Article

Extraction of Lead and Zinc from a Rotary Kiln Oxidizing Roasting Cinder

Junhui Xiao 1,2,3,* , Kai Zou 1,3, Wei Ding 1,3, Yang Peng 1,3 and Tao Chen 1,3

1 Sichuan Engineering Lab of Non-Metallic Mineral Powder Modification and High-Value Utilization, Southwest University of Science and Technology, Mianyang 621010, China; zoukaiswust@163.com (K.Z.); dingwei@mails.swust.edu.cn (W.D.); pengyang@mails.swust.edu.cn (Y.P.); chentao@mails.swust.edu.cn (T.C.)
2 Key Laboratory of Sichuan Province for Comprehensive Utilization of Vanadium and Titanium Resources, Panzhihua University, Panzhihua 61700, China
3 Key Laboratory of Ministry of Education for Solid Waste Treatment and Resource Recycle, Southwest University of Science and Technology, Mianyang 621010, China

* Correspondence: xiaojunhui@swust.edu.cn or xiaojunhui33@163.com; Tel.: +86-139-9019-0544

Received: 28 February 2020; Accepted: 1 April 2020; Published: 2 April 2020

Abstract: In this study, sulfuric acid leaching and gravity shaking-table separation by shaking a table are used to extract lead and zinc from a Pb-Zn oxidizing roasting cinder. The oxidizing roasting cinder—containing 16.9% Pb, 30.5% Zn, 10.3% Fe and 25.1% S—was obtained from a Pb-Zn sulfide ore in the Hanyuan area of China by a flotation-rotary kiln oxidizing roasting process. Anglesite and lead oxide were the main Pb-bearing minerals, while zinc sulfate, zinc oxide and zinc ferrite were the main Zn-bearing minerals. The results show that a part of lead contained in lead oxide is transformed to anglesite, and a 3PbO·PbSO₄·H₂O-dominated new lead mineral phase after acid leaching. A zinc leaching efficiency of 96.7% was obtained under the leaching conditions used: a leaching temperature of 55 °C; a leaching time of 90 min; a sulfuric acid dosage of 20%; a sulfurous acid dosage of 4%; a cinder particle size of <0.3 mm; and a solid-liquid ratio of R = 1:4. After the gravity shaking-table separation, a lead concentrate with 50.2% Pb, 2.33% Zn and lead recovery of 86.0% was produced. The main chemical compounds in leaching residue are anglesite, 3PbO·PbSO₄·H₂O, SiO₂ and ZnFe₂O₄, while the main chemical compounds in lead concentrate are anglesite, 3PbO·PbSO₄·H₂O and SiO₂.

Keywords: lead; zinc; oxidizing roasting cinder; acid leaching; gravity separation

1. Introduction

Lead and zinc mineral resources in China are abundant and widely distributed, but relatively concentrated. According to the statistical data of the United States geological survey, the world’s confirmed reserves of lead were 89 million tons in 2013, of which China’s reserves were 14 million tons, accounting for 15.7% of the total. The global reserves of zinc were 250 million tons, of which China’s reserves were 43 million tons, accounting for 17.2% of the total. Chinese reserves of both metals are ranked second in the world. The mineral resources report of the Ministry of Land and Resources shows that the confirmed reserves of lead and zinc were 73.849 million tons and 144.861 million tons in China, respectively. According to the degree of ore oxidation, lead-zinc ore can be divided into sulfide ore (lead or zinc oxidation < 10%), mixed ore (lead or zinc oxidation 10–30%) and oxidized ore (lead or zinc oxidation > 30%). The degree of ore oxidation is closely related to the selection of the separation method and technological process used for metal recovery. Sulfide ore accounts for the majority of lead-zinc ore in China, as well as worldwide. According to the differences in mineral floatability and floating speed, the process for lead-zinc ore can be divided into three categories: selective flotation; bulk flotation; and combined flow. On this basis, according to specific ore properties, many technological processes have
been derived, such as the direct selective flotation process, partial selective flotation process, floatable flotation process, asynchronous flotation process, partial bulk flotation process, fully bulk flotation process, branch series flotation process, gravity separation-flotation process and flotation-gravity separation process, etc. Sometimes a combined process of beneficiation and metallurgy is used to process extremely refractory bulk lead-zinc ores or lead-zinc oxide ores [1–3].

There are a large amount of Cu-Pb-Zn polymetallic sulfide ores in the Hanyuan area of China, of which the main metal-containing minerals are chalcopyrite, galena, sphalerite, marmatite and pyrite. The main gangue minerals are dolomite, calcite, quartz, feldspar, mica, chlorite, montmorillonite, etc. Assemblages of galena, sphalerite and marmatite (Fe-sphalerite) are currently produced as solid solutions with a fine grain size, and occur in these ores. Copper concentrate with more than 20% Cu, lead concentrate with more than 62% Pb and mixed Pb-Zn sulfide concentrate with about 40% Pb + Zn were obtained by flotation in the local dressing plant. The elements associated with the sulfide minerals are sulfur, silver, cadmium, gallium, indium, arsenic and antimony. The separation of lead and zinc from the lead-zinc sulfide ore is difficult using just flotation, due to the close association of lead with zinc. With the development of the market, the price of lead-zinc mixed concentrate has tended to decrease, while a large number of these concentrates are unsalable, neither of which are conducive to the improvement of economic benefits. Therefore, it is crucial that the effective separation of lead and zinc mixed lead-zinc concentrate is studied [4–9].

At present, sulfating roasting-leaching and high-pressure acid leaching-extraction separation are the main metallurgical methods to process Pb-Zn bulk concentrate. Zinc sulfate is obtained by the leaching and formation of crystal line products, while the lead sulfate remains in the leaching residue. The high-pressure acid leaching process is used to dissolve lead and zinc into Pb\(^{2+}\) and Zn\(^{2+}\) ions, respectively. Then, lead and zinc are further extracted by electrodeposition and other processes to achieve effective separation [10–16]. In the local mining enterprises, lead-zinc bulk concentrate is treated in a rotary kiln, and the schematic diagram is shown in Figure 1.

![Schematic diagram of rotary kiln in the local factory.](image)

**Figure 1.** Schematic diagram of rotary kiln in the local factory.

The roasting temperature and roasting atmosphere are the two key factors, and are the most difficult to control in the oxidizing roasting process of mixed lead-zinc concentrate. The amount of air in and out of the blower is used to control the roasting atmosphere. If the oxygen content is sufficient, the roasting products are mainly sulfates. If the oxygen content is insufficient, the roasting products are mainly oxides. It is difficult to accurately control the roasting temperature of a rotary kiln, which is generally controlled by temperature installed sensors. The rotary kiln (B-C) region represents the high temperature belt, while the rotary kiln (C-D) region represents the middle temperature zone and the rotary kiln (D-E) region represents the low temperature zone. The mixed lead-zinc concentrate can react with oxygen in the middle and high temperate zones, so the local factory can only control the roasting temperature to fluctuate within a certain range in the production process, resulting in the mixture of
metal oxide and metal sulfate in the oxidized roasting cinder. The separation of lead and zinc from oxidized calcined slag by water leaching and the spiral chute gravity separation process was not ideal. At present, more than 60% of lead and over 70% of zinc can be recovered by oxidizing roasting, water leaching and spiral chute gravity separation from the mixed Pb-Zn sulfide concentrate. However, as the atmosphere is difficult to control during rotary kiln roasting, some lead oxide, zinc oxide and zinc ferrite mineral phases still exist in the oxidizing roasting cinders, resulting in the poor separation of lead and zinc. Therefore, separation tests of lead and zinc from the oxidizing roasting cinder produced from the mixed Pb-Zn sulfide concentrate were carried out. From this study, a technical scheme for the resource utilization of lead-zinc sulfide ore resources in the Hanyuan area of China was developed.

2. Materials and Methods

2.1. Sample Characterization

The main sulfide minerals identified are galena, sphalerite, marmatite and pyrite; while the main gangue minerals in the mixed Pb-Zn sulfide concentrate are calcite, dolomite, dolomite, mica, chlorite, feldspar, etc. Galena reacts with oxygen to form anglesite (PbSO$_4$) and lead oxide (PbO), while sphalerite reacts with oxygen to form zinc sulfate (ZnSO$_4$) and zinc oxide (ZnO), and marmatite reacts with oxygen to form zinc sulfate (ZnSO$_4$), zinc oxide (ZnO) and zinc ferrite (Zn$_2$FeO$_4$). Pyrite reacts with oxygen to form hematite (Fe$_2$O$_3$) or magnetite (Fe$_3$O$_4$). The main chemical reactions that may occur in the sulfuric acid leaching system are shown in Equations (1)–(16), and these are confirmed by characterization results, as described below.

\[
\begin{align*}
2\text{PbS} (s) + 3\text{O}_2(g) & \rightarrow 2\text{PbO} (s) + 2\text{SO}_2(g) \\
\text{PbO} (s) + \text{SO}_2(g) + 0.5\text{O}_2(g) & \rightarrow \text{PbSO}_4(s) \\
2\text{ZnS} (s) + 3\text{O}_2(g) & \rightarrow 2\text{ZnO} (s) + 2\text{SO}_2(g) \\
\text{ZnO} (s) + \text{SO}_2(g) + 1/2\text{O}_2(g) & \rightarrow \text{ZnSO}_4(s) \\
(\text{Zn,Fe})\text{S} (s) + 2\text{O}_2(g) & \rightarrow \text{ZnO} (s) + \text{PbO} (s) + \text{SO}_2(g) \\
4\text{FeS}_2(s) + 7\text{O}_2(g) & \rightarrow 2\text{Fe}_2\text{O}_3(s) + 4\text{SO}_2(g) \\
3\text{FeS}_2(s) + 8\text{O}_2(g) & \rightarrow \text{Fe}_3\text{O}_4(s) + 6\text{SO}_2(g) \\
\text{ZnO} (s) + \text{Fe}_2\text{O}_3(s) & \rightarrow \text{ZnFe}_2\text{O}_4(s) \\
\text{CaCO}_3(s) & \rightarrow \text{CaO}(s) + \text{CO}_3(g) \\
\text{CaMg(CO}_3)_2(s) & \rightarrow \text{CaO}(s) + \text{MgO}(s) + 2\text{CO}_2(g) \\
\text{CaO} (s) + \text{Fe}_2\text{O}_3(s) & \rightarrow \text{CaFe}_2\text{O}_4(s) \\
\text{MgO}(s) + \text{Fe}_2\text{O}_3(s) & \rightarrow \text{MgFe}_2\text{O}_4(s) \\
\text{CaO} (s) + \text{SiO}_2(s) & \rightarrow \text{CaO-SiO}_2(s) \\
\text{MgO}(s) + \text{SiO}_2(s) & \rightarrow \text{MgO-SiO}_2(s) \\
\text{CaO} (s) + \text{Al}_2\text{O}_3(s) & \rightarrow \text{CaO-Al}_2\text{O}_3(s) \\
\text{MgO}(s) + \text{Al}_2\text{O}_3(s) & \rightarrow \text{MgO-Al}_2\text{O}_3(s)
\end{align*}
\]

The sample was collected from the Pb-Zn sulfide ore dressing plant by the flotation-oxidizing roasting process. The oxidizing roasting cinders contained 16.9% Pb, 30.5% Zn, 10.3% Fe and 25.1% S. Anglesite (PbSO$_4$) and lead oxide (PbO) were the main Pb-bearing minerals, while zinc sulfate (ZnSO$_4$), zinc oxide (ZnO) and zinc ferrite (Zn$_2$FeO$_4$) were the main Zn-bearing minerals. Gangue minerals were
quartz (SiO₂), calcium ferrite (CaFe₂O₄), magnesium ferrite (MgFe₂O₄), calcium aluminate (Ca₂Al₂O₄), etc. The chemical composition analysis of the sample is shown in Table 1. The lead and zinc mineral phase analyses for the main elements are shown in Tables 2 and 3, respectively, while a size fraction is shown in Table 4, and the X-ray diffraction (XRD, X Pert pro, Panaco, the Netherlands) analysis is shown in Figure 2.

**Table 1.** Main chemical composition of the oxidizing roasting cinder (wt %).

|   | Pb | Zn | Fe | S   | As | CaO | SiO₂ | Al₂O₃ | MgO | Na₂O |
|---|----|----|----|-----|----|-----|------|-------|-----|------|
|   | 16.9 | 30.5 | 3.36 | 15.1 | 0.01 | 3.22 | 8.36 | 4.23  | 2.89 | 1.66 |

**Table 2.** Lead phase analysis of the oxidizing roasting cinder (wt %).

| Lead in | Lead Sulfate | Lead in Lead Oxide | Lead in Lead Sulfide | Lead in Lead Carbonate |
|---------|--------------|--------------------|----------------------|------------------------|
|         | 10.3         | 6.52               | 0.02                 | 0.06                   |

**Table 3.** Zinc phase analysis of the oxidizing roasting cinder (wt %).

| Zinc in | Zinc Sulfate | Zinc in Zinc Oxide | Zinc in Lead Sulfide | Zinc in Zinc Carbonate |
|---------|--------------|--------------------|----------------------|------------------------|
|         | 20.2         | 10.2               | 0.06                 | 0.04                   |

**Table 4.** Size fraction analysis of the oxidizing roasting cinder.

| Fractions (mm) | Content (wt %) | Grade (wt %) | Distribution (wt %) |
|----------------|----------------|--------------|---------------------|
|                |                | Pb | Zn | Pb | Zn |
| −2.00~+1.00    | 25.7           | 15.4 | 28.7 | 23.4 | 24.1 |
| −1.00~+0.50    | 25.1           | 17.8 | 31.2 | 26.5 | 25.8 |
| −0.50~+0.25    | 16.6           | 18.3 | 27.9 | 18.0 | 15.2 |
| −0.25~+0.15    | 11.8           | 15.9 | 30.6 | 11.0 | 11.8 |
| −0.15~+0.10    | 15.9           | 16.9 | 34.4 | 16.0 | 18.0 |
| −0.10~0        | 4.90           | 17.3 | 31.8 | 5.10 | 5.10 |
| **Totals**     | **100**        | **16.9** | **30.5** | **100** | **100** |

**Figure 2.** XRD diffractogram and identified phases of the oxidizing roasting cinder.

2.2. Chemical Reagent and Equipment

The main chemical reagents used in this test are sulfuric acid (purity 98%) and sulfurous acid (purity 99.5%), both obtained by Chengdu Jinshan Chemical Reagent Co., Ltd. (Chengdu, China). The main equipment used for the experiment was a magnetic stirrer (1.5 dm³, Jilin Exploration Machinery Factory,
Sulfuric acid leaching and gravity shaking-table separation were used to separate lead and zinc from the oxidizing roasting cinder, and this process is shown in Figure 3. To conduct acid leaching, raw materials (a mass of 100 g for each test) are mixed with the sulfuric acid in a 5-30% proportion and placed into the stirrer. Water was added to adjust the solid:liquid ratio to the target value, and the sulfuric acid reacts with the oxidizing roasting cinder to generate insoluble PbSO$_4$ and soluble ZnSO$_4$. After solid-liquid separation, ZnSO$_4$ reports to the lixivium and PbSO$_4$ to the leaching residue. Zinc-bearing lixivium is used for the preparation of ZnSO$_4$·7H$_2$O. Sulfuric acid leaching residue (a mass of 500 g for each test) and water were mixed in a 30-40% portion and gravity shaking-table to recover lead. The contents of lead and zinc in the sulfuric acid leaching residue were analyzed to calculate the leaching efficiency for zinc, and evaluate the separation effect of zinc and enrichment of lead. The contents of lead in the gravity shaking-table separation concentrate and tailings were analyzed to calculate the lead recovery. The calculation formula for zinc leaching efficiency is shown in Equation (17), and lead recovery is shown in Equation (18).

\[
\text{Zinc leaching efficiency} = \frac{(Q_1 \times \alpha_{Zn} - Q_2 \times \theta_{Zn})}{Q_1 \times \alpha_{Zn}} \quad (17)
\]

\[
\text{Lead recovery} = \frac{Q_5 \times \beta_{Pb}}{(Q_5 \times \beta_{Pb} + Q_4 \times \theta_{Pb})} \quad (18)
\]

where $Q_1$ is the weight of the oxidizing roasting cinder (g); $Q_2$ is the weight of the leaching residue (g); $Q_3$ is the weight of the gravity shaking-table separation concentrate (g); $Q_4$ is the weight of the gravity shaking-table separation tailings (g); $\alpha_{Zn}$ is content of the oxidizing roasting cinder (%); $\theta_{Zn}$ is the content of leaching residue (%); $\beta_{Pb}$ is content of gravity shaking-table separation concentrate (%); and $\theta_{Pb}$ is content of gravity shaking-table separation tailings (%).

![Figure 3. Scheme of the extraction of lead and zinc process from the oxidizing roasting cinder.](image-url)
2.4. Analysis and Characterization

The chemical composition of solid materials was analyzed by a Z-2000 atomic absorption spectrophotometer (Hitachi Co., Ltd., Tokyo, Japan); the diffraction grating was Zenier-tana type, 1800 lines/mm; the flash wavelength was 200 nm, the wavelength range was 190–900 nm; and the automatic peak seeking setting and spectral bandwidth were set to 1.3 nm and 2.6 nm, respectively, in order to analyze the chemical composition of the solid. Inductively coupled plasma mass spectrometry (8800 ICP-MS/MS, Agilent Technologies Inc., Santa Clara, CA, USA) was used to determine the Zn, Pb and Fe contents of lixivium. The phase compositions of solid substances (the oxidizing roasting cinders, leaching residue, lead concentrate and gravity shaking-table separation tailings) were analyzed by XRD. The microstructure of the solid products was observed by SEM (S440, Hirschmann Laborgerate GmbH & Co. KG, Eberstadt, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector (Ultra55, CarlzeissNTS GmbH, Hirschmann Laborgerate GmbH & Co. KG, Eberstadt, Germany).

3. Results and Discussion

3.1. Separation of Zinc Using Sulfuric Acid Leaching

3.1.1. Sulfuric Acid Dosage

Hydrochloric acid, sulfuric acid and nitric acid are commonly used to extract lead and zinc by acid leaching. If hydrochloric acid or nitric acid is used as the leaching agent, PbCl₂ or Pb(NO₃)₂ and ZnCl₂ or Zn(NO₃)₂ will enter into the leaching solution at the same time, which prevents the effective separation of lead and zinc. When sulfuric acid is used as the leaching agent, the products are an insoluble PbSO₄ precipitate and soluble ZnSO₄, and lead and zinc can be separated by solid-liquid separation. The effect of using different sulfuric acid dosages is shown in Figure 4a.

![Figure 4](image)

Figure 4. Effect of sulfuric acid dosage (a) and leaching time (b) on the leaching efficiency of zinc and metal grades in the leaching residue.

Results in Figure 4a confirm that increasing sulfuric acid dosage was conducive to improving zinc leaching efficiency and enriching lead grade in the leaching residue. When the amount of sulfuric acid exceeded 20%, the leaching efficiency of zinc increases slightly. Considering the cost of reducing acid consumption in the production process and the corrosion of equipment by high concentration acid, a sulfuric acid dosage of 20% was suitable. The leaching efficiency of zinc was 79.2%, and the grades of lead and zinc in leaching residue were 25.5% and 8.86%, respectively.
3.1.2. Leaching Time

The test results for different leaching times are shown in Figure 4b. Prolonging the leaching time is conducive to the dissolution of zinc, and the leaching reaction is more complete. However, when the leaching time is too long, it becomes easier to dissolve non-target elements in the sample. This increases the impurity content in the leaching solution, and therefore affects the separation and purification of the zinc in the leaching solution. When the leaching time was extended to 90 min, the leaching efficiency of zinc increased slightly. Compared with the leaching time of 120 min, the leaching efficiency of zinc increased from 84.8% to 85.5%. The main reason for this small change is that as the reaction time increases, the acid in the system is consumed, and there is little impetus for the reaction to continue. Therefore, a leaching time of 90 min was selected as most appropriate, the leaching efficiency of zinc was 84.8%, and the grades of lead and zinc in the leaching residue were 25.7% and 7.08%, respectively.

3.1.3. Leaching Temperature

The effects of different leaching temperatures are shown in Figure 5a. The results show that temperature has a significant influence on the leaching efficiency. When the leaching temperature rose to 55 °C, the leaching efficiency of zinc was 89.1%; when the leaching temperature was further increased to 75 °C, the increase of the leaching efficiency of zinc was relatively small. With the increase of temperature, the influence of sulfate ions in the solution on minerals increases, which is beneficial to the leaching of valuable metal zinc. When the temperature reached 55 °C, the leaching efficiency of other elements will increase significantly as the temperature continues to increase. Therefore, the leaching temperature was 55 °C, the leaching efficiency of zinc was 89.2%, the lead grade was increased to 28.8%, and the zinc grade was reduced to 5.66% in the leaching residue.

![Figure 5. Effect of leaching temperature (a) and fineness (b) on the leaching efficiency of zinc and the metal grades in the leaching residue.](image)

3.1.4. Fineness of the Oxidizing Roasting Cinder

The effects of different particle size fractions are shown in Figure 5b. Since the mixed lead-zinc concentrate was oxidized in a rotary kiln, zinc sulfate and lead sulfate are both present in the roasting cinder. If wet grinding is adopted to change the material size, it is not conducive to the control of the liquid-solid ratio in subsequent leaching tests and the concentration of Zn²⁺ in the leaching solution. Furthermore, it is not conducive to the subsequent separation or the recovery of zinc in the leaching solution. The results show that decreasing the particle size of the oxidizing roasting residue is beneficial to increase the leaching efficiency of zinc and the lead grade in leaching residue. However, the decrease of feed size also means an increase in the grinding cost. As the size of the roasting ore decreases, its specific surface area increases, and mineral liberation is enhanced. Both of these changes are conducive.
to the leaching reaction, so the leaching efficiency also increases gradually. When the particle size of leaching materials was <0.3 mm, the leaching efficiency of zinc was 90.1%, the lead grade was enriched to 30.5%, and the zinc grade was reduced to 5.12% in leaching residue.

3.1.5. Solid-Liquid Ratio ($R = m_{\text{solid}}:m_{\text{liquid}}$)

The test results of different solid-liquid ratios are shown in Figure 6a. Once the solid-liquid ratio reached 1:4, the viscosity of the leaching solution changed little. Hence, diffusion rates of species to and from the reacting mineral surfaces did not increase significantly with the further decrease of the solid-liquid ratio. Hence, the leaching efficiency increased slowly. A solid-liquid ratio for the leaching of $R = 1:4$ was therefore suitable. The leaching efficiency of zinc was 91.4%, the lead grade was enriched to 32.8%, and the zinc grade was reduced to 5.08% in leaching residue.

![Figure 6. Effect of the solid-liquid ratio (a) and sulfurous acid dosage (b) on the leaching efficiency of zinc and the metal grades in the leaching residue.](image)

3.1.6. Additive Dosage

The effects of different sulfurous acid dosage are shown in Figure 6b. The mineral analysis of the sample indicated the presence of ZnFe$_2$O$_4$, which does not readily react with sulfuric acid to produce ZnSO$_4$ and Fe$_2$(SO$_4$)$_3$ during the leaching process. Combining this with the previous relevant study, the addition of oxidizer in the leaching process was beneficial to improve the leaching efficiency. The predominance diagram of $\phi$-$pH$ for the SO$_2$-ZnFe$_2$O$_4$-H$_2$O system at different temperatures is shown in Figure 7. There are two mechanisms for the decomposition of ZnFe$_2$O$_4$ under acidic conditions. Under the oxidizing conditions, the first step of ZnFe$_2$O$_4$ decomposition is into Fe$_2$O$_3$ and Zn$^{2+}$, and the second step is Fe$^{3+}$ dissolution from Fe$_2$O$_3$. Under the reducing conditions, after ZnFe$_2$O$_4$ is decomposed into Fe$_2$O$_3$ and Zn$^{2+}$, Fe$_2$O$_3$ is reductively dissolved to Fe$^{2+}$. When the redox potential was controlled in the (B) region, zinc in ZnFe$_2$O$_4$ entered the solution in the form of Zn$^{2+}$, while iron remained in the residue in the form of Fe$_2$O$_3$. When the redox potential was controlled in the (D), (E) and (F) regions, zinc and iron in ZnFe$_2$O$_4$ entered the solution in the form of Zn$^{2+}$ and Fe$^{2+}$, respectively [17–20].

The results in Figure 5b show that increasing the appropriate amount of sulfurous acid is conducive to improving the extraction efficiency of zinc. When the amount of sulfuric acid exceeded 4%, the leaching efficiency of zinc changes little. These results indicated that sulfuric acid can play a synergistic role in enhancing the leaching efficiency of zinc using sulfuric acid. A 4% dosage of sulfurous acid was deemed sufficient, and allowed the redox potential to be controlled within the (D), and with a zinc leaching efficiency of 96.5%. The lead grade was enriched to 33.6% and the zinc grade was reduced to 2.12% in the leaching residue.
Figure 7. Predominance diagram of $\phi$-pH for SO$_2$-ZnFe$_2$O$_4$-H$_2$O system (25 °C—Full lines, 100 °C—Dashed lines).

3.1.7. Repeated Scale-up Test

In order to further validate test repeatability, repeated scale-up tests were carried out under the conditions employed as follows: a sulfuric acid dosage of 20%; a leaching time of 60 min; a leaching temperature of 55 °C; a cinder particle size of <0.3 mm; and a solid-liquid ratio of $R = 1:3$. These tests scaled to the ore mass up to 3000 g for each test, and the results are shown in Table 5. These results show that the index of repeated experiments is superior to the conditions of results. Lead enters into the leaching residue, and is enriched in the leaching residue from 16.9% to 33.8%. The impurity elements also report to the residue at significant concentrations (Table 6).

Table 5. Repeated scale-up test results (wt %).

| Repeat | Contents in the Oxidizing Roasting Cinder | Contents in Leaching Residue | Leaching Efficiency of Zinc |
|--------|-------------------------------------|-----------------------------|-----------------------------|
|        | Pb       | Zn   | Pb   | Zn   |                                    |
| 1      | 16.8     | 30.6 | 33.9 | 2.08 | 96.7                                |
| 2      | 17.1     | 30.4 | 33.6 | 2.12 | 96.6                                |
| 3      | 16.9     | 30.4 | 33.9 | 2.05 | 97.1                                |
| 4      | 17.0     | 30.6 | 33.7 | 2.11 | 96.5                                |
| 5      | 16.7     | 30.5 | 33.9 | 2.06 | 96.7                                |
| 6      | 16.8     | 30.4 | 33.7 | 2.07 | 96.7                                |
| Average| 16.9     | 30.5 | 33.8 | 2.08 | 96.7                                |

Range ($R = E_{\text{max}} - E_{\text{min}}$) = 0.60

Arithmetic mean error ($\delta = \frac{\sum |d_i|}{N}$) = 96.7

Sum square variation $SS = \sum (E_i - \bar{E})^2 = \sum_{i=1}^{N} (E_i - \bar{E})^2 = 0.21$

Average deviation $MS = \frac{SS}{N} = 0.04$

Standard deviation $s = \sqrt{\frac{(E_i - \bar{E})^2}{N-1}} = \sqrt{MS} = 0.20$
Table 6. Average main element analysis of leaching residues (wt %).

| Pb   | Zn  | Fe  | S   | CaO | SiO₂ | Al₂O₃ | MgO |
|------|-----|-----|-----|-----|------|-------|-----|
| 33.8 | 2.07| 0.26| 5.12| 9.18| 36.9 | 0.25  | 0.45|

3.2. Recovering Lead from Leaching Residue by Table Gravity Separation

Gravity shaking-table separation was adopted to further recover lead from the acid leaching residue, and the test procedure is shown in Figure 8. The test results are shown in Table 7, and the main element analysis results for the lead concentrate generated are shown in Table 8. The lead concentrate with a lead grade of 50.2% and recovery of 86.0% was obtained by two stages of grinding and three stages of gravity shaking-table separation. According to the quality standard for lead concentrate in China, the lead concentrate meets the requirement for level four lead concentrate, with a lead content of more than 50%.

![Figure 8. Scheme for recovering lead from the leaching residue.](image-url)
3.3. Lead and Zinc Phase Transformation Mechanism in Sulphuric Acid Leaching Process

According to the phase of sample analysis results, the oxidizing roasting of valuable metals in ore—mainly lead and zinc sulfate and oxides—exists in the form of different mineral phases, the oxidizing roasting cinder in different mineral dissolution mechanisms for the understanding of valuable metals such as lead, zinc and iron, magnesium, calcium and aluminum impurities such as leaching behavior have important significance. From the chemical composition, minerals composition and grain-sized analysis of the complex oxidizing roasting cinder, zinc was first extracted by sulphuric acid. The valuable metallic lead and zinc mainly exist in the mineral phases of lead sulfate, lead oxide, zinc oxide, zinc sulfate and zinc ferrite. At the same time, there are also corresponding chemical reactions for calcium, magnesium, aluminum compounds and sulfuric acid [21–25].

Therefore, it is very important to investigate the dissolution process of different mineral phases in acid solution. According to the X-ray diffraction (XRD) mineral analysis of the raw ore, the main mineral phases in the oxidizing roasting cinder were lead sulfate (PbSO$_4$), lead oxide (PbO), zinc sulfate (ZnSO$_4$), zinc oxide (ZnO), zinc ferrite (ZnFe$_2$O$_4$), calcium ferrite (CaFe$_2$O$_4$), magnesium ferrite (MgFe$_2$O$_4$) and calcium aluminate (Ca$_2$Al$_2$O$_4$). The main chemical reactions that may occur in the sulfuric acid leaching system were shown in Equations (19)–(24).

\[
PbO(s) + H_2SO_4(l) \rightarrow PbSO_4(s) + H_2O(l) \quad (19)
\]
\[
ZnO(s) + H_2SO_4(l) \rightarrow ZnSO_4(l) + H_2O(l) \quad (20)
\]
\[
ZnFe_2O_4(s) + 4H_2SO_3(l) + 2O_2(g) \rightarrow ZnSO_4(l) + Fe_2(SO_4)_3(l) + 4H_2O(l) \quad (21)
\]
\[
CaFe_2O_4(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + 2FeSO_4(l) + H_2O(l) \quad (22)
\]
\[
MgFe_2O_4(s) + 2H_2SO_4(l) \rightarrow MgSO_4(l) + 2FeSO_4(l) + 2H_2O(l) \quad (23)
\]
\[
Ca_2Al_2O_4(s) + 2H_2SO_4(l) \rightarrow 2CaSO_4(s) + Al_2(SO_4)_3(l) + H_2O(l) \quad (24)
\]

XRD, scanning electron microscopy (SEM) and energy dispersive X-ray (EDS) are used to characterize the leaching residue and lead concentrate, and analyze the leaching mechanism of sulfuric acid system solution. SEM-EDS analysis results of leaching residue and lead concentrate are shown in Figure 9, and XRD analysis results for leaching residue and lead concentrate are shown in Figure 10.
A sulfuric acid leaching—gravity shaking-table separation process was used to recover lead and zinc from the oxidizing roasting cinder which contained 16.9% Pb, 30.5% Zn, 10.3% Fe and 25.1% S. Based on the results obtained in this work, we drew the following conclusions:

1. An oxidizing roasting cinder which contained 16.9% Pb, 30.5% Zn, 10.3% Fe and 25.1% S was obtained from a Pb-Zn sulphide ore dressing plant in the Hanyuan area of China. Anglesite and lead oxide were the main Pb-bearing minerals. Zinc oxide, zinc sulfate and zinc ferrite were the main Zn-bearing minerals.

2. A sulfuric acid leaching—gravity shaking-table separation process was used to recover lead and zinc from the oxidizing roasting cinder. The zinc leaching efficiency of 96.7% was obtained under the leaching conditions used: a leaching temperature of 55 °C; a leaching time of 90 min; a sulfuric acid dosage of 20%; a sulfurous acid dosage of 4%; a cinder particle size of <0.3 mm; and a solid-liquid ratio of R = 1:4. After the gravity shaking-table separation, a lead concentrate with 50.2% Pb, 2.33% Zn and a lead recovery of 86.0% was produced.

It can be seen from Figures 9 and 10 that after leaching, the amount of lead sulfate phase increased significantly, while the amounts of zinc oxide and lead oxide phases decreased significantly. At the same time, some impurities such as calcium, magnesium and aluminum react with sulfuric acid to form corresponding salts that can either report to the residue, e.g., gypsum, or remain in the liquid phase. In addition, after the co-leaching of sulfuric acid and sulfurous acid, zinc was transformed from zinc oxide and zinc ferrite into ZnSO₄ into a liquid phase, while lead was transformed into anglesite and 3PbO·PbSO₄·H₂O in the residue [26]. The characteristics of ZnSO₄ as a soluble salt and PbSO₄ and 3PbO·PbSO₄·H₂O as an insoluble salt were utilized to realize the effective separation of lead and zinc.

4. Conclusions

Based on the results obtained in this work, we drew the following conclusions:

1. An oxidizing roasting cinder which contained 16.9% Pb, 30.5% Zn, 10.3% Fe and 25.1% S was obtained from a Pb-Zn sulphide ore dressing plant in the Hanyuan area of China. Anglesite and lead oxide were the main Pb-bearing minerals. Zinc oxide, zinc sulfate and zinc ferrite were the main Zn-bearing minerals.

2. A sulfuric acid leaching—gravity shaking-table separation process was used to recover lead and zinc from the oxidizing roasting cinder. The zinc leaching efficiency of 96.7% was obtained under the leaching conditions used: a leaching temperature of 55 °C; a leaching time of 90 min; a sulfuric acid dosage of 20%; a sulfurous acid dosage of 4%; a cinder particle size of <0.3 mm; and a solid-liquid ratio of R = 1:4. After the gravity shaking-table separation, a lead concentrate with 50.2% Pb, 2.33% Zn and a lead recovery of 86.0% was produced.

**Figure 9.** SEM images of leaching residue (a) and lead concentrate (b); EDS images of leaching residue (c) and lead concentrate (d).

**Figure 10.** XRD diffractogram of leaching residue (a) and lead concentrate (b).
XRD, SEM and EDS analysis of the leaching residue and lead concentrate show that the main minerals phase in the leaching residue are anglesite, $3\text{PbO-PbSO}_4\cdot\text{H}_2\text{O}$, $\text{SiO}_2$ and $\text{ZnFe}_2\text{O}_4$, and the main minerals phase in lead concentrate are anglesite, $3\text{PbO-PbSO}_4\cdot\text{H}_2\text{O}$ and $\text{SiO}_2$. A small amount of gangue compounds such as $\text{SiO}_2$ is generated in the lead concentrate due to mechanical entrainment.

**Author Contributions:** This is a joint work of the five authors; each author was in charge of their expertise and capability: J.X. for writing, formal analysis and original draft preparation, T.C. for validation, K.Z. for methodology and J.X. for investigation. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Acknowledgments:** This work was supported by the Sichuan Science and Technology Program (Grant Nos. 2018FZ0092); Key Laboratory of Sichuan Province for Comprehensive Utilization of Vanadium and Titanium Resources Foundation (2018FTSZ235); and the China Geological Big Survey (Grant No. DD20190694).

**Conflicts of Interest:** On behalf of all authors, the corresponding author states that there is no conflict of interest.

**References**

1. Zhu, L.Y.; Su, W.C.; Shen, N.P.; Dong, W.D.; Cai, J.L.; Zhang, Z.W.; Zhao, H.; Xie, P. Fluid inclusion and sulfur isotopic studies of lead-zinc deposits, northwestern Guizhou, China. *Acta Petrol. Sin.* **2016**, *32*, 3431–3440.
2. Asadi, T.; Azizi, A.; Lee, J.C.; Jahani, M. Leaching of zinc from a lead-zinc flotation tailing sample using ferric sulphate and sulfuric acid media. *J. Environ. Chem. Eng.* **2017**, *5*, 4769–4775. [CrossRef]
3. Liu, D.F.; Fan, X.X.; Shi, Y.F.; Yang, K.B. Leaching ecological behavior of indium from lead-containing copper matte using oxidation leaching-releasing technique. *Ekoloji* **2018**, *27*, 667–676.
4. Chen, L.Z.; Wang, C.B.; Zheng, Y.X.; Lv, J.F.; Lai, Z.N.; Pang, J. Flotation of a low-grade zinc oxide ore after surface modification at high temperature. *JOM* **2019**, *71*, 3166–3172. [CrossRef]
5. Xiao, J.H.; Zhang, Y.S. Extraction of cobalt and iron from refractory Co-bearing sulfur concentrate. *Processes* **2020**, *8*, 200. [CrossRef]
6. Zheng, Y.X.; Liu, W.; Qin, W.Q.; Han, J.W.; Yang, K.; Luo, H.L. Selective reduction of PbSO$_4$ to PbS with carbon and flotation treatment of synthetic galena. *Physicochem. Probl. Miner. Process.* **2015**, *51*, 533–546.
7. Ding, W.; Xiao, J.H.; Peng, Y.; Shen, S.Y.; Chen, T. Iron extraction from red mud using roasting with sodium salt. *Miner. Process. Extr. Metall. Rev.* **2019**. [CrossRef]
8. Xiao, J.H.; Zhang, Y.S. Recovering Cobalt and Sulfur in Low Grade Cobalt-Bearing V–Ti Magnetite Tailings Using Flotation Process. *Processes* **2019**, *7*, 536. [CrossRef]
9. Dong, J.C.; Wei, Y.G.; Zhou, S.W.; Li, B.; Yang, Y.D.; Mclean, A. The effect of additives on extraction of Ni, Fe and Co from nickel laterite ores. *JOM* **2018**, *70*, 2265–2277. [CrossRef]
10. Hyk, W.; Kitka, K.; Rudnicki, D. Selective recovery of zinc from metallurgical waste materials from processing zinc and lead ores. *Molecules* **2019**, *24*, 2275. [CrossRef]
11. Xiao, J.H.; Ding, W.; Peng, Y.; Wu, Q.; Chen, Z.Q.; Wang, Z.; Wang, J.M.; Peng, T.F. Upgrading iron and removing phosphorus of high phosphorus oolitic iron ore by segregation roasting with Calcium chloride and Calcium hypochlorite. *J. Min. Metall. Sect. B* **2019**, *55*, 305–314. [CrossRef]
12. Kim, E.; Honckmans, L.; Spooren, J.; Vrancken, K.C.; Quaghebeur, M.; Broos, K. Selective leaching of Pb, Cu, Ni and Zn from secondary lead smelting residues. *Hydrometallurgy* **2017**, *169*, 372–381. [CrossRef]
13. Liao, Y.L.; Zhou, J.; Huang, F.R.; Wang, Y.Y. Leaching kinetics of calcification roasting calcinate from multimetallic sulfide copper concentrate containing high content of lead and iron. *Sep. Purif. Technol.* **2015**, *149*, 190–196. [CrossRef]
14. Tian, D.; Shen, X.Y.; Zhai, Y.C.; Xiao, P.; Webley, P. Extraction of iron and aluminum from high-iron bauxite by ammonium sulfate roasting and water leaching. *J. Iron Steel Res. Int.* **2019**, *26*, 578–584. [CrossRef]
15. Peng, Y.; Xiao, J.H.; Deng, B.; Wang, Z.; Liu, N.Y.; Yang, D.G.; Ding, W.; Chen, T.; Wu, Q. Study on separation of fine-particle ilmenite and mechanism using flocculation flotation with sodium oleate and polyacrylamide. *Physicochem. Probl. Miner. Process.* **2020**, *56*, 161–172.
16. Rodriguez, N.R.; Onghena, B.; Binnemans, K. Recovery of lead and silver from zinc leaching residue using methanesulfonic acid. *ACS Sustainable Chem. Eng.* **2019**, *7*, 19807–19815. [CrossRef]
17. Xiao, J.H.; Peng, Y.; Ding, W.; Chen, T.; Zou, K.; Wang, Z. Recovering Scandium from Scandium Rough Concentrate Using Roasting-Hydrolysis-Leaching Process. *Processes* 2020, *8*, 365. [CrossRef]

18. Zhang, C.; Min, X.B.; Zhang, J.Q.; Wang, M.; Li, Y.C. Mechanisms and kinetics on reductive leaching of zinc from neutral leaching residue. *Trans. Nonferrous Met. Soc. Chin.* 2016, *26*, 197–203. (In Chinese)

19. Zhang, Y.J.; Li, X.H.; Pan, L.P.; Wei, Y.S. Influence of mechanical activation on dissolution kinetics and physicochemical properties of indium-bearing zinc ferrite. *Trans. Nonferrous Met. Soc. Chin.* 2012, *22*, 315–323. (In Chinese)

20. Zheng, Y.; Deng, Z.G.; Fan, G.; Wei, C.; Fan, G.; Li, X.B.; Li, C.X.; Li, M.T. Reductive decomposition of zinc ferrite and zinc residues by sulfur dioxide. *Trans. Nonferrous Met. Soc. Chin.* 2019, *29*, 170–178. (In Chinese)

21. Coelho, F.E.B.; Balarini, J.C.; Araujo, E.M.R.; Miranda, T.L.S.; Peres, A.E.C.; Martins, A.H.; Salum, A. Roasted zinc concentrate leaching: Population balance modeling and validation. *Hydrometallurgy* 2018, *175*, 208–217. [CrossRef]

22. Xiao, J.H.; Zhou, L.L. Increasing Iron and Reducing Phosphorus Grades of Magnetic-Roasted High-Phosphorus Oolitic Iron Ore by Low-Intensity Magnetic Separation–Reverse Flotation. *Processes* 2019, *7*, 388. [CrossRef]

23. Yang, K.; Zhang, L.B.; Zhu, X.C.; Peng, J.H.; Li, S.W.; Ma, A.Y.; Li, H.Y.; Zhu, F. Role of manganese dioxide in the recovery of oxide-sulphide zinc ore. *J. Hazard. Mater.* 2018, *343*, 315–323. [CrossRef] [PubMed]

24. Azevedo, A.; Oliveira, H.A.; Rubio, J. Treatment and water reuse of lead-zinc sulphide ore mill wastewaters by high rate dissolved air flotation. *Miner. Eng.* 2018, *127*, 114–121. [CrossRef]

25. Cui, F.H.; Mu, W.N.; Wang, S.; Xin, H.X.; Xu, Q.; Zhai, Y.C.; Luo, S.H. Sodium sulfate activation mechanism on co-sulfating roasting to nickel copper sulfide concentrate in metal extractions, microtopography and kinetics. *Miner. Eng.* 2018, *123*, 104–116. [CrossRef]

26. Steele, I.M.; Pluth, J.J.; Richardson, J.W., Jr. Crystal Structure of Tribasic Lead Sulfate (3PbO·PbSO₄·H₂O) by X-Rays and Neutrons: An Intermediate Phase in the Production of Lead Acid Batteries. *J. Solid State Chem.* 1997, *132*, 173–181. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).