates after grinding and to select the appropriate particle size in order to reduce the energy consumption during the grinding process. For example, copper and zinc are finely distributed in the ore, but both are present in the mineral in the form of sulphide, so the sulphide aggregate can be considered as the target mineral for flotation. The mineralogical characteristics of ore and mineral aggregates after crushing and grinding are listed in this paper. The particle size distribution characteristics of aggregate and single minerals are explored, and the optimal process parameters of flotation after the rough grinding of lead–zinc ore are determined, which provides theoretical guidance for similar polymetallic sulfide ores.

The sulfide ore used in this paper comes from the Inner Mongolia Autonomous Region of China. The ore contains a high cryptocrystalline graphite, low lead and zinc content, and fine intercalation particle size, but the sulfide aggregate has a coarser particle size and simple intergrowth relationship. Therefore, the improvement in zinc recovery depends on the recovery of lead–zinc sulfide.

## 2. Experimental

### *2.1. Experimental Materials*

The chemicals employed, e.g., $Na_2CO_3$, CaO, etc., were purchased from Shanghai Guoyao Chemical Reagent Co., Ltd. (Shanghai, China), and the sulfide ore was sampled from the Nei Monggol Autonomous Region of China.

### *2.2. Experimental Methods*

The experimental equipment used include a ball mill (Luoke, XMQ-Φ240×90, Shaoxing, China), three flotation machine (Balike, XFD12, 0.5 L, 1 L, 4 L, Nanchang, China), a balance (Mettler toledo, AR1140, Shanghai, China), a filter (Hengcheng, XTLZ, Nanchang, China), an ultrasonicator (Ruibo, BRC-20A, Beijing, China), and a drying oven (Shuangxu, PH050, Shanghai, China).

The chemical composition of the samples was analyzed by an atomic absorption spectrophotometer (Rayleigh, UV-9600, Beijing, China). The total carbon and total sulfur of the samples were analyzed by a carbon and sulfur analyzer (Horiba, EMIA-920V2, Kyoto, Japan). The mineral composition of ore and the dynamic XRD images obtained in the reacting process were examined by an MLA (FEI, FEI MLA 250, Hillsboro, OR, USA) and an XRD (Rigaku, TTRIII, Tokyo, Japan), respectively. The process morphologies of the ore adopted were determined by a reflection macroscope (Leica, DM4500P, Weztlar, Germany).

#### 2.2.1. Mineral Composition

The ore was crushed so that 100% of it passes through a 2 mm sieve, and it was tested using MLA. MLA was used to quantify the mineral phases present in the ore. At the same time, it can also perform electron backscatter diffraction imaging and XRD on the particles. Then, the ore sample was crushed to 100% by passing it through a 0.074 mm sieve and then tested with a XRD.

#### 2.2.2. Mineral Liberation

A rod mill was used to grind the sample at a pulp density of 30% solid. The liberation degree was tested by MLA, determined by the area percentage and density of a certain mineral in the particle. If the degree of liberation is greater than 90%, it is considered to be completely liberated; if it is less than 10%, it is considered to be unliberated.

#### 2.2.3. The Grade and Recovery of Concentrate

The grade of Pb/Zn was tested by an atomic absorption spectrophotometer, directly, and then the recovery of Pb/Zn during separation was calculated using Equation (1):

$$\varepsilon = \frac{\beta}{\alpha} \cdot \gamma \times 100\% \tag{1}$$

$\varepsilon$, the recovery of Pb/Zn during separation, %;
$\alpha$, the grade of Pb/Zn in the ore, %;
$\beta$, the grade of Pb/Zn in the concentrate, %;
$\gamma$, the yield of concentrate during separation, %.

### 2.2.4. Grinding and Flotation Experiments

First of all, the raw ore is crushed into −2 mm particles. After crushing, the minerals need to be dried and weighed. The pulp density is controlled at 50%. The ore was fed to the rod mill with the moisture content <2%, and the filling ratio of the grinding medium was 20%. The optimized conditions for the flotation experiment include whether to remove carbon, the grinding size, the type of collector, collector dosage, pH, and #2 oil dosage. The ores of −0.074 mm (69%) and −0.074 mm (48%) were compared under the same type and dosage of flotation reagent, and the possibility of coarsening the particle size of the flotation feedstock was explored. A sieve was used to determine the size of the feeding ores. In each unit flotation, 300 g of ore was adopted to prepare the ore pulp, and the volumes of the flotation cells used were 0.5, 1, and 2 L. The flotation's pulp density is 53.33%.

## *2.3. Technical Route*

The technical route of the current investigation is shown in Figure 1.

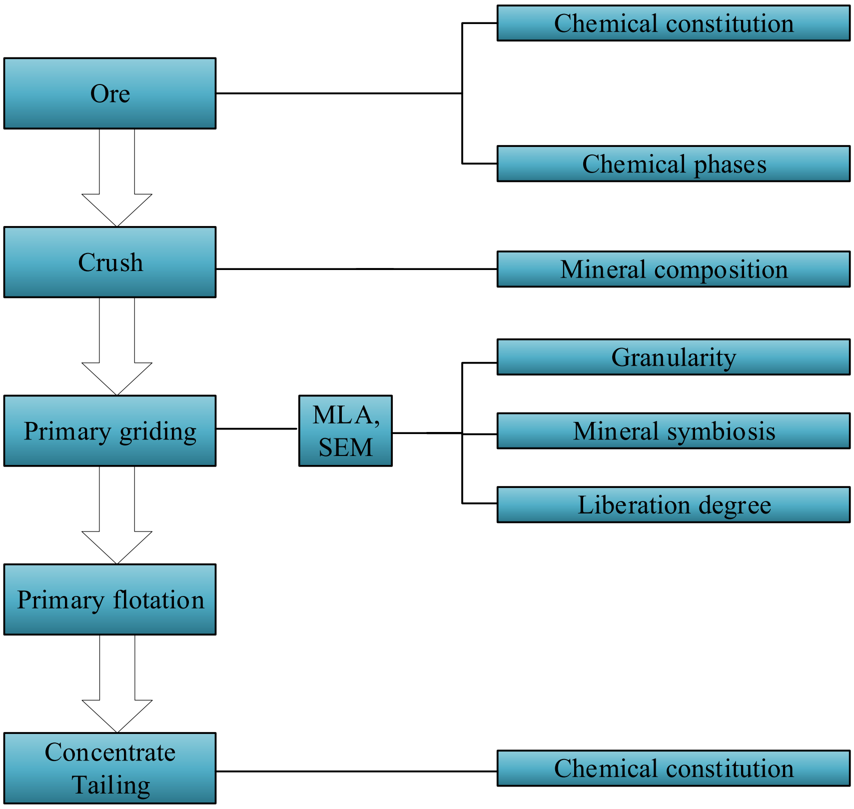


**Figure 1.** The technical route of the current investigation.

## 3. Results and Discussions

### *3.1. Ore's Mineralogical Characteristics*

The lead–zinc sulfide ore adopted is classified into cryptocrystalline graphite mica quartz schist type lead–zinc sulfide ore. Through the study of process mineralogy, the subject has ascertained the ore size composition, chemical composition, mineral composition, and the occurrence state of lead, zinc, copper, and sulfur minerals, and systematically studied the mineralogical characteristics of the lead–zinc deposit in China. The content of cryptocrystalline graphite is as high as 5.01%, while the content of lead, zinc, and copper is small, totaling 4.01%, with fine-grained intercalation. However, the coarser intergrowth of sulfide mineral aggregations and the relatively simple symbiosis relationship are typical mineralogical characteristics of the ore.

### 3.1.1. Chemical Composition

The chemical compositions of ore are shown in Table 1.

**Table 1.** Analysis results for the composition of ore.

| Composition | Pb | Zn | Cu | K | Fe | TS | TC | Al | Mg | Ca | Mn | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Contents (%) | 0.86 | 3.09 | 0.06 | 1.81 | 17.10 | 11.56 | 7.50 | 3.16 | 2.42 | 1.88 | 0.49 | 0.18 |

It found that the recyclable elements of the ore adopted included lead, zinc, as well as copper, which has comprehensive recovery value. The carbon content in gangue minerals is relatively high, and its beneficiation indicators need to be considered when throwing coarse particles.

### 3.1.2. Chemical Phase Analysis

The chemical phase of the ore adopted is shown in Table 2.

**Table 2.** Analysis results of lead, zinc, and carbon chemical phases in raw ore.

| Elements | Phases | Contents/% | Distribution Rate/% |
|---|---|---|---|
| Lead | Sulfide | 0.74 | 86.04 |
| | Oxide | 0.06 | 6.98 |
| | Others | 0.06 | 6.98 |
| | Sum | 0.86 | 100.00 |
| Zinc | Sulfide | 2.72 | 88.03 |
| | Oxide | 0.32 | 10.36 |
| | Others | 0.05 | 1.61 |
| | Sum | 3.09 | 100.00 |
| Carbon | Graphite | 5.01 | 66.80 |
| | Carbonate | 2.49 | 33.20 |
| | Sum | 7.50 | 100.00 |

Lead and zinc are the main elements recoverable from sulfide minerals. Table 2 shows that very few lead and zinc minerals has been oxidized, 86.04% of lead minerals exist in the form of sulfide, and that for zinc is 88.03%. Sulfides are beneficial to the flotation and recovery of lead and zinc; carbon minerals mainly exist in the form of graphite and carbonate, and graphite is cryptocrystalline. It is easy to adsorb reagents in the flotation process, causing the consumption of reagents and worsening the flotation index. Therefore, the floatability of lead, zinc minerals, and cryptocrystalline graphite became the first mineralogical characteristic of the ore in this study.

### 3.1.3. Analysis of Ore Material's Composition

The XRD pattern of the ore is shown in Figure 2, the distribution characteristics of the ore are shown in Figure 3, and the types and contents of minerals are shown in Table 3.

**Table 3.** Types and contents of ore materials.

| Minerals | Metallic Minerals | Gangue Minerals |
|---|---|---|
| Major minerals | Pyrite + Marcasite: 14%±<br>Pyrrhotite: 8%±<br>Sphalerite: 5%± | Quartz: 40%±<br>Dolomite: 12%±<br>Muscovite: 8% |
| Minor minerals | Galena: 1%±<br>Chalcopyrite: 0.1%± | Graphite: 5%±<br>Apatite: 2%± |
| Trace minerals | Bornite | Tourmaline, Calcite, Chlorite, etc. |

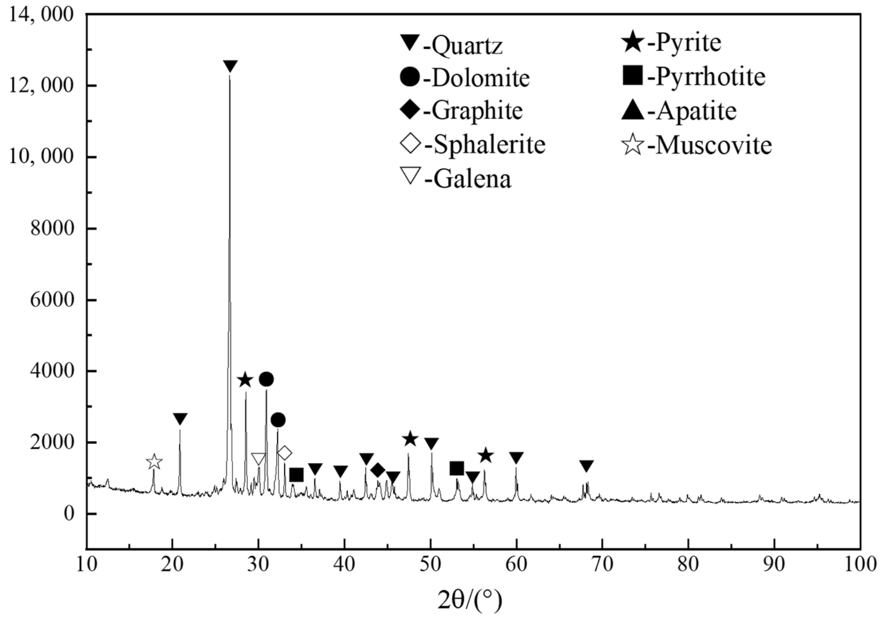


**Figure 2.** XRD pattern of the ore.

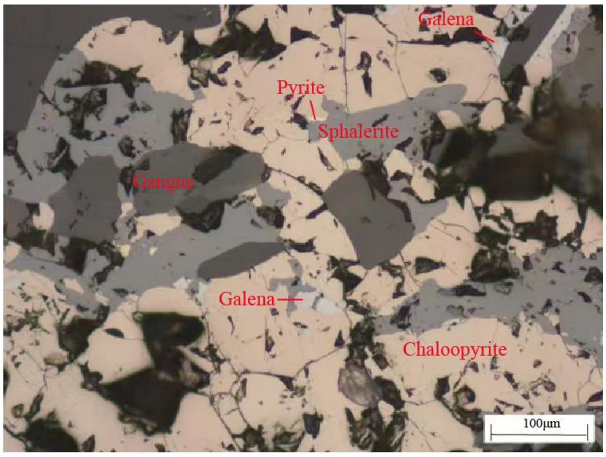


**Figure 3.** Symbiotic relationship of sulfide ore (reflective, ×100).

The XRD pattern shows that the major metal minerals in ore mainly include pyrite ($FeS_2$), pyrrhotite ($Fe_{0\cdot18}S$), and sphalerite ($ZnS$). The minor metal minerals are galena ($PbS$), chalcopyrite ($CuFeS_2$), and bornite ($Cu_5FeS_4$). The major gangue minerals include quartz ($SiO_2$), muscovite ($K\{Al_2[Si_3AlO_{10}](OH)_2\}$), and dolomite($CaMg(CO_3)_2$), and a small amount of graphite (C) and apatite ($Ca_5[PO_4]_3F$), etc. From Tables 2 and 3, we can find that metallic minerals account for 28.1% of the total mass of minerals, with 86.04% of total lead existing in galena, and 88.03% of total zinc existing in sphalerite.

The distribution characteristics of the ore in Figure 3 indicate that part of the pyrite in ore is filled with sphalerite and a small amount of chalcopyrite or their aggregation bodies, forming a complex structure.

Quantitative analysis of minerals by a reflection microscope shows that the content of sulfide minerals such as pyrite (marcasite) and pyrrhotite in the ore is much higher than that of sphalerite and galena. The content of chalcopyrite is about 0.1%, which only presents a comprehensive utilization value. In other words, the content of pyrite (marcasite) and pyrrhotite in lead–zinc ore are much higher than the sulfide minerals of lead, zinc, and copper in ore, which become the other mineralogical characteristics of the ore. Lead-oxidized minerals and zinc-oxidized minerals are discarded during the rougher flotation of sulfides.

### 3.1.4. Analysis of the Embedded Characteristics of Sulfide Minerals

The surface distributions of elements in lead–zinc ore are shown in Figure 4.

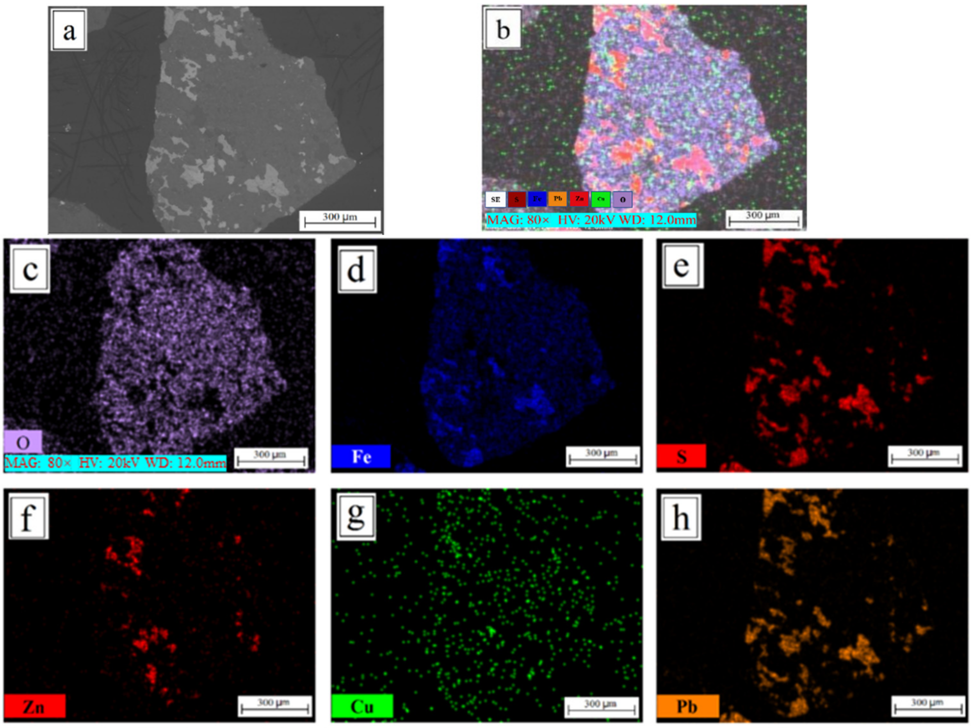


**Figure 4.** Surface distribution of elements in lead–zinc ore.

As shown in Figure 4, the element of Fe in ore is evenly distributed in sulfide aggregations. The Fe in ore mainly exists in the form of sulfide minerals such as pyrite, marcasite, and pyrrhotite, etc. The even distribution of Fe indicates that the Pb and Zn that are contained in sulfide minerals also closely coexist with their carrier sulfide minerals. However, the distribution of Cu elements was found distributing dispersedly in sulfide aggregations, and the embedded particle size is extremely fine.

When −0.074 mm accounts for 48%, the distribution of minerals in the lead–zinc mine is shown in Figure 5. Combining sulfur, lead, zinc, and copper minerals, the resulting sulfide mineral's conjoined distribution is shown in Figure 6.

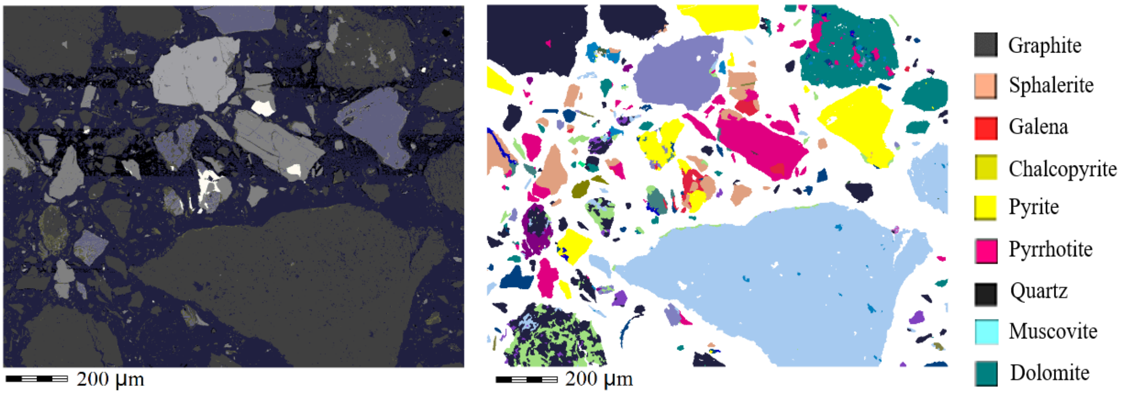


**Figure 5.** Mineral distribution in the lead–zinc mine.

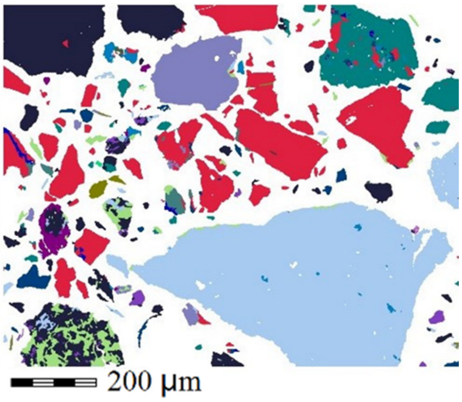


**Figure 6.** Distribution of sulfide minerals in the lead–zinc mine (red part).

As shown in Figure 5, the red and beige areas are galena and sphalerite, respectively. Studies have shown that the particle size of lead and zinc minerals is fine, and the monomer dissociation is low. It is difficult to achieve the monomer dissociation when the grinding fineness is −0.074 mm, accounting for 48%, and it is impossible to achieve high-efficiency flotation.

As shown in Figure 6, the particle size of the aggregate is coarser than that of a single sulfide. In the grinding process, the aggregates will be more easily dissociated from the gangue minerals because of the coarse dissociation granularity of the aggregates. At the same time, the floatability of the aggregates is very good because they are formed by fine-grained and floatable sulfide particles. As can be seen from Figures 5 and 6, sulfide monomers are difficult to dissociate and float compared to sulfide aggregates. Therefore, at a certain grinding size, flotation can be used to complete the beneficiation of the aggregates. Initially, the sulphide aggregate in the ore is separated from a large number of gangues, saving grinding energy for the subsequent recovery of the sulphide aggregate and avoiding the overgrinding of the gangues and the influence of their fines on the Pb and Zn index. The granularity and distribution of single sulfide minerals and their aggregates are the second mineralogical characteristic of the ore in this study.

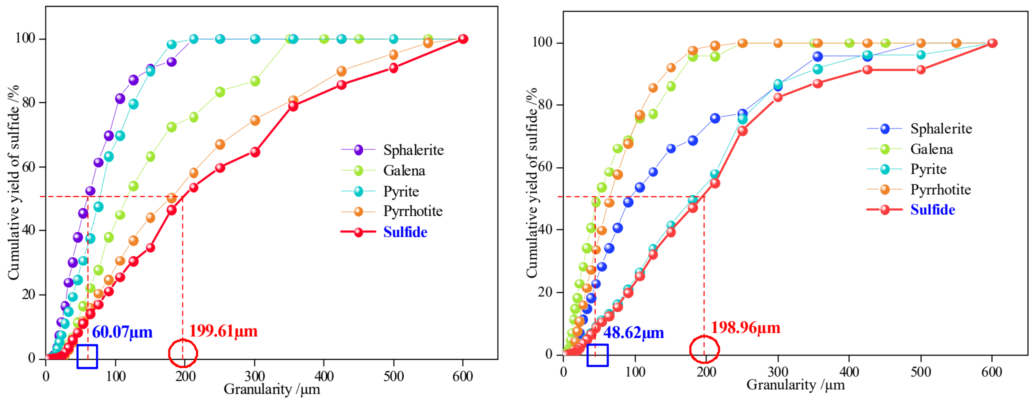
## *3.2. Fragment's Mineralogical Characteristics*

Based on the aforementioned mineralogical characteristics, the selection of sulfide aggregates for recovery is conducive to coarsening the grinding size before primary flotation. The granularity distribution of sulfide minerals after grinding is important information for studying mineralogical characteristics Therefore, two samples were prepared. The grinding fineness of the first sample is −0.074 mm, accounting for 69%. Compared with the sample with the grinding fineness of −0.074 mm accounting for 48%, the two samples were studied using the MLA.

### 3.2.1. Granularity Dissemination of Minerals after Primary Grinding

Under the condition that the grinding fineness is −0.074 mm, accounting for 48% and 69%, combining sulfur, lead, and zinc minerals, the particle size distribution of the obtained sulfide mineral conjoined body is shown in Figure 7a,b.

The D50 of the sulfide mineral aggregations under different grinding fineness conditions are 199.61 µm and 198.96 µm, respectively, with small changes, but the minimum embedded particle size D50 is 60.07 µm for sphalerite, which changed to 48.62 µm for galena. However, from Fig 9, we can find that the sulfide monomer with too fine of a particle size is difficult to be recovered by flotation.



(**a**) (**b**)

**Figure 7.** The granularity dissemination of most of the sulfide minerals and aggregates. (**a**) −0.074 mm (48%); (**b**) −0.074 mm (69%).

#### 3.2.2. Particle Size and Liberation Degree of Sulfide Aggregates

The liberation characteristics of sulfide minerals in grinding products under the conditions of −0.074 mm, accounting for 48% and 69%, are shown in Table 4.

The study found that under the grinding fineness of −0.074 mm accounting for 48%, the liberation degree of the sulfide aggregates can reach 69.88%. When the grinding size increases, the liberation degree also increases. The grinding size increases to −0.074 mm, accounting for 69%, and the liberation degree of the sulfide aggregates is 83.56%. More importantly, the liberation degree of sulfide aggregates is higher than that of most sulfide monomers.

**Table 4.** Dissociation characteristics of major metal minerals under two kinds of grinding conditions.

| Mineral | −0.074 mm Accounts for 48% | | | −0.074 mm Accounts for 69% | | |
|---|---|---|---|---|---|---|
| | D50/μm | Maximum Particle Size/μm | Monomer Liberation Degree/% | D50/μm | Maximum Particle Size/μm | Monomer Liberation Degree/% |
| Sphalerite | 88 | 500 | 23.92 | 50 | 180 | 46.04 |
| Galena | 53 | 250 | 32.52 | 36 | 106 | 61.15 |
| Pyrite | 88 | 600 | 59.62 | 75 | 210 | 73.63 |
| Pyrrhotite | 103 | 475 | 69.91 | 67 | 250 | 81.85 |
| Sulfide aggregates | 136 | 600 | 69.88 | 68 | 242 | 83.56 |

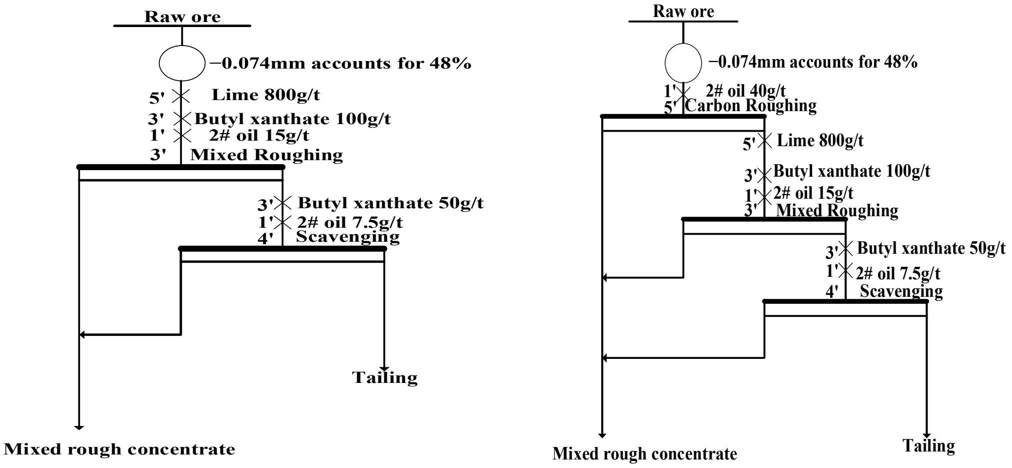
### *3.3. Primary Flotation*

The primary ores of Pb and Zn are similar in mineral composition and have a similar affinity for organic matter [27]. According to the analysis of the mineralogical characteristics of the original ore, the sulfide aggregate has great advantages as a flotation recovery object; for example, flotation can be carried out at a relatively coarse particle size, and the liberation degree of object granularity can be larger. Therefore, we will explore the possibility of recovering sulfide aggregates and optimizing the conditions in the process of recovering sulfide aggregates.

#### 3.3.1. Effects of Grinding Fineness and Carbon

As the carbon content of the lead–zinc sulfide ore is as high as 7.50%, most of it exists in the form of cryptocrystalline graphite. The floatability of this part of graphite is quite different, and some of the carbon has good floatability. It is easy to float with lead and zinc during the flotation process, which reduces the quality of lead and zinc concentrates. At the same time, large amounts of reagents will be adsorbed, causing consumption of the reagents. The existence of cryptocrystalline graphite is not conducive to the flotation recovery of lead and zinc. Therefore, the experiment explored two options to remove and retain carbon. The test slurry concentration is 53.33%, and the stirring speed is 2430 r/min.

The grinding fineness test process is shown in Figure 8, and the influence of the grinding fineness on the recovery of lead and zinc flotation is shown in Figure 9.



(**a**) (**b**)

**Figure 8.** The flow sheet for flotation experiments. (**a**) Undecarbonized; (**b**) Decarburized.

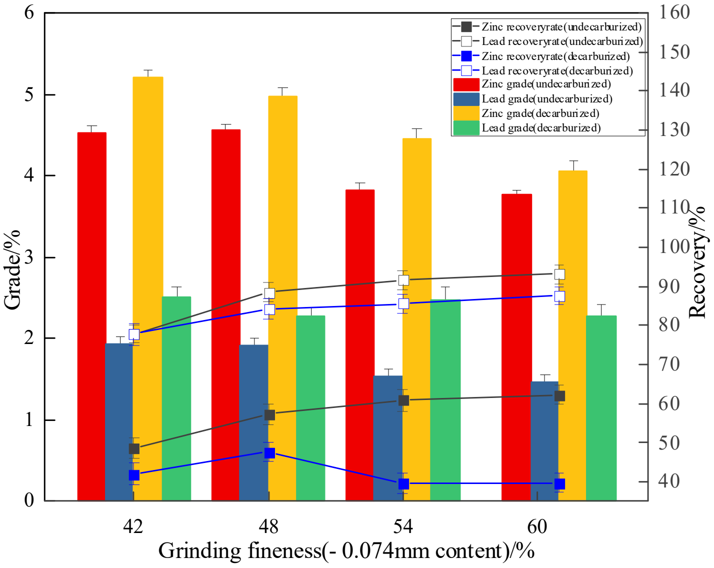


**Figure 9.** Effect of grinding fineness and carbon on sulfide aggregates.

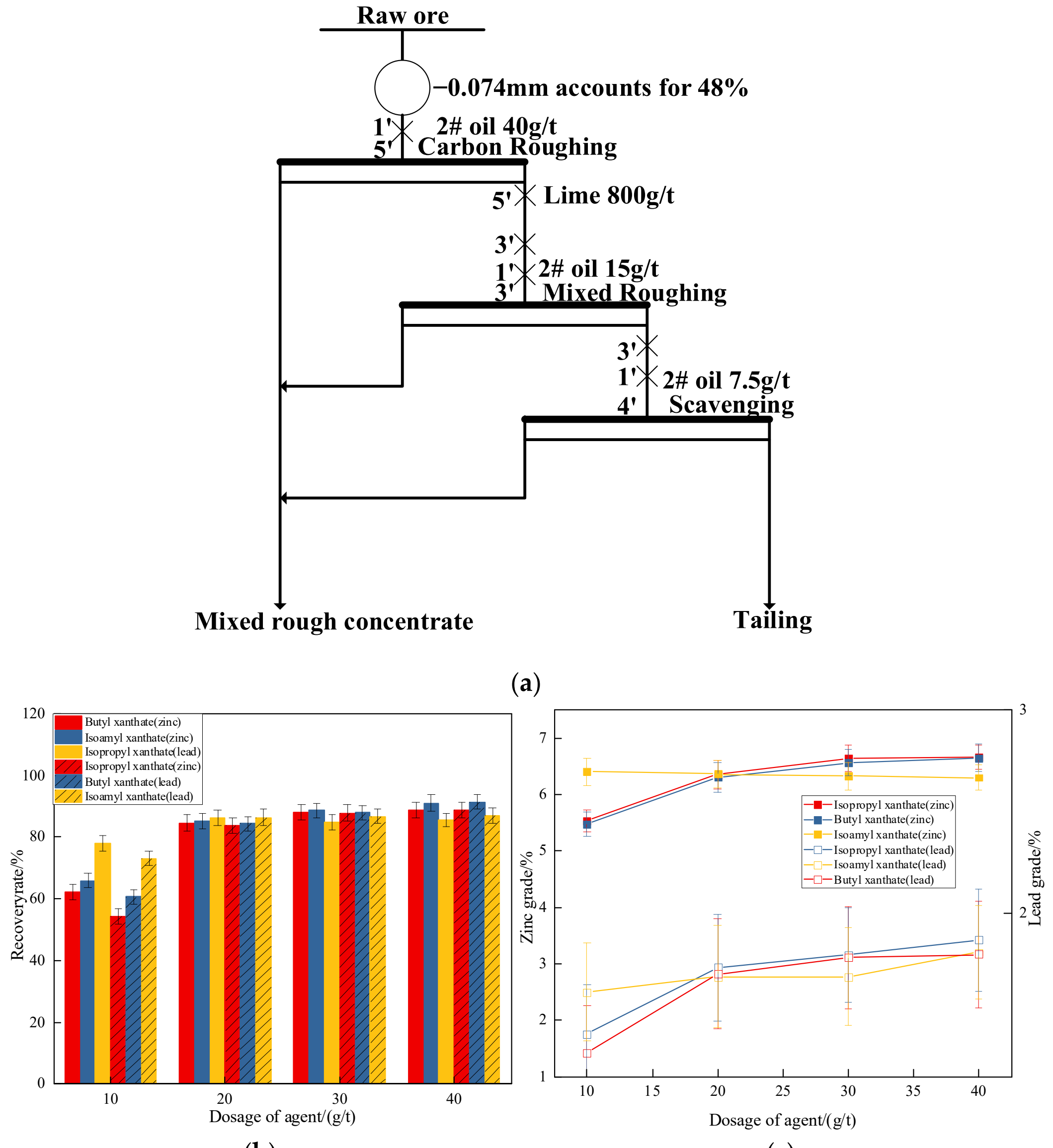
As shown in Figure 9, The grades and recoveries of zinc and lead did not change significantly with the increase in the grinding size. As the optimal grinding particle size, −0.074 mm (48%) was selected because as the grinding fineness increases, the recovery rate of lead and zinc does not increase significantly, but as the particle size becomes smaller, grinding will consume more energy.

At the same time, fine particles become more difficult to select in flotation. The grade of decarburized lead and zinc is better than those undecarburized, but the recovery rate is lower. The recovery rate of the undecarburized group is higher than that of the decarburized group, which may be because some fine-grained lead and zinc minerals are adsorbed on the carbon and taken away during the decarburization process. Pre-separation of useless minerals before flotation is of great significance to improve flotation efficiency and product indicators and reduce reagent consumption. Pre-removal carbon is beneficial to the flotation recovery of lead and zinc. In summary, the flotation removal carbon process was selected in the study, and the grinding fineness was initially determined to be −0.074 mm, accounting for 48%.

### 3.3.2. Effects of Type and Dosage of Collector

Xanthate has the advantages of good water solubility and stability in alkaline conditions, as well as easy storage and transportation and a low price [28].

As shown in Figure 10b,c, the difference is not obvious, but as a collector, isoamyl xanthate shows better effects on lead and zinc grades than other collectors. The different effects of these drugs are mainly due to the different hydrocarbon chain lengths and structures of xanthate [29]. It can be found from Figure 10b that under the dosage of 20 g/t, isoamyl xanthate has the best recovery effect on lead and zinc. The recovery rate of lead and zinc changes obviously when the dosage of the collector is increased from 10 g/t to 20 g/t. The grade of lead and zinc does not change much when the amount of collector exceeds 20 g/t. In primary flotation, a high recovery is more important than a high grade. Therefore, in order to reduce the cost, the reagent dosage is 20 g/t. Isoamyl xanthate was selected as the best collector.



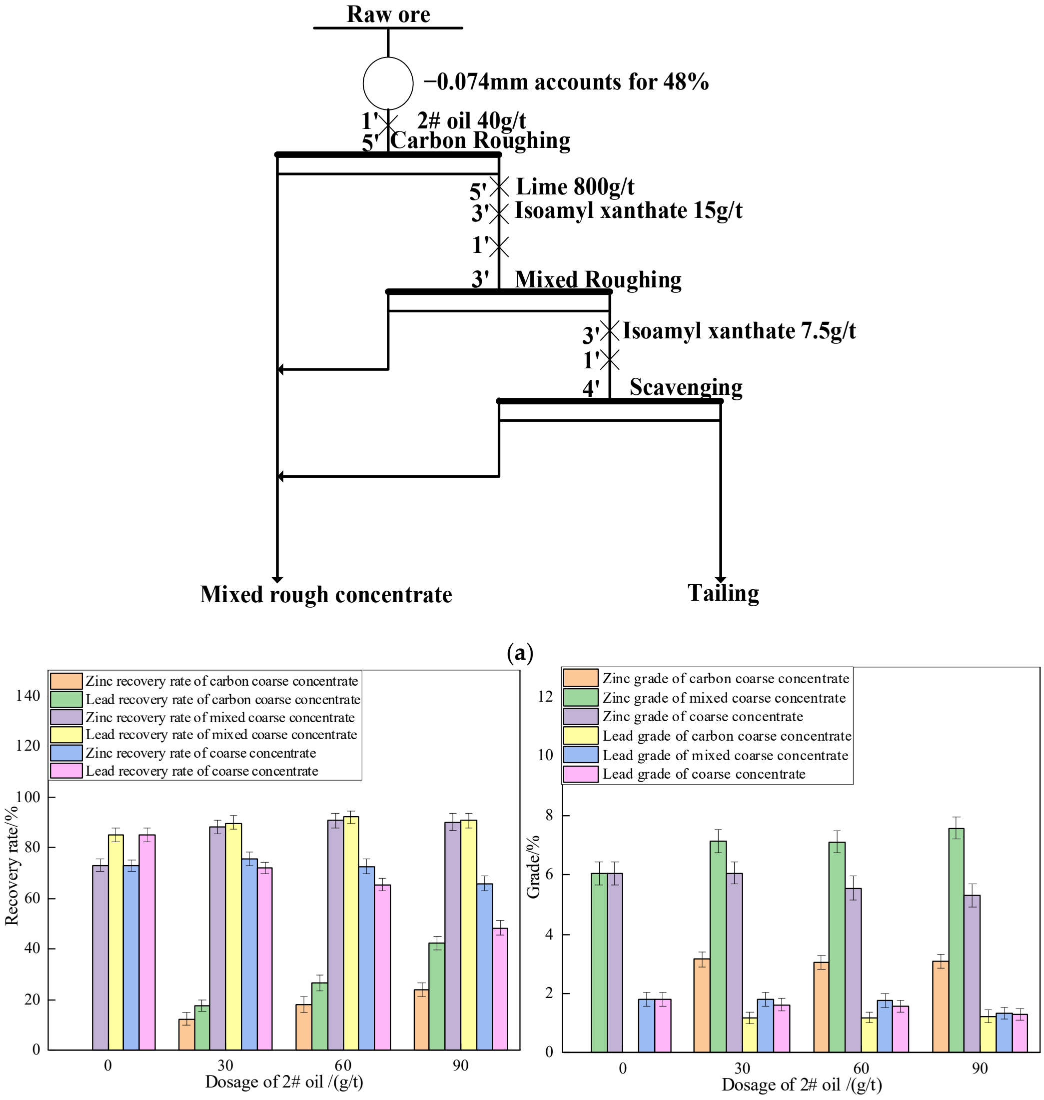
(a)

(b) (c)

**Figure 10.** Effects of collector type and dosage on sulfide aggregates. (**a**) The flowsheet for flotation experiments; (**b**) effects of collector type and dosage on the recovery of sulfide aggregates; (**c**) effects of collector type and dosage on the grade of sulfide aggregates.

### 3.3.3. Effect of #2 Oil Dosage

Figure 11 shows that the recovery rate and grade of lead and zinc change strongly when the dosage of #2 oil is from 0 g/t to 30 g/t. The recovery rate and grade of lead and zinc in the coarse concentrate do not change obviously when the dosage of #2 oil exceeds 30 g/t. The lead–zinc minerals in the coarse carbon concentrate will be discarded.



(**a**)

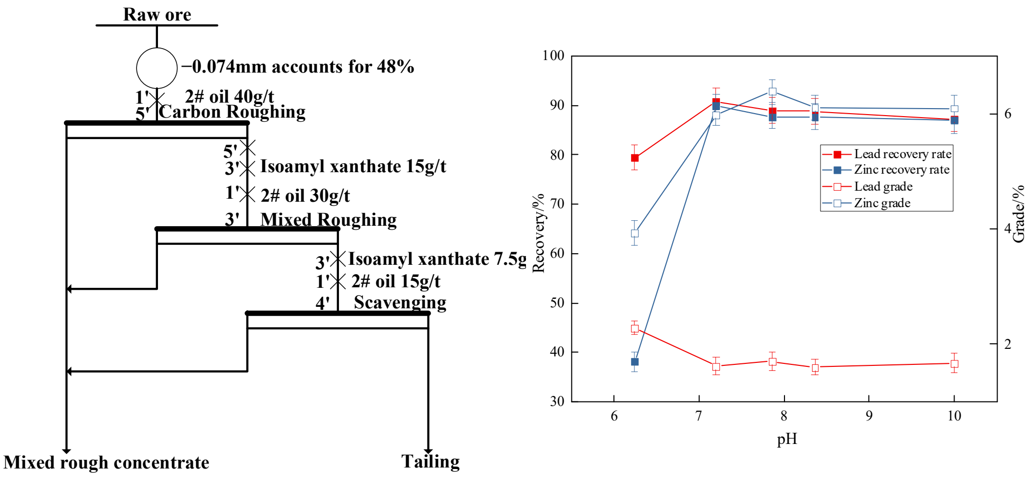
(**b**) (**c**)

**Figure 11.** Effects of #2 oil dosage on the recovery rate of sulfide aggregates. (**a**) The flow chart for flotation experiments; (**b**) effects of 2 # oil dosage on the recovery rate of lead and zinc flotation; (**c**) effects of 2 # oil dosage on the grade of lead and zinc flotation.

Therefore, combining the above two figures, it can be concluded that when the dosage of #2 oil is 30 g/t, lead and zinc concentrates with a higher recovery rate and grade can be obtained.

### 3.3.4. Effect of pH

CaO is used to adjust the pH of the pulp. From Figure 12b, it can be seen that as the pH increases, the zinc grade keeps increasing until the pH reaches 7.86, and the recovery rate of zinc reaches the maximum at pH 7.2, so the optimal pH for zinc flotation is 7.2. With the increase in pH, the grade of lead will drop first and then become stable. The recovery rate of lead increases first and then does not change much. The optimal pH of lead flotation is 7.2. Therefore, the final determined optimal pulp pH is 7.2.



(**a**) (**b**)

**Figure 12.** Effect of pH value on the recovery of sulfide aggregates. (**a**) The flow chart for flotation experiments; (**b**) effect of pH value on the flotation recovery.

### *3.4. Product Inspection*

The final process parameters of a coarse-grained mixed flotation process are adopted, that is, the slurry concentration is 53.33%, the stirring speed is 2340 r/min, the amount of #2 oil added for removal carbon is 40 g/t, the pH value of the mixed roughing is 7.2, isopropyl xanthate 20 g/t and #2 oil 30 g/t were subjected to removal carbon tailing to carry out a roughing and one scavenging test. The indexes of each concentrate product are shown in Table 5.

**Table 5.** Results of coarse-grain mixed flotation test.

| Product Name | Yield/% | Grade/% | | Recovery Rate/% | |
|---|---|---|---|---|---|
| | | Pb | Zn | Pb | Zn |
| Carbon Coarse Concentrate | 19.50 | 0.95 | 2.92 | 21.50 | 18.60 |
| Rough concentrate | 29.90 | 2.03 | 8.40 | 70.28 | 82.04 |
| Mixed rough concentrate | 49.40 | 1.60 | 5.71 | 91.78 | 92.07 |
| Tailings | 50.60 | 0.14 | 0.47 | 8.22 | 7.93 |
| Raw ore | 100.00 | 0.86 | 3.06 | 100.00 | 100.00 |

Research shows that under the condition of a grinding fineness of −0.074 mm accounting for 48%, after roughing, lead and zinc grades of 2.03% and 8.4% can be obtained, respectively, lead and zinc recovery rates are 70.28% and 82.04%, and the tailing rate is 70.1%, but the recovery rate is low. In order to improve the recovery rate of roughing, the roughing tailings are re-beneficiated, and the re-beneficiation concentrate is merged into the rough concentrate. The rough particle flotation and tailing can significantly improve the grinding grade of the subsequent fine grinding process, thereby reducing the grinding cost.

In order to investigate the loss of each size of lead and zinc in the tailings, the size of the tailings was analyzed. The results are shown in Table 6.

Table 6 shows that galena and sphalerite are mostly lost to a −0.4 + 0.3 mm grain size, and the distribution rate of lead and zinc in the +0.3 mm grain size reaches 41.20% and 54.50%, indicating that rough-grained minerals are not easy to float. The reason why the rough particles are difficult to float may be caused by the high density of mineral aggregates, which are not easy to float during the flotation process or are easy to fall off during the ascent.

**Table 6.** Results of particle size analysis of coarse-grain mixed flotation tailings.

| Grain Grade/mm | Yield/% | Grade | | Distribution Rate | | Negative Accumulation | |
|---|---|---|---|---|---|---|---|
| | | Pb | Zn | Pb | Zn | Pb | Zn |
| +0.6 | 0.37 | 0.22 | 0.66 | 0.56 | 0.51 | 100.00 | 100.00 |
| 0.6 + 0.45 | 1.50 | 0.17 | 0.67 | 1.78 | 2.11 | 99.44 | 99.49 |
| −0.45 + 0.4 | 6.11 | 0.20 | 0.70 | 8.54 | 9.02 | 97.66 | 97.37 |
| −0.4 + 0.3 | 27.10 | 0.16 | 0.75 | 30.32 | 42.86 | 89.11 | 88.36 |
| −0.3 + 0.2 | 14.05 | 0.18 | 0.74 | 17.69 | 21.93 | 58.80 | 45.50 |
| −0.2 + 0.15 | 9.78 | 0.13 | 0.36 | 8.89 | 7.42 | 41.11 | 23.57 |
| −0.15 + 0.1 | 8.55 | 0.10 | 0.17 | 5.98 | 3.07 | 32.22 | 16.15 |
| −0.1 + 0.074 | 6.11 | 0.10 | 0.15 | 4.06 | 1.93 | 26.24 | 13.08 |
| −0.074 | 26.44 | 0.12 | 0.20 | 22.18 | 11.15 | 22.18 | 11.15 |
| Total | 100.00 | 0.14 | 0.47 | 100.00 | 100.00 | | |

To sum up, after coarse grinding, the raw ore is finely ground to −0.074 mm, accounting for 48%, and the sulfide ore-rich contiguous body is used as the recovery object to obtain a higher roughing recovery rate. Studies have shown that the identifiable mineral fragments after coarse grinding are sulfide mineral-rich conglomerates. The fineness of grinding can be selected by referring to the liberation degree of sulfide mineral-rich conglomerates of about 70%. That is, the fineness of grinding is determined by the grain size of the sulfide mineral aggregations, so that the liberation degree of the sulfide mineral-rich conglomerate in the first grinding product can reach 70% to achieve high-efficiency rough particle flotation tailing.

## 4. Conclusions

(1) The MLA technology is used to measure two grinding products with a grinding fineness of −0.074 mm, accounting for 48% and 69%. With a grinding fineness of −0.074 mm accounting for 48%, it is more technically reasonable to use the sulfide aggregates as the recovery objects to carry out the rough particle flotation tailings;

(2) Determine the characteristics of the aggregates fragments that can be re-covered after coarse grinding. The recovery object of coarse-grained mixed flotation is a sulfide mineral-rich conglomerate, which can be thrown after the liberation degree reaches 70%;

(3) Galena and sphalerite are mostly lost to a −0.4 + 0.3 mm particle size, and the distribution rate of lead and zinc for the +0.4 mm particle size is higher, indicating that coarse-grained minerals are not easy to float;

(4) The optimized process conditions: In the first step of flotation, the carbon in lead–zinc sulfide ore was removed, by adding #2 oil to the flotation tank at a dosage of 40 g/t. In the second flotation process, the pH was adjusted to 7.2, the dosage of isopropyl xanthate was 20 g/t, the dosage of #2 oil was 30 g/t; the flotation reagent in the third step was isopropyl xanthate, and the dosage was 7.5 g/t, with 15 g/t of #2 oil. At the selected conditions, the recoveries of Pb and Zn were 91.78% and 92.07%, respectively. Moreover, the grades of Pb and Zn were 1.6% and 5.71%, respectively, with the tailing discard rate reaching 50.6%.

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