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Recycling of spent lead-acid battery for lead extraction with sulfur conservation

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ABSTRACT

This study proposed a cleaner pyrometallurgical lead-acid battery (LAB) recycling method for lead extraction and sulfur conservation without excessive amount of SO₂ generation. Reducing atmosphere was introduced to the lead paste recycling system to selectively reduce PbSO₄ to PbS. At the same time, PbO and PbO₂ components contained in the lead paste was also reduced to metallic Pb. Then the intermediate PbS further reacted with sulfur-fixing agent, typically Fe₃O₄, to generate PbO and FeS. Sulfur was transformed from PbSO₄ to PbS and conserved as FeS finally. Thus SO₂ emissions and pollution were significantly eliminated. This work investigated the thermodynamic and experimental feasibility and phase conversion mechanism of this method proposed, the detailed lead extraction and sulfur fixing mechanisms were clarified, and the phase transformation and microstructural evolution processes were characterized. Additionally, bench experimental of industrial, end-of-life LAB paste was conducted to detect the lead recovery and sulfur fixation efficiency.

INTRODUCTION

Advances in the automobile, chemical, energy, transportation, and telecommunication industries are increasingly expanding both the demand for lead-acid battery (LAB) and also its scrap volume growth worldwide ¹. The reported amounts of scrap LAB annually in China total more than 2.6 million metric tons ¹⁻³, around 1.79 Mt in the Americas ⁴, and approximately 1.5 Mt in Europe ^{1,2}. LABs are a solid waste and classified as hazardous materials in many countries. Their disposal has become a significant environmental concern ⁵. However, considering the shortage of primary lead ores, increasing interest is being shown in recycling lead from scrap LABs. Typically, an end-of-life LAB consists of four main components: waste electrolyte (11~30%), polymeric materials (22~30%), lead alloy grids (24~30%), and lead paste (30~40%). Of these, lead paste is the most difficult to recycle ⁶. It is a mixture of 50~60% PbSO₄, 15~35% PbO₂, 5~10% PbO/Pb(OH)₂, 2~5% metallic Pb, and a small amount of impurities, such as iron, antimony, tin, and barium ⁶.

Lead produced in recycling increasingly dominates the world's lead market ⁷. More than 95% of the LABs used in the US and Europe are recycled ^{8,9}. In China, the production of secondary lead in 2018 was approximately 2.15 Mt, accounting for only 46% of total lead production. The recycling degree is alarmingly low. Currently, LAB paste recycling processes contain pre-desulfurization followed by pyrometallurgical process, pure hydrometallurgy, combined-smelting with primary lead concentrate and direct smelting without pre-desulfurization. Among them, pyrometallurgy is presently the predominant route worldwide for recycling LAB ⁸, in which the high-temperature treatment of spent LABs in a blast, electric, reverberatory, or rotary furnace without pre-desulfurization is employed ^{10, 11}. In the hydrometallurgical process ^{4,12}, a pre-desulfurization step ¹³ is necessary. Na₂CO₃, NaOH, K₂CO₃ solutions or citric acid and citrate salts are usually adopted as desulfurization reagents. The desulfurized lead paste usually is further processed via pyrometallurgical route. But some pure hydrometallurgical routes for the recycling of LABs are also combined with leaching and electrowinning ¹⁰. Additionally, some emerging lead paste recycling routes are developed, such as preparing of PbO, PbS, PbCO₃, PbCl₂ and PbSO₄ (nano-) powders ¹⁴. However, the treatment of spent LABs always involves a potential health and environmental risk ^{15,16}, and the current LAB recycling techniques are multi-step recycling techniques, and always bonded with tedious procedures; SO₂ emissions and pollution; large amounts of generated unmanageable waste water; and high electricity consumption. Therefore, the lead recycling industry is keen to seek novel technologies to treat secondary lead-containing materials economically and efficiently, as well as to reduce

SO₂ emissions and lead-involved pollutions ^{17,18}. This includes the storage of lead residues, and emissions of lead-containing particle dusts ^{8,18}.

In this study, an environment-friendly lead-acid battery paste recycling method is proposed ^{19,20}, as Figure 1(a) shows. The novelties of this process were co-treatment of industrial iron-containing by-products, sulfur fixation and conservation, a much shorter flowsheet, and wide adaptability for secondary materials. In this process, a reducing atmosphere was introduced to a blast furnace to directly reduce PbSO₄, PbO and PbO₂ components in the lead paste. Lead in the PbSO₄ was extracted with the help of sulfur-fixing agent, typically Fe₂O₃-containing materials. Lead oxides (PbO and PbO₂) can be directly reduced to metallic Pb and thus recycled. Sulfur was finally converted and recycled as sulfide matte instead of generating sulfur-containing gaseous products. The emission and pollution of SO₂ during this process can be significantly eliminated. Additionally, various lead-containing secondary materials, such as lead ash and lead slag generated in Pb/Zn smelting, lead anode slime, and lead sludge produced in the electrolytic refining, can be recycled in this process. At the same time, iron-containing by-products, including jarosite residue, pyrite cinder, zinc leaching residue in rotary kiln and so on, generated in metallurgical and chemical industry can be employed as sulfur-fixing agent in this process and recycled thus ¹¹.

This work examined PbSO₄ reaction behavior in the reducing atmosphere, and further investigated the detailed lead extraction and sulfur-fixing mechanisms in the intermediate products PbS-Fe₃O₄-C reaction system, thermodynamically and experimentally. The phase transformations and microstructural evolution processes were characterized with the help of XRD and SEM-EDS analyses, and the lead extraction and sulfur fixing reaction mechanisms were clarified. In addition, batch experimental of the real LAB paste was conducted to verify the feasibility and reliability of the proposed process. At the same time, the products obtained were characterized.

Figure 1. Cont.

Fig.1. (a) The proposed reductive sulfur-fixing smelting process for lead- and iron-containing wastes recycling; (b) Schematic of the experimental apparatus and temperature profile of the furnace employed.

EXPERIMENTAL MATERIALS AND METHODS

PbSO₄ was selected as the model compound in the reaction mechanism investigation, since it is the major as well as the most difficult component to deal with in spent lead paste. Analytical purity materials employed in this study, including PbSO₄, PbS, Fe₂O₃, Fe₃O₄, CaO, SiO₂ and carbon powder, were obtained from Aladdin Industrial Corporation (China). The LAB paste, Fe₂O₃, coke and pure SiO₂ and CaO were adopted in the batch processing tests. The LAB paste employed was separated from scrap LABs and supplied by Yuguang Gold & Lead Co., Henan, China. Fe₂O₃ was employed as sulfur-fixing agent. The coke was used as reductant and 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, USA). The assays are shown in Table 1.

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

Materials	Pb	S	Fe	SiO ₂	CaO	Na	Mg	Al	Ba	Sb
	72.90	5.77	0.02	5.48	0.22	0.33	0.06	0.03	0.14	0.09
Lead paste	PbSO ₄	PbO	PbO ₂	Pb						
	54.68	8.49	22.05	8.53						
Industrial analysis (%)					Chemical composition of the ash (%)					
Coke	Fixed Carbon		Volatile	Ash	Fe _{total}	SiO ₂	Al ₂ O ₃	CaO	MgO	
	84.05		1.13	13.94	15.96	30.96	18.18	4.05	1.45	

The reaction process of the lead paste recycling system was firstly simulated by HSC vs. 9.2.6 thermodynamic modeling software and its database. Based on the modeling results, 5 g PbSO₄ or PbS were employed as a model compound to synthesize PbSO₄-C reaction system and intermediate products PbS-Fe₃O₄-C reaction system according to their potential reaction stoichiometry. The detailed reaction paths took place in each raw material component were investigated at different reaction temperatures and time. The specimens were mixed carefully and pressed uniaxially under 15 MPa into cylindrical samples of 10 mm diameter. Each specimen was loaded in an alumina crucible, and pushed into the constant temperature zone of a horizontal tube furnace, shown in Figure 1(b). The argon gas with a purity of 99.9 vol% pure was used as protective gas, and the gas flow was fixed at 0.1 L/min during the reaction mechanism

investigations. After the required reaction time, the sample was taken out rapidly from the furnace and quenched in liquid nitrogen. The phase compositions of synthesis $\text{PbSO}_4\text{-C}$ and $\text{PbS-Fe}_3\text{O}_4\text{-C}$ samples were characterized by XRD (D/max 2550PC, Rigaku Co., Ltd; Tokyo, Japan) with Cu-K α radiation. The XRD data were collected in the range of $2\theta=10\text{--}80^\circ$ with a 2θ step width of 1° . The recorded spectra were evaluated by comparison with entries from the PDF-2 database²¹. At the same time, the selected samples were polished, carbon-coated and subjected to Scanning electron microscope and energy dispersive spectroscopy (SEM-EDS, Carl Zeiss LEO 1450, Oberkochen, Germany; EDS, INCA Wave 8570, Oxford Instruments, Oxford, UK) analysis to determine the phase compositions and microstructures.

In the batch experimental of real lead paste, 200 g of lead paste was mixed evenly with coke, Fe_2O_3 and other fluxes (CaO and SiO_2) for every test. The mixture was placed into the hot zone of the tube furnace to smelt for a preset treatment time. After that, the crucible was rapidly quenched in liquid nitrogen and weighed. Then the crucible was broken to carefully separate and weigh the smelting produces, crude lead, ferrous matte and slag. Each sample was well prepared for ICP-AES analysis. The direct Pb recovery rate (η) and sulfur-fixing rate (γ) were calculated based on following equations (1) and (2), respectively:

$$\eta = \frac{\text{Mass of Pb in the crude lead}}{\text{Mass of Pb in the initial feed materials}} \times 100\% \quad (1)$$

$$\gamma = \frac{\text{Mass of sulfur in the ferrous matte and slag}}{\text{Mass of sulfur in the initial feed materials}} \times 100\% \quad (2)$$

THERMODYNAMIC CALCULATIONS

PbSO_4 can be reduced to PbS at relative high temperature^{22, 23}. PbS will probably continually react with sulfur fixing agent to transform sulfur. Lead oxides will also be reduced to metallic and thus be recovered. The entire reaction path can be described as following, where the Gibbs free energies ΔG_T^θ of the reactions below were calculated by HSC 9.2.6 and its database²⁴ (unit of ΔG_T^θ is kJ/mol , temperature T is $^\circ\text{C}$):

Fig.2. (a) ΔG_T^θ versus T diagram and (b) a reductive sulfur-fixing equilibrium diagram in presented lead paste recycling process (data from the HSC 9.2.6 database).

Figure 2 illustrates the ΔG_T^θ vs. T and the $\text{Log}(P_{\text{CO}}/P_{\text{CO}_2})$ vs. T diagrams of the corresponding reactions. Figure 2(a) indicates that extraction of metallic lead was thermodynamically favorable in a temperature range of 700~1200°C, in the presence of Fe_2O_3 and a reductant. Increasing the temperature will promote reactions. The reductive equilibrium diagram presented in Figure 2(b) further illustrates that PbSO_4 was easily reduced to PbS in weakly reducing conditions. In the same domain, Fe_2O_3 will also be reduced to Fe_3O_4 . The technical difficulty of the process associated with implementation mainly lie in the controlling of reducing atmosphere. As $P_{\text{CO}}/P_{\text{CO}_2}$ was increased, Pb extraction reactions took place between PbS and Fe_3O_4 ²². Metallic Pb and FeS generated. Sulfur will transfer from PbS to FeS and finally become fixed as sulfide matte. All main components in the lead paste, including PbSO_4 , PbO , and PbO_2 , can be reduced and further recycled as metallic Pb.

RESULTS AND DISCUSSION

Reaction mechanisms of PbSO_4 in the reductive atmosphere

The phase transformation mechanisms of PbSO_4 in the presence of carbon at different reaction temperatures and times are presented in Figure 3(a)-(b). Figure 3(a) illustrates that in 900 °C PbSO_4 can selectively be reduced to PbS within 5 min reaction time. A limited amount of by-products appeared, e.g., $\text{PbO} \cdot \text{PbSO}_4$ and $2\text{PbO} \cdot \text{PbSO}_4$. As reaction time extended, metallic Pb generated and its diffraction peaks intensified gradually. This indicates that the lead oxide in the $x\text{PbO} \cdot \text{PbSO}_4$ ($x=1$ and 2) was reduced to metallic Pb. After 30 min reaction at 900 °C, the final products were PbS and a small fraction of metallic Pb. Figure 3(b) shows the PbSO_4 phase evolution paths at different temperatures. It was observed that at 650 °C, PbSO_4 was reduced to PbS in the first 30 min reaction time. As temperature increased, a small amount of $\text{PbO} \cdot \text{PbSO}_4$ and $2\text{PbO} \cdot \text{PbSO}_4$ were also detected. Metallic Pb generated at 850 °C after 30 min reaction. Temperature continually increased to 1000 °C, the diffraction peaks of PbS and Pb increased, PbS was the main final product and it will be stable in the reductive atmosphere.

Fig. 3. XRD patterns of (a) the PbSO₄-C mixture (molar ratio 1:6) after different reaction times and (b) at different temperatures; (c) the PbS-Fe₃O₄-C (molar ratio 3:1:16) mixture after different reaction times and (d) at different temperatures.

The above investigations imply that PbSO₄ is able to be selectively reduced PbS by reductant. Sulfur in the PbSO₄ will be conserved as PbS. At the same time, the intermediate product lead oxide can be reduced to metallic Pb. Therefore, lead paste, as its main components are PbSO₄, PbO₂, PbO and Pb, can be transformed and recycled to PbS and metallic Pb without excessive SO₂/SO₃ generation and emissions in the presence of a reductant. However, further extraction of lead from PbS was needed to reach an acceptable lead paste recycling rate.

Reaction mechanisms in the PbS-Fe₃O₄-C system

The thermodynamic calculation results presented in Figure 2 indicate that PbS and Fe₃O₄ can react and generate metallic Pb and FeS. Fe₃O₄, reduced from Fe₂O₃, was able to help extract lead from PbS at reductive atmosphere, and at the same time, recycle and conserve sulfur from PbS as FeS. Figure 3(c)-(d) presents the XRD patterns of the experimental reaction products in the PbS-Fe₃O₄-C reaction system. Figure 3(c) shows that at 950 °C, exchange reactions took place gradually between PbS and Fe₃O₄. Thus PbO and FeS appeared. Metallic Pb was also reduced from PbO. The phase transformation mechanisms in PbS-Fe₃O₄-C system at different temperatures are shown in Figure 3(d). It was observed that at low temperature, a small fraction of PbS will be oxidized to PbSO₄ if the atmosphere was not reducing enough. As temperature increased, FeS and metallic Pb appeared. This implies that lead extraction reactions and sulfur conservation reactions occurred between PbS and Fe₃O₄ at reducing atmosphere. Lead was extracted from PbS with the help of Fe₃O₄. Reductive atmosphere and reaction temperature are the critical factor affecting the lead extraction and sulfur fixation.

Microstructural phase evolution mechanisms

The SEM-EDS micrographs of products generated in the PbS-Fe₃O₄-C reaction system are illustrated in Figure 4. The results show that some Pb particles were surrounded by PbS, and metallic Pb particle usually contained unreduced PbO. This indicates that the metallic Pb was extracted through the sequence of $\text{PbS} \xrightarrow{\text{Fe}_3\text{O}_4} \text{PbO} \xrightarrow{\text{CO}/\text{CO}_2} \text{Pb}$. At the same time, some other metallic Pb particles were also founded to be surrounded by FeS. This implies that sulfur in the PbS was transformed to FeS. Therefore, lead paste recycling can be conducted by a pyrometallurgical carbon thermal reduction process with the help of iron oxide to extract metallic lead and to conserve sulfur as well.

Fig. 4. SEM micrographs of products in the PbS-Fe₃O₄-C (molar ratio 3:1:16) mixture at 950 °C and 1000 °C after 10~30 min reaction time

Iron-containing wastes or secondary materials, such as hematite, jarosite residue and pyrite cinder etc., can be selected as sulfur-fixing agent to conserve sulfur during the lead paste recycling process²³. The recycling and extraction mechanisms of lead paste through reductive sulfur-fixing smelting process are illustrated in Figure 5. At relatively high temperature, PbSO₄ in the lead paste will selectively be reduced to PbS by reductant. At the same time, Fe₂O₃ was also gradually reduced to Fe₃O₄. Then the exchange reactions happened between PbS and Fe₃O₄. PbS was converted to intermediate PbO and sulfur was transformed and fixed as FeS. The intermediate PbO and oxides (PbO and PbO₂) in the lead paste were continually reduced to metallic lead. As a result, lead was extracted and recycled from lead paste through $\text{PbSO}_4 \xrightarrow{\text{CO/CO}_2} \text{PbS} \xrightarrow{\text{Fe}_3\text{O}_4} \text{PbO} \xrightarrow{\text{CO/CO}_2} \text{Pb}$. Additionally, sulfur contained in the lead paste was simultaneously conversed and recovered as marketable FeS product.

Fig. 5. Schematic of lead paste recycling mechanisms through reductive sulfur-fixing smelting process.

Therefore, lead extraction and recycling from lead paste can be realized through a pyrometallurgical route and the stages followed below:

Experimental verification of lead extraction from lead paste

The reaction mechanism investigations proved that lead can be extracted from PbSO_4 and lead oxides included PbO and PbO_2 at reducing atmosphere with sulfur conservation. The real LAB paste was employed to investigate experimental reliability of the process proposed. Fe_2O_3 and coke were used as sulfur-fixing agent and reductant, respectively. CaO and SiO_2 were employed to form slag.

Figure 6 presents the bench experimental results with a scale of 200 g lead paste in each test. It was found from Figure 6(a)–(b) that the lead recovery and sulfur-fixing rate increased gradually along with the coke and Fe_2O_3 addition. An adequate coke and Fe_2O_3 addition is necessary to obtain an acceptable lead recovery and sulfur fixation. When coke addition was less than 15 % or Fe_2O_3 addition was less than 18 %, the reaction $\text{PbS} + \text{Fe}_3\text{O}_4 \xrightarrow{\text{C/CO}} \text{PbO} + 3\text{FeS}$ cannot take place adequately, the formation of crude lead and matte was limited and insufficient after 2 h smelting and settling times. The reductive atmosphere is the critical parameter to guarantee an adequate formation volume of matte and exchange and reduction of lead paste. Coke and Fe_2O_3 addition exceeded 15% and 18%, respectively, more than 92% of the lead can be recovered to crude lead and 97% of the sulfur can be fixed in the ferrous matte and slag. The influence of treatment temperature and time on the lead recovery and sulfur-fixing rate are illustrated in Figure 8(c)–(d). The results indicate that within 2 h smelting lead recovery rose from 86.4% to 93.3%, and sulfur fixation from 95.2% to 98.9% when temperature increased from 1150 °C to 1250 °C. 1250 °C was the optimal recycling temperature to obtain a high lead and sulfur recovery. Furthermore, at 1250 °C, as treatment time extended from 1 h to 3 h, direct lead recovery increased steadily from 83.1% to 94.9%, while, the sulfur-fixing rate remained constant at around 98%. A declining trend of lead recovery was observed when the treatment time exceeded 3 h because of the increasing volatilization of lead. Therefore, 3 h was an acceptable recycling time for sulfur fixation, lead alloy settling and enrichment.

Fig. 6. The bench-scale experimental results of lead paste using the proposed reductive sulfur-fixing smelting process;

- (a) $W_{\text{lead paste}} : W_{\text{Fe}_2\text{O}_3} : W_{\text{SiO}_2} : W_{\text{CaO}} = 200 : 40 : 7 : 6 \text{ g}$, 1200°C, 2 h;
- (b) $W_{\text{lead paste}} : W_{\text{coke}} : W_{\text{SiO}_2} : W_{\text{CaO}} = 200 : 30 : 7 : 6 \text{ g}$, 1200°C, 2 h;
- (c) $W_{\text{lead paste}} : W_{\text{Fe}_2\text{O}_3} : W_{\text{coke}} : W_{\text{SiO}_2} : W_{\text{CaO}} = 200 : 36 : 30 : 7 : 6 \text{ g}$, 2 h;
- (d) $W_{\text{lead paste}} : W_{\text{Fe}_2\text{O}_3} : W_{\text{coke}} : W_{\text{SiO}_2} : W_{\text{CaO}} = 200 : 36 : 30 : 7 : 6 \text{ g}$, 1250°C;

Two comprehensive bench-scale experiments were conducted under the obtained optimal conditions of $W_{\text{lead paste}} : W_{\text{Fe}_2\text{O}_3} : W_{\text{coke}} : W_{\text{SiO}_2} : W_{\text{CaO}} = 400 : 72 : 60 : 14 : 12 \text{ g}$, at 1250°C and 3 h smelting time. The experimental results validate the thermodynamic calculation and reaction mechanism investigation results. Three products, crude lead bullion, matte, and slag, were simultaneously obtained and visibly separated as three distinct layers. Lead in the initial lead paste was extracted and enriched in lead bullion. Sulfur-fixing product formed a sulfide matte. The compact slag floated on the surface of the condensed ferrous matte, and crude lead settled at the bottom due to density differences. Thus the sulfur, not only lead, in the lead paste was also immobilized and conserved as a marketable condensed sulfide matte. Table II shows the chemical compositions of different products obtained in the comprehensive bench-scale experiments. The results indicate that the purity of crude lead bullion obtained reached 98.8%, and lead concentrations in the matte and slag were below 4.3% and 1.1%, respectively. Calculated according to the equations (1)~(2), it shows that direct recovery of lead, i.e. the yields without subsequent slag cleaning and matte processing, reaches more than 93%, and the sulfur-fixing rate is generally higher than 98.7%. Therefore, this novel reductive sulfur-fixing smelting process can significantly inhibit the generation of SO_2 and largely decrease the SO_2 emissions.

Table II. Chemical compositions of products obtained in comprehensive bench-scale experiments under a condition of $W_{\text{lead paste}} : W_{\text{Fe}_2\text{O}_3} : W_{\text{coke}} : W_{\text{SiO}_2} : W_{\text{CaO}} = 400 : 72 : 60 : 14 : 12 \text{ g}$, at 1250°C and 3 h.

No.	Product	Chemical compositions (wt.%)						
		Pb	Fe	S	Sb	Ba	SiO ₂	CaO
1	Crude lead	99.11	0.089	0.05	0.064	0.001	--	--
2		98.48	0.12	0.10	0.085	0.001	--	--
Average		98.80	0.105	0.075	0.075	0.001	--	--
1	Ferrous matte	3.21	57.65	24.78	--	0.062	--	--
2		4.23	56.32	25.37	--	0.078	--	--
Average		3.72	56.99	25.08	--	0.07	--	--
1	Slag	0.78	20.72	5.13	--	0.87	21.03	9.84

2	1.09	22.49	4.28	--	0.93	23.67	11.62
Average	0.94	21.61	4.71	--	0.90	22.35	10.73

The feasibility and reliability of the proposed reductive sulfur-fixing smelting process for lead recovery and sulfur conservation from scrap LAB paste were confirmed. Fe_2O_3 -containing materials, such as hematite, pyrite cinder²⁵ and jarosite residue, can be used as sulfur-fixing agent to recycle LAB paste in a reducing atmosphere. The reductive sulfur-fixing smelting process is also a potentially effective technology for both recovering metals and protecting the environment. In addition to LAB paste recycling, this new process provides a promising alternative recycling and treatment for various waste (hazardous) materials and residues containing lead, iron, zinc, antimony, bismuth, and copper²³. It is an environment friendly and high-efficiency technique that offers multiple applications in the fields of materials recycling.

CONCLUSION

Lead extraction and sulfur conservation from LAB paste in a reducing atmosphere with the help of sulfur-fixing agent, iron-containing waste, was shown to be feasible, thermodynamically and experimentally. Phase transformation in the PbSO_4 -C reveals that PbSO_4 can be selectively reduced to PbS by reductant without generating excessive fraction of SO_2/SO_3 . Phase evolution in the intermediate $\text{PbS-Fe}_3\text{O}_4$ -C reaction system shows that the presence of Fe_3O_4 helped to transform sulfur from PbS to FeS. Thus PbS was converted to PbO and further reduced to metallic lead. Therefore, all components in the lead paste, including PbSO_4 , PbO and PbO_2 , can be recycled as metallic Pb.

The bench-scale experimental results of lead paste show that an adequate coke and Fe_2O_3 addition is necessary to obtain an acceptable lead recovery and sulfur fixation. The reductive atmosphere is the critical parameter to guarantee an adequate formation volume of matte and exchange and reduction of lead paste. Three products, crude lead bullion, matte, and slag, can simultaneously obtain and visibly separate as three distinct layers. More than 93 % lead in the lead paste can be directly enriched in the crude lead without subsequent slag cleaning and matte processing. 98.7 % sulfur was fixed as sulfide mattes instead of emitting excessive amount of SO_2 . The purity of crude lead bullion reached 98.8 %, and lead concentrations in the matte and slag were below 4.3 % and 1.1 %, respectively. Furthermore, iron-containing wastes were able to be co-treated and recycled in this process. Iron and sulfur were conserved as marketable FeS as well. This novel process can be used for co-treatment of various lead- and iron-containing solid wastes and residues, and for comprehensively recycling a variety of valuable metals compatible with iron matte and metallic lead.

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