Li, Yun; Yang, Shenghai; Taskinen, Pekka; Chen, Yongming; Tang, Chaobo; Jokilaakso, Ari

Cleaner Recycling of Spent Lead-Acid Battery Paste and Co-Treatment of Pyrite Cinder via a Reductive Sulfur-Fixing Method for Valuable Metal Recovery and Sulfur Conservation

Published in:
Metals

DOI:
10.3390/met9080911

Published: 01/08/2019

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:
Li, Y., Yang, S., Taskinen, P., Chen, Y., Tang, C., & Jokilaakso, A. (2019). Cleaner Recycling of Spent Lead-Acid Battery Paste and Co-Treatment of Pyrite Cinder via a Reductive Sulfur-Fixing Method for Valuable Metal Recovery and Sulfur Conservation. Metals, 9(8), [911]. https://doi.org/10.3390/met9080911

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Cleaner Recycling of Spent Lead-Acid Battery Paste and Co-Treatment of Pyrite Cinder via a Reductive Sulfur-Fixing Method for Valuable Metal Recovery and Sulfur Conservation

Yun Li 1,2, Shenghai Yang 1, Pekka Taskinen 2, Yongming Chen 1,* 1, Chaobo Tang 1,* and Ari Jokilaakso 1,2,*

1 School of Metallurgy and Environment, Central South University, Changsha 410083, China
2 Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, P.O. Box 16100, 02150 Espoo, Finland
* Correspondence: csuchenyongming@163.com (Y.C.); chaobotang@163.com (C.T.); ari.jokilaakso@aalto.fi (A.J.); Tel.: +86-731-8883-0470 (C.T.); +358-50-3138-885 (A.J.); Fax: +86-731-8883-0470 (Y.C.)

Received: 28 July 2019; Accepted: 16 August 2019; Published: 20 August 2019

Abstract: This study proposes a cleaner lead-acid battery (LAB) paste and pyrite cinder (PyC) recycling method without excessive generation of SO₂. PyCs were employed as sulfur-fixing reagents to conserve sulfur as condensed sulfides, which prevented SO₂ emissions. In this work, the phase transformation mechanisms in a PbSO₄-Na₂CO₃-Fe₃O₄-C reaction system were studied in detail. Furthermore, the co-treatment of spent LAB and PyCs was conducted to determine the optimal recycling conditions and to detect the influences of different processing parameters on lead recovery and sulfur fixation. In addition, a bench-scale experiment was carried out to confirm the feasibility and reliability of this novel process. The results reveal that the products were separated into three distinct layers: slag, ferrous matte, and crude lead. 98.3% of lead and 99% of silver in the feed materials were directly enriched in crude lead. Crude lead with purity of more than 98 wt.% (weight percent) was obtained by a one-step extraction. Lead contents in the produced matte and slag were below 2.7 wt.% and 0.6 wt.%, respectively. At the same time, 99.2% total sulfur was fixed and recovered.

Keywords: lead-acid battery recycling; pyrite cinder treatment; lead bullion; sulfide matte; SO₂ emissions; pilot plant

1. Introduction

Lead-acid batteries (LABs) are widely applied in automobiles and electric bicycles. Recently, advances in energy, transportation, and telecommunication industries have increasingly expanded its demand, and its scrap volume grows worldwide [1]. It has been estimated that the number of spent LABs would be multiplied annually based on the mean lifetime of 2–3 years and will continue to grow, especially in China and other emerging economies [2]. As a result, it has become the most significant secondary lead source worldwide [3]. About 80–85% of total secondary lead is recycled from lead paste [4]. Typically, a spent LAB consists of four main components: lead paste (30–40%), lead alloy grids (24–30%), polymeric materials (22–30%), and waste electrolytes (11–30%) [5,6]. Of these, lead paste is the most difficult to deal with [7].
Spent LABs are of great environmental concern [8,9] because of the toxicity of lead [10]. It will be a serious problem to environmental protection and human health if disposed and treated improperly [11]. In many countries, spent LAB is classified as a hazardous waste. In China, plants without a certificate for hazardous waste treatment are not allowed to handle or process spent LABs [10,12]. Currently, pyrometallurgy is the predominant methodology for LAB recycling worldwide [13]; spent lead paste is recovered as metallic lead through an energy-intensive decomposition process using traditional pyrometallurgical processes [14]. Reverberatory furnaces, shaft furnaces, electric furnaces, rotary furnaces [15], and bottom blowing methods [16] are usually selected to smelt lead-containing residues and wastes [15]. Although the traditional recycling technology of spent LABs through smelting is relatively mature, occasional and serious pollution is still possible [2], for example, in form of lead particulates, discharge of toxic and unstable sludge, slag, and wastewater [14]. Since 2009, there has been more than 10 major lead poisoning accidents recorded in China, and nearly 4000 children have been affected by these accidents [10].

Some emerging technologies [9,17,18], including electrowinning, solid phase electrolysis, biological technique, vacuum methods [19], and so on, are being developed and applied. However, in most methods, some problems still exist and need to be solved (e.g., sulfur footprint removal; lead-containing dust, industrial SO_2 emissions and pollution in pyrometallurgy [20,21]; tedious procedures; large amounts of generated unmanageable waste water; and high electricity consumption [22] in hydrometallurgy).

In addition, pyrite cinder (PyC), another hazardous waste, is produced in large quantities in industrial sulfuric acid manufacture. Only in China, the production of PyCs annually exceeds 12 million tons [23]. It often contains toxic metals, including Pb, Cd, As, and so on, as well as appreciable quantities of valuable metals such as Cu, Co, In, Au, and Ag [24]. The recycling or harmless treatment of PyCs is a huge challenge, even in developed countries. The recycling status of PyCs is not encouraging: the recycling rate in USA is about 80%–85% and about 70%–80% in Japan. China recycles only around 50% of PyCs, and large quantities of PyCs are simply landfilled or dumped without any treatment [23]. A limited amount of PyCs is recycled to produce cement, bricks, iron oxide pigments, or iron sponges [23,24]. This leads to serious consequences including occupation of considerable land resources, dust problems, and contamination of soil and ground water [24].

In view of environmental regulations, treatment costs, and limited availability of landfill/disposal sites, the search for new and cost-effective practices for the recycling of LABs and, in recent years, valorization of PyCs has become increasingly important [10]. In this article a novel, integrated resourcing treatment method of LABs and PyCs, a reductive sulfur-fixing recycling process [25,26], was proposed to recover valuable metals, recycle iron and sulfur values, as well as to co-treat hazardous materials. The novelties of this process are SO_2-free generation, sulfur fixation and conservation, a much shorter flowsheet, absence of harmful by-products, and a wide adaptability for different secondary materials. This work investigated the experimental feasibility and reliability of this novel process. The fundamental phase conversion mechanisms and reaction paths in the treatment were further examined.

2. Experimental Parameters

2.1. Materials

The materials employed in the reaction mechanism investigations included PbSO_4, Na_2CO_3, Fe_3O_4, and carbon powder. They were of analytical grade (≥99.9 wt.%) and purchased from Aladin Industrial Corporation, China. Nitrogen with a purity of 99% was applied as a protective gas. LAB paste, pyrite cinder, and metallurgical coke were adopted in the batch processing tests. The lead paste used was separated from scrap LABs and supplied by Yuguang Gold & Lead Co., Henan, China. The coke and sulfur-fixing agent, pyrite cinder, were supplied by Jiuquan Iron & Steel Co., Ltd., Gansu, China. Their chemical compositions were analyzed by inductively coupled plasma-atomic emission
spectrometry (ICP-AES, Perkin Elmer, Optima 3000, Norwalk, CT, USA). The assays are shown in Table 1. The concentration of the various metal oxides in LAB and PyC and phase compositions of lead in LAB paste were determined by EDTA (Ethylene Diamine Tetracetic Acid) titration. The contents of PbO, PbO₂, and metallic Pb components presented in Table 1 were determined by dissolving each individual component in turn into solution, followed by EDTA titration. Firstly, lead paste was added to 5% (mass fraction) acetum to dissolve the PbO component. Secondly, the residue was moved and further dissolved in HNO₃ solution (1 + 1 volume fraction) to separate metallic Pb. Then, the remaining residue was dissolved in the mixed solution of 1 + 1 HNO₃ and 1 + 40 H₂O₂ to separate PbO₂. Thus, the contents of PbO, PbO₂, and metallic Pb can be titrated in the corresponding solution by means of EDTA (0.05 mol/L) titration. The PbSO₄ component in lead paste was determined by sulfur concentrate. It suggests that the lead paste comprised 54.7 wt.% PbSO₄, 22.1 wt.% PbO₂, 8.5 wt.% Pb, and 8.5 wt.% PbO.

Table 1. Chemical composition of the corresponding materials (wt.%), * g/t.

| Materials | Pb | S  | Fe | SiO₂ | CaO | Na  | Mg  | Al  | Ba  | Sb |
|-----------|----|----|----|------|-----|-----|-----|-----|-----|----|
| Lead paste | 72.90 | 5.77 | 0.02 | 5.48 | 0.22 | 0.33 | 0.06 | 0.03 | 0.14 | 0.09 |
| PbSO₄    | PbO | PbO₂ | Pb  | -    | -   | -   | -   | -   | -   | -  |
| Coke     | Pb | S  | Fe | SiO₂ | CaO | Na  | MgO | Al₂O₃ | Cu | Ag* |
| Pyrite cinder | 0.02 | 1.31 | 58.23 | 9.68 | 1.02 | 0.01 | 0.19 | 2.06 | 0.05 | 324 |

| Coke | Industrial analysis (%) | Chemical composition of the ash (%) |
|------|-------------------------|-----------------------------------|
|      | Fixed Carbon | Volatile | Ash | Fe_total | SiO₂ | Al₂O₃ | CaO | MgO |
|      | 84.05 | 1.13 | 13.94 | 15.96 | 30.96 | 18.18 | 4.05 | 1.45 |

2.2. Apparatus

The equipment used in this investigation is shown in Figure 1. Equipment included a horizontal tube furnace equipped with a gas controller and temperature controller (SR3-8P-N-90-100Z, SHIMADEN Co., Ltd., Tokyo, Japan, accuracy ±1 °C) and two S-type thermocouples. Silicon carbide (Si-C) heating elements were used to heat the furnace. An alumina crucible was used to carry the reaction mixture. The solid products were quenched in liquid N₂. The tail gas was absorbed by a NaOH solution.
2.3. Procedure

When investigating the reaction mechanism, pure PbSO$_4$ was selected as the model compound because it is the major and most difficult component to deal with in lead paste. In order to reveal the reaction paths, the PbSO$_4$-Fe$_2$O$_3$-Na$_2$CO$_3$-C reaction mixture was synthesized using pure chemicals according to their potential reaction stoichiometry. Five grams of PbSO$_4$ was employed in each synthesized specimen. The specimens were pressed uniaxially under 15 MPa to obtain cylindrical samples 10 mm in diameter, loaded into the alumina crucible, and pushed into the constant temperature zone of the furnace at the desired temperature for 5, 10, 15, 20, or 30 min. The protective N$_2$ gas flow rate was fixed at 0.5 L/min. After the preset reaction time, the product was taken out rapidly and quenched in liquid nitrogen. The phase compositions were characterized by XRD (D/max 2550PC, Rigaku Co., Ltd., Tokyo, Japan) with Cu-Ka radiation. The XRD data were collected in the range of 2θ = 10°–80° with a 2θ step width of 1°. The recorded spectra were evaluated by comparison with entries from the PDF-2 database [27].

In the batch experiments of real lead paste, 200 g of lead paste was mixed evenly with a given amount of coke, pyrite cinder, Na$_2$CO$_3$, and other fluxes (CaO and SiO$_2$) for every test. The mixture was placed into an alumina crucible and positioned in the furnace. After the required treatment time, the crucible was rapidly quenched in liquid nitrogen and weighed. The crucible was broken to carefully separate and weigh crude lead, ferrous matte, and slag. Each sample was well prepared for ICP-AES analysis. The microstructures of matte and slag samples were characterized by a scanning electron microscope and energy diffraction spectrum (SEM-EDS, Carl Zeiss LEO 1450, Oberkochen, Germany; EDS, INCA Wave 8570, Oxford Instruments, Oxford, UK). The direct Pb recovery rate ($\eta$) and sulfur-fixing rate ($\gamma$) were calculated based on following Equations (1) and (2), respectively:

$$\eta = \frac{\text{Mass of Pb in the crude lead}}{\text{Mass of Pb in the initial feed materials}} \times 100\%;$$  

(1)

$$\gamma = \frac{\text{Mass of sulfur in the ferrous matte and slag}}{\text{Mass of sulfur in the initial feed materials}} \times 100\%.$$  

(2)

3. Results and Discussion

3.1. Phase Transformation Mechanisms

The XRD patterns of the PbSO$_4$-Na$_2$CO$_3$-Fe$_2$O$_3$-C reaction system are presented in Figure 2. It is observed from Figure 2a that exchange reactions between PbSO$_4$ and Na$_2$CO$_3$ occurred above 500 °C. At 650 °C, xPbO·PbSO$_4$ (x can be 1, 2, or 4), PbO, and Na$_4$CO$_3$SO$_4$ were detected. This indicates that the reactions between PbSO$_4$ and Na$_2$CO$_3$ were a multistage process. PbO was generated from PbSO$_4$ in the presence of Na$_2$CO$_3$ through the following sequence: PbSO$_4$→PbO-PbSO$_4$→2PbO-PbSO$_4$→4PbO-PbSO$_4$→PbO. A schematic of the reaction path is shown in

Figure 1. (a) Schematic of the experimental apparatus and (b) temperature profile of the furnace.

---

**Equations:**

1. \( \eta = \frac{\text{Mass of Pb in the crude lead}}{\text{Mass of Pb in the initial feed materials}} \times 100\%; \)
2. \( \gamma = \frac{\text{Mass of sulfur in the ferrous matte and slag}}{\text{Mass of sulfur in the initial feed materials}} \times 100\% . \)
Figure 3a. Thus, SO₃ in PbSO₄ transferred to Na₂SO₄. With increased temperature, PbS and metallic Pb emerged at 750 °C, and the main products after 30 min reaction were Pb, PbS, PbO, Fe₃O₄, and Na₂SO₄. It indicates that a part of PbSO₄ was reduced to PbS. At the same time, PbO was reduced to metallic Pb. When temperature rose to 850 °C, NaFeS₂ was generated after 30 min lead time. This suggests that iron oxide was involved in the sulfur-fixation reactions. Sulfur in PbS and Na₂SO₄ was transferred to NaFeS₂. Metallic Pb emerged and settled from the reaction mixture as a metal layer. When temperature increased to 1000 °C, intermediate products—sodium iron oxides, sodium lead oxides, and lead iron oxides—were detected, and as temperature rose from 1100 °C to 1200 °C, their generation grew. However, the main products were Pb, NaFeS₂, and FeS.

![XRD pattern of the PbSO₄-Na₂CO₃-Fe₃O₄-C mixture (molar ratio 3:3:1:18) at (a) different temperatures and (b) reaction times.](image-url)
The above results indicate that the presence of Na$_2$CO$_3$ and reductant is a critical factor to ensure sufficient sulfur and lead recovery. At low temperatures and weakly reductive atmospheres, as Figure 3a shows, PbSO$_4$ first reacted with Na$_2$CO$_3$ to convert to PbO and Na$_2$SO$_4$, which helped the decomposition of PbSO$_4$ and ensured that sulfur was conserved in the recycling system in the solid state (as Na$_2$SO$_4$) without generating and emitting SO$_2$ gas. As temperature increased, unconverted PbSO$_4$ was selectively reduced to PbS. Then, the sulfur-fixing agent, Fe$_3$O$_4$, reacted with PbS, as shown in Figure 3b. The sulfur in PbS was further immobilized and finally recycled as FeS and NaFeS$_2$.

The entire reaction path can be described as follows, where the Gibbs free energies $\Delta G^\circ_T$ of the reactions below are calculated by HSC 9.2.6 and its database [28] (unit of $\Delta G^\circ_T$ is kJ/mol, temperature $T$ is °C):

$$\text{PbSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{PbO} + \text{Na}_2\text{SO}_4 + \text{CO}_2(g); \Delta G^\circ_T = -0.149 T + 7.586; \quad (3)$$

$$\text{C} + \text{CO}_2(g) = \text{CO}_2(g); \Delta G^\circ_T = -0.173 T + 121.52; \quad (4)$$

$$\text{PbSO}_4 + 4\text{CO}(g) = \text{PbS} + 4\text{CO}_2(g); \Delta G^\circ_T = -0.681 T + 166.39; \quad (5)$$

$$3\text{PbS} + \text{Fe}_3\text{O}_4 + 4\text{CO}(g) = 3\text{Pb} + 3\text{FeS} + 4\text{CO}_2(g); \Delta G^\circ_T = -0.066 T - 24.284; \quad (6)$$

$$\text{PbS} + \text{Na}_2\text{CO}_3 + \text{CO}(g) = \text{Na}_2\text{S} + \text{Pb} + 2\text{CO}_2(g); \Delta G^\circ_T = -0.132 T + 128.00; \quad (7)$$

**Figure 3.** Schematic of (a) the multistage process between PbSO$_4$ and Na$_2$CO$_3$ and (b) lead extraction reactions between PbS and Fe$_3$O$_4$. 

Figure 2b suggests that Na$_2$CO$_3$ first reacted with PbSO$_4$ to convert it to PbO. At the same time, PbO can be reduced to metallic Pb at 850 °C. The unconverted PbSO$_4$ will also be reduced to PbS. After 5 min reaction, the products comprised Pb, PbS, Na$_2$SO$_4$, PbO, and Fe$_3$O$_4$. As reaction time extended, the diffraction intensity of metallic Pb increased steadily, and that of PbO decreased. Fe$_3$O$_4$ did not react with PbS within around the first 20 min but 30 min later when NaFeS$_2$ emerged.
\[
PbO + CO_{(g)} = Pb + CO_{2(g)}; \quad \Delta G^0_T = -0.013 \, T - 67.25,
\]
\[T \leq 900 \, ^\circ C; \quad \Delta G^0_T = 0.014 \, T - 90.546, \quad T \geq 900 \, ^\circ C;\]
\[Na_2SO_4 + 4CO_{(g)} = Na_2S + 4CO_{2(g)}; \quad \Delta G^0_T = 0.034 \, T - 127.88;\]
\[4Na_2SO_4 + Fe_2O_3 + 16CO_{(g)} = 2NaFeS_2 + 3Na_2O + 16CO_{2(g)}; \quad \Delta G^0_T = 0.207T - 126.14;\]
\[6Na_2SO_4 + Fe_2O_4 + 23.5CO_{(g)} = 3NaFeS_2 + 4.5Na_2O + 23.5CO_{2(g)}; \quad \Delta G^0_T = 0.339 \, T - 164.05;\]
\[2Na_2SO_4 + 2FeS + 7CO_{(g)} = 2NaFeS_2 + Na_2O + 7CO_{2(g)}; \quad \Delta G^0_T = 0.1884 \, T - 122.67.\]

Figure 4 illustrates the \(\Delta G^0_T\) versus \(T\), \(\log(pS_2)\) versus \(T\), and \(\log(pSO_2)\) versus \(T\) diagrams of the reaction system. The thermodynamic calculation results agreed well with the experimental reaction mechanism. \(\text{PbSO}_4 \rightarrow \text{PbO}\) and \(\text{PbSO}_4 \rightarrow \text{PbS}\) reactions tended to take place firstly at a low temperature. Then, lead was extracted from PbS and PbO with the help of \(\text{Fe}_3\text{O}_4\) [29] and \(\text{Na}_2\text{CO}_3\) [30]. Sulfur was conserved as \(\text{FeS}, \text{Na}_2\text{S}\), and \(\text{NaFeS}_2\).

Figure 4. (a) The \(\Delta G^0_T\) and \(T\) diagram, (b) \(\log(pS_2)\) and \(T\) equilibrium diagram, and (c) \(\log(pSO_2)\) and \(T\) equilibrium diagram in the boundary condition of \(\text{FeO-Fe}_3\text{O}_4\) equilibria (data from HSC 9.2.6 database).

The reaction systems in Figure 4b,c were defined by oxygen pressures based on the \(\text{FeO-Fe}_3\text{O}_4\) boundary conditions. Thus, the activity of elemental carbon, gaseous sulfur polymers, and \(CO_{(g)}\) can be calculated from the results obtained, and they will not violate the equilibria by any means. It was found from Figure 4b,c that the \(\text{Pb}, \text{Na}_2\text{S}_2\), and \(\text{Na}_2\text{SO}_4\) equilibrium domains formed before \(\text{FeS}\). It indicated that \(\text{Na}_2\text{CO}_3\) will first react with \(\text{PbSO}_4\) to extract metallic \(\text{Pb}\). The results coincide with previous experimental results. Additionally, the \(\text{Na}_2\text{O}/\text{Na}_2\text{SO}_4\) equilibrium generated the lowest \(\text{SO}_2\).
partial pressure (i.e., allows the smallest SO₂ losses to gas). Therefore, it is essential for sulfur (dioxide) emissions to have Na₂CO₃ in the raw materials.

3.2. Batch Experiments of End of Life (EoL) Lead Paste

3.2.1. Influence of Coke Addition

Lab-scale batch experiments using real EoL (end of life) lead battery paste were carried out to investigate the effect of major recycling parameters on direct lead recovery and sulfur fixation efficiency. The results of increasing coke addition are presented in Figure 5. It reveals that the direct Pb recovery and sulfur-fixation rates increased with increasing coke dosage and were stable after 12% coke addition, where 95.9% lead was recovered and enriched in crude lead, and 97.7% sulfur was recovered in the ferrous matte and slag. This indicates that the reductive atmosphere was a significant factor for lead recovery and sulfur fixation. As the results shown in Figure 2 indicate, lead extraction from PbSO₄, PbS, and PbO, as well as sulfur conversion from PbSO₄, PbS, and Na₂SO₄, should rely on carbothermal reduction. A suitable coke addition can notably improve lead recovery and sulfur fixation according to Equations (1) and (2), respectively.

![Figure 5. The effects of coke dosage on lead recovery and sulfur fixation. (W_{lead paste}:W_{Na₂CO₃}:W_{pyrite cinder} = 200:16:50 g, FeO/SiO₂ = 1.3, CaO/SiO₂ = 0.4, 1200 °C, 2 h).](image)

3.2.2. Influence of Na₂CO₃ Addition

The effects of Na₂CO₃ addition on direct Pb recovery and sulfur fixation are depicted in Figure 6. It illustrates that lead recovery and sulfur fixation rates gradually increased as Na₂CO₃ dosage increased from 0% to 4%, where 97.0% lead was recovered, and 99.2% sulfur was made immovable. Without Na₂CO₃ addition, PbSO₄ could be directly reduced to PbS, and it further was converted to PbO with the help of sulfur-fixing agent Fe₃O₄. As a result, metallic Pb was extracted and recovered from lead oxide. However, when the Na₂CO₃ addition exceeded 4%, direct Pb recovery and sulfur-fixing rates no longer increased and were maintained at around 96% and 98%, respectively. This means that the active Na₂CO₃ reached saturation. Excess Na₂CO₃ was unable to further increase the capacities of lead recovery and sulfur fixation.
3.2.3. Influence of Treatment Temperature

The influences of temperature on lead recovery and sulfur-fixing rates are presented in Figure 7. The results show that 1200 °C was the optimal recycling temperature to obtain a high lead and sulfur recovery, where 97.0% lead was recovered in crude lead. The sulfur fixation rate was maintained at around 98% when temperature increased from 1150 °C to 1350 °C. This indicates that the sulfur-fixation reactions had completed before 1150 °C. Excessive temperature was unbeneficial for lead enrichment because volatilization of lead will intensify at high temperatures. The above presented XRD results of the PbSO₄-Na₂CO₃-Fe₂O₃-C mixtures also indicate that the intermediate products, lead oxides, tended to combine with sodium oxide and iron oxides at high temperatures, which limited further reduction of lead oxide to metallic lead.

3.2.4. Influence of Treatment Time

The direct Pb recovery and sulfur-fixation rates at different treatment times are presented in Figure 8. It implies that 1.5 h was an acceptable recycling time for sulfur fixation, lead alloy settling, and enrichment, where more than 96.7% of lead and 99.5% of sulfur were recovered. A declining trend was observed when the treatment time exceeded 1.5 h because of the increasing volatilization of lead and sodium salt. The results in Figure 2b reveal that the lead extraction and sulfur fixing reactions could take place in minutes. However, an acceptable lead recovery and sulfur fixation rate relied on reactions between PbS and Fe₃O₄. Adequate completion of these reactions would take time.
3.3. Comprehensive Experiments and Characterization of Products

3.3.1. Comprehensive Experimental Results

Comprehensive bench-pilot experiments with 1500 g lead paste were conducted to detect the repeatability and reliability of this novel process. The above obtained optimal recycling conditions were used—$W_{\text{lead paste}}:W_{\text{Na}_2\text{CO}_3}:W_{\text{pyrite cinder}}:W_{\text{coke}} = 200:8:50:24$ g, FeO/SiO$_2 = 1.3$, CaO/SiO$_2 = 0.4$, 1200 °C.

3.3.2. SEM-EDS Characterization of Products

Physical macrograph and corresponding XRD patterns of recycling products. It is clear that the products were separated into three distinct layers: slag, ferrous matte, and crude lead bullion. Table 2 shows the chemical compositions of different products obtained.

![Physical macrograph and corresponding XRD patterns](image)

Figure 8. The effects of treatment time on lead recovery and sulfur fixation. ($W_{\text{lead paste}}:W_{\text{Na}_2\text{CO}_3}:W_{\text{pyrite cinder}}:W_{\text{coke}} = 200:8:50:24$ g, FeO/SiO$_2 = 1.3$, CaO/SiO$_2 = 0.4$, 1200 °C).

Figure 9. Physical macrograph (a) and corresponding XRD patterns (b) of the recycling products. ($W_{\text{lead paste}}:W_{\text{Na}_2\text{CO}_3}:W_{\text{pyrite cinder}}:W_{\text{coke}} = 1500:60:375:180$ g, FeO/SiO$_2 = 1.3$, CaO/SiO$_2 = 0.4$, 1200 °C, 1.5 h).
Table 2. Chemical compositions of recycling products in the comprehensive expansion experiments (wt. %), * g/t.

| No. | Product            | Chemical Compositions (wt. %) |  |  |  |  |  |
|-----|--------------------|-------------------------------|---|---|---|---|---|
|     |                    | Pb   | Fe   | S   | Na | Sb | Ag * | SiO₂ | CaO | Al₂O₃ |
| 1   | Crude lead         | 98.87 | 0.26 | 0.04 | -  | 0.075 | 136 | -   | -   | -   |
| 2   |                    | 98.02 | 0.38 | 0.07 | -  | 0.089 | 115 | -   | -   | -   |
|     | Average            | 98.45 | 0.32 | 0.06 | -  | 0.082 | 126 | -   | -   | -   |
| 1   | Ferrous matte      | 2.37  | 53.25 | 22.54 | 9.56 | -    | -   | -   | -   | -   |
| 2   |                    | 2.73  | 52.66 | 24.39 | 9.68 | -    | -   | -   | -   | -   |
|     | Average            | 2.55  | 53.09 | 23.47 | 9.62 | -    | -   | -   | -   | -   |
| 1   | Slag               | 0.39  | 22.96 | 3.24 | 9.79 | -    | 31.22 | 18.86 | 6.83 |
| 2   |                    | 0.59  | 24.31 | 3.19 | 9.88 | -    | 30.72 | 18.50 | 6.14 |
|     | Average            | 0.49  | 23.64 | 3.22 | 9.84 | -    | 30.97 | 18.68 | 6.49 |

The results show that 98.3% lead and 99% silver were directly enriched in crude lead in the pilot test. More than 98% purity crude lead was obtained by a one-step extraction. Lead contents in the matte and slag were 2.7% and 0.6%, respectively. At the same time, 99.2% of total sulfur was fixed and recovered in the treatment system (85.9% in ferrous matte and 13.3% in slag), which helped to prevent the generation and emission of SO₂. The main phases in the solidified matte were FeS, Fe₃O₄, and NaFeS₂. Some unreacted PbS and entrained gangue materials, such as Ca₃Al₂(SiO₄)₃, FeSiO₃, Ca₂(Al(AlSi)O₇), and CaSiO₃, were also detected. The matte can be sold directly or used for sulfuric acid manufacture and regenerate the sulfur-fixing agent. The slag comprised Ca₂(Al(AlSi)O₇), Fe₂SiO₄, Fe₃O₄, Na₂Si₂O₅, NaAlSiO₄, CaSiO₃, Ca₃Al₂(SiO₄)₃, and some entrained FeS. It is harmless and can be used as raw material for cement production after water-quenching and granulation.

3.3.2. SEM-EDS Characterization of Products

The recycling products obtained, ferrous matte and slag, were characterized by SEM-EDS techniques. The results are presented in Figures 10 and 11. Figure 10 illustrates that ferrous oxide FeO and few metallic Fe droplets were embedded in the ferrous sulfide and its FeS minerals. At the same time, iron spinel (magnetite) Fe₃O₄ was adjacent to FeS. Some metallic lead and lead oxide particles were embedded and entrained in FeS minerals. It helps to confirm that lead extraction from PbS was carried out by exchange reactions between iron oxide (Fe₃O₄ and FeO) and PbS.

The SEM-EDS results presented in Figure 11 show that magnetite Fe₃O₄ tended to combine with sodium silicate Na₂Si₃O₈. Carnegieite Na₂AlSiO₄ particles were found embedded in magnetite and fayalite. Mackinawite FeS was found to be mainly entrained on the interfaces between gehlenite Ca₂(Al(AlSi)O₇) and fayalite Fe₂SiO₄.
The recycling products obtained, ferrous matte and slag, were characterized by SEM-EDS. Figure 10 shows SEM-EDS results of the matte produced from conditions of \( W_{\text{lead paste}}:W_{\text{Na}_2\text{CO}_3}:W_{\text{pyrite cinder}}:W_{\text{coke}} = 1500:60:375:180 \text{ g}, \) \( \text{FeO/}\text{SiO}_2 = 1.3, \) \( \text{CaO/}\text{SiO}_2 = 0.4, \) \( 1200{\circ} \text{C}, \) and \( 1.5 \text{ h}. \)

Figure 11 shows SEM-EDS results of the slag produced from conditions of \( W_{\text{lead paste}}:W_{\text{Na}_2\text{CO}_3}:W_{\text{pyrite cinder}}:W_{\text{coke}} = 1500:60:375:180 \text{ g}, \) \( \text{FeO/}\text{SiO}_2 = 1.3, \) \( \text{CaO/}\text{SiO}_2 = 0.4, \) \( 1200{\circ} \text{C}, \) and \( 1.5 \text{ h}. \)
4. Conclusions

A cleaner recycling of lead from EoL LAB paste and co-treatment of PyCs by a reductive sulfur-fixing recycling technique was experimentally confirmed to be feasible. The optimal treatment conditions were determined as $W_{\text{lead paste}}:W_{\text{Na}_2\text{CO}_3}:W_{\text{pyrite cinder}}:W_{\text{coke}} = 100:4:25:12$ g, $\text{FeO}/\text{SiO}_2 = 1.3$, $\text{CaO}/\text{SiO}_2 = 0.4$, treatment temperature 1200 °C, and time 1.5 h. Under these conditions, 98.3% lead in the raw materials was directly enriched and recovered in crude lead, and 99.2% total sulfur was fixed and recovered to matte and slag. Crude lead of 98% purity was obtained in a one-step extraction. Lead contents in matte and slag were 2.7% and 0.6%, respectively.

The phase transformation mechanisms were clarified. PbSO$_4$ originally reacted at low temperatures with Na$_2$CO$_3$ to convert to PbO and Na$_2$SO$_4$, which avoided decomposition of PbSO$_4$ and ensured that sulfur was conserved in the recycling system in the solid state (Na$_2$SO$_4$) without generating and emitting SO$_2$ gas. As temperature increased, unconverted PbSO$_4$ was selectively reduced to PbS. Then, Fe$_3$O$_4$ reacted with PbS. The sulfur in PbS was further transferred and finally fixed as FeS and NaFeS$_2$. This new process provides a promising alternative recycling and treatment method for various secondary lead-containing materials and iron-bearing industrial wastes.

**Author Contributions:** Y.L. organized the research plan, performed the experiments, and wrote and revised the manuscript according to the comments from the co-authors. S.Y., Y.C., and C.T. were in charge of project administration and assisted with the supervising work; P.T. modified the thermodynamic section; A.J. and P.T. reviewed and checked the language of the manuscript.

**Funding:** This research was funded by Specialized Research Project of Guangdong Provincial Applied Science and Technology, China, grant number 2016B020242001; Hunan Provincial Science Fund for Distinguished Young Scholars, China, grant number 2018J1044; National Natural Science Foundation of China, China, grant number 51234009 and 51604105; and CMEco by Business Finland, Finland, grant number 2116781.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Tian, X.; Wu, Y.; Gong, Y.; Zuo, T. The lead-acid battery industry in China: outlook for production and recycling. *Waste Manage. Res.* 2015, 33, 986–994. [CrossRef] [PubMed]
2. Zhu, X.; He, X.; Yang, J.; Gao, L.; Liu, J.; Yang, D.; Sun, X.; Zhang, W.; Wang, Q.; Kumar, R.V. Leaching of spent lead acid battery paste components by sodium citrate and acetic acid. *J. Hazard. Mater.* 2013, 250, 387–396. [CrossRef] [PubMed]
3. Zhang, Q. The current status on the recycling of lead-acid batteries in China. *Int. J. Electrochem Sci.* 2013, 8, 6457–6466.
4. Huggins, R.A. *Lead-Acid Batteries*; Springer: Boston, MA, USA, 2016; pp. 237–250.
5. Li, Y.; Chen, Y.; Tang, C.; Yang, S.; Klemettinen, L.; Rämä, M.; Wan, X.; Jokilaakso, A. A New Pyrometallurgical Recycling Technique for Lead Battery Paste without SO$_2$ Generation—A Thermodynamical and Experimental Investigation. *Extraction 2018* 2018, 1109–1120. [CrossRef]
6. Li, Y.; Tang, C.; Chen, Y.; Yang, S.; Guo, L.; He, J.; Tang, M. One-Step Extraction of Lead from Spent Lead-Acid Battery Paste via Reductive Sulfur-Fixing Smelting: Thermodynamic Analysis. In *8th International Symposium on High-Temperature Metallurgical Processing*; Springer: Cham, Switzerland, 2017; pp. 767–777. [CrossRef]
7. Lin, D.; Qiu, K. Recycling of waste lead storage battery by vacuum methods. *Waste Manage.* 2011, 31, 1547–1552. [CrossRef] [PubMed]
8. Van der Kuijp, T.J.; Huang, L.; Cherry, C.R. Health hazards of China’s lead-acid battery industry: A review of its market drivers, production processes, and health impacts. *Environ. Health* 2013, 12, 61. [CrossRef] [PubMed]
9. Tian, X.; Wu, Y.; Hou, P.; Liang, S.; Qu, S.; Xu, M.; Zuo, T. Environmental impact and economic assessment of secondary lead production: Comparison of main spent lead-acid battery recycling processes in China. *J. Clean. Prod.* 2017, 144, 142–148. [CrossRef]
10. Sun, Z.; Cao, H.; Zhang, X.; Lin, X.; Zheng, W.; Cao, G.; Sun, Y.; Zhang, Y. Spent lead-acid battery recycling in China–A review and sustainable analyses on mass flow of lead. *Waste Manage.* 2017, 64, 190–201. [CrossRef]
11. Liu, T.; Qiu, K. Removing antimony from waste lead storage batteries alloy by vacuum displacement reaction technology. *J. Hazard. Mater.* **2018**, *347*, 334–340. [CrossRef]

12. Ma, Y.; Qiu, K. Recovery of lead from lead paste in spent lead acid battery by hydrometallurgical desulfurization and vacuum thermal reduction. *Waste Manage.* **2015**, *40*, 151–156. [CrossRef]

13. Kreusch, M.A.; Ponte, M.J.J.S.; Ponte, H.A.; Kaminari, N.M.S.; Marino, C.E.B.; Myymrin, V. Technological improvements in automotive battery recycling. *Resour. Conserv. Recy.* **2007**, *52*, 368–380. [CrossRef]

14. Lassin, A.; Piantone, P.; Burnol, A.; Bodénan, F.; Chateau, L.; Lerouge, C.; Crouzet, C.; Guyonnet, D.; Bailly, L. Reactivity of waste generated during lead recycling: An integrated study. *J. Hazard. Mater.* **2007**, *139*, 430. [CrossRef] [PubMed]

15. Queneau, P.B.; Leiby, R.; Robinson, R. Recycling lead and zinc in the United States. *World of Metallurgy-ERZMETALL* **2015**, *68*, 149.

16. Li, W.F.; Jiang, L.H.; Zhan, J.; Zhang, C.F.; Li, G.; Hwang, J.Y. Thermodynamics Analysis and Industrial Trials of Bottom-Blowing Smelting for Processing Lead Sulfate-Containing Materials. In *6th International Symposium on High-Temperature Metallurgical Processing*; Springer: Cham, Switzerland, 2015; pp. 507–514.

17. Zhang, X.; Li, L.; Fan, E.; Xue, Q.; Bian, Y.; Wu, F.; Chen, R. Toward sustainable and systematic recycling of spent rechargeable batteries. *Chem. Soc. Rev.* **2018**, *47*, 7239–7302. [CrossRef] [PubMed]

18. Dutta, T.; Kim, K.H.; Deep, A.; Szulêjko, J.E.; Vellingiri, K.; Kumar, S.; Kwon, E.E.; Yun, S.T. Recovery of nanomaterials from battery and electronic wastes: A new paradigm of environmental waste management. *Renew. Sustain. Energ. Rev.* **2018**, *82*, 3694–3704. [CrossRef]

19. Liu, K.; Yang, J.; Liang, S.; Hou, H.; Chen, Y.; Wang, J.; Liu, B.; Xiao, K.; Hu, J.; Wang, J. An Emission-Free Vacuum Chlorinating Process for Simultaneous Sulfur Fixation and Lead Recovery from Spent Lead-Acid Batteries. *Environ. Sci. Technol.* **2018**, *52*, 2235–2241. [CrossRef] [PubMed]

20. Wei, J.; Guo, X.; Marinova, D.; Fan, J. Industrial SO₂ pollution and agricultural losses in China: evidence from heavy air polluters. *J. Clean. Prod.* **2014**, *64*, 404–413. [CrossRef]

21. Mohanty, C.; Adapala, S.; Meikap, B. Removal of hazardous gaseous pollutants from industrial flue gases by a novel multi-stage fluidized bed desulfurizer. *J. Hazard. Mater.* **2009**, *165*, 427–434. [CrossRef] [PubMed]

22. Zhang, W.; Yang, J.; Wu, X.; Hu, Y.; Yu, W.; Wang, J.; Dong, J.; Li, M.; Liang, S.; Hu, J. A critical review on secondary lead recycling technology and its prospect. *Renew. Sustain. Energ. Rev.* **2016**, *61*, 108–122. [CrossRef]

23. Zhang, J.; Yan, Y.; Hu, Z.; Fan, X.; Zheng, Y. Utilization of low-grade pyrite cinder for synthesis of microwave heating ceramics and their microwave deicing performance in dense-graded asphalt mixtures. *J. Clean. Prod.* **2018**, *170*, 486–495. [CrossRef]

24. Alp, I.; Deveci, H.; Yazıcı, E.; Türk, T.; Sümüng, Y. Potential use of pyrite cinders as raw material in cement production: Results of industrial scale trial operations. *J. Hazard. Mater.* **2009**, *166*, 144–149. [CrossRef] [PubMed]

25. Hu, Y.; Tang, C.; Tang, M.; Chen, Y.; Yang, J.; Yang, S.; He, J. Reductive smelting of spent lead-acid battery colloid slag in molten salt of sodium at low temperature. *Chin. Nonferr. Metall.* **2014**, *24*, 75–79.

26. Ye, L.; Tang, C.; Chen, Y.; Yang, S.; Yang, J.; Zhang, W. One-step extraction of antimony from low-grade stibnite in Sodium Carbonate–Sodium Chloride binary molten salt. *J. Clean. Prod.* **2015**, *93*, 134–139. [CrossRef]

27. Toby, B. CMPR-a powder diffraction toolkit. *J. Appl. Crystallogr.* **2005**, *38*, 1040–1041. [CrossRef]

28. Roine, A. Outotec HSC Chemistry. Available online: www.hsc-chemistry.com (accessed on 19 August 2019).

29. Li, Y.; Yang, S.; Taskinen, P.; He, J.; Liao, F.; Zhu, R.; Chen, Y.; Tang, C.; Wang, Y.; Jokilaakso, A. Novel recycling process for lead-acid battery paste without SO₂ generation-Reaction mechanism and industrial pilot campaign. *J. Clean. Prod.* **2017**, *217*, 162–171. [CrossRef]

30. Li, Y.; Yang, S.; Taskinen, P.; He, J.; Chen, Y.; Tang, C.; Wang, Y.; Jokilaakso, A. Spent Lead-Acid Battery Recycling via Reductive Sulfur-Fixing Smelting and Its Reaction Mechanism in the PbSO₄-Fe₂O₃-Na₂CO₃-C System. *JOM* **2019**, *71*, 1–12. [CrossRef]

© 2019 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/).