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Molten salt mediated low-temperature direct roasting of spent lead paste



Abstract: - Traditional pyrometallurgy for recovery of spent lead paste suffered from high energy consumption, massive reducing agent and toxic SO_x gas emission. Here, a sustainable molten nitrate salt mediated approach was proposed to realize low-temperature (500 °C) direct roasting of waste lead paste. Efficient desulfurization could not be realized via single direct smelting of the mixture containing spent lead paste, Na₂CO₃ and NaNO₃. The introduction of Na₂CO₃ desulfurizer could promote the chemical conversion with PbSO₄, while the process still required relatively high temperature above 900 °C to realize relatively high desulfurization efficiency. After the introduction of NaNO₃ molten salt into spent lead paste-Na₂CO₃ system, the original solid-solid reaction in spent lead paste-Na₂CO₃ system was changed to solid-liquid-solid contract, providing more reaction probability between Na₂CO₃ and PbSO₄ phase in spent lead paste. As a result, high-purity lead oxide powders were obtained with 98.7% desulfurization and 99.2% lead recovery ratio. A profit of \$378.2 per ton spent lead paste could be achieved from the economically evaluations. The proposed novel pyrometallurgy approach eliminated the emission of harmful SO_x from the decomposition of PbSO₄ phase and releases of lead containing wastewater, offering a robust lead oxide recovery substitute from secondary lead resources while possessing significant environmental and economic benefits.

Keywords: Spent lead paste, Pyrometallurgical recovery, Desulfurization, Molten salt medium, Low-temperature roasting.

I. INTRODUCTION

Lead-acid batteries (LABs) possess the features including low cost, high safety benefits, mature manufacturing technology and 99% recycling ratio, etc.[1] Currently, LABs still occupy a significant position in the market of rechargeable battery, which are extensively employed in the fields of electric power, uninterruptible power supply, starter power supply and energy storage systems.[2] Recycling of spent LABs is regarded as an important issue for the sustainable development of waste lead resources, which not only effectively reduces the serious environmental problems caused by the discharge of lead-containing substances into the environment, but also provides great significance for the recovery of valuable materials.[3, 4] As the largest raw material of secondary lead, waste LABs are mainly composed of metal grids, lead paste, H₂SO₄ electrolyte and plastic shells. Spent lead paste (SLP) is regarded as important secondary lead resource, which usually consists of PbSO₄, PbO₂, PbO and metallic Pb. The composition of SLP is complex, making it difficult to recycle. Hence, the efficient and green recycling has become a key and difficult part of secondary lead industry.[5]

At present, the prevailing technical methods for recovery of SLP include pyrometallurgy and hydrometallurgy approaches.[6] Pyrometallurgical technology is considered as the most popular technical approach to recover secondary lead resources from SLP, which was directly smelted in reflector furnace, blast

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furnace, electric furnace, top-blown bath or rotary furnace. The whole processes deliver the characteristics of relatively simple plant operation and strong adaptability of raw materials, and has achieved great success in the recovery of SLP.[7] However, the traditional pyrometallurgical processes employ coal or coke as the reducing agent and fuel, where the roasting temperature reaches as high as 1000 °C.[8] In addition, the emission of acid SO_x gas from the decomposition of PbSO₄ phase will inevitably lead to lead dust particles, which will be discharged into the air/ground environment and obtained a low lead recovery rate of only 80-90%.[9, 10] Hydrometallurgical processes are summarised as desulphurisation, leaching, electrodeposition, etc. [11-14], and have received growing attention benefitting from the advantages of weak environmental pollution, low energy consumption and flexible scale. During the combined hydrometallurgy-pyrometallurgy recovery process, PbSO₄ in SLP is first converted into PbCO₃ or lead precursors after the introduction of desulphurisation agents (for example, Na₂CO₃, (NH₄)₂CO₃) [15]. Then, PbCO₃ powders are pyrolyzed to lead oxide powder, where the smelting temperature is reduced to below 600°C, increasing the lead recovery rate to more than 98%.[16, 17] However, the complicated process still required a large amount of desulphurisation solvent while generating waste water.

Hence, due to the disadvantages listed before, a molten salt mediated low-temperature direct roasting approach of SLP is proposed, as schematically illustrated in Scheme 1. The mixture including spent lead paste powder, desulphurisation agent (Na₂CO₃) and low melting point reagent (NaNO₃) was directly placed in the heating furnace and roasted under pre-determined calcination temperature in oxygen enriched air condition. As a result, low melting-point nitrates can be regarded as medium for the effective contact between Na₂CO₃ desulfurizer and PbSO₄ phase in SLP, increasing the lead recovery and desulfurization efficiencies.



Scheme 1 Schematic diagram of flow chart of the molten nitrate salt assisted approach for direct smelting of spent lead paste

II. EXPERIMENTAL METHODS

The raw waste lead paste samples were obtained from Kunming Hendera Technology Co. Ltd. The original waste lead paste was dried under vacuum environment, crushed, and ground to achieve the powder. All chemical reagents including PbSO₄, Na₂CO₃, and NaNO₃ were of analytical grade without further purification.

Before the roasting, waste lead paste (or PbSO₄), Na₂CO₃ and NaNO₃ were mixed in a pre-determined molar ratio, which was loaded into stainless steel molds and then pressed into tablets. The mixture was loaded in a quartz boat and put into an oxygen-rich furnace. The oxygen-rich furnace was then heated to the designed temperatures with a heating rate of 5 °C min⁻¹ and maintained for different holding time. After cooling the furnace to room temperature, the solid residues were dissolved in deionized water to obtain the final products after vacuum filtration.

Formula (1) and (2) were employed to calculate the lead oxide recovery and desulfurization ratio during the roasting of SPL, respectively.

$$\text{Lead oxide recovery ratio} = \frac{M_1}{M_2}$$

M1 represents the molar amount of PbO in the final product, M2 refers to the total molar amount of Pb in raw SPL.

$$\text{Desulfurization ratio} = 1 - \frac{M_3}{M_4}$$

M3 is the mass of PbSO₄ in the final product, and M4 stands for the weight of PbSO₄ in raw SPL.

The TG-DSC profiles were recorded to examine thermochemical reaction changes and possible thermodynamics kinetics. The identification of major element composition and crystal phase were evaluated by powder X-ray diffractometer (XRD, D2 Advance, Bruker, Germany) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The contents of PbO₂, PbSO₄, PbO, and metal lead in waste lead paste were determined by chemical titration. The surface morphological properties and major element compositions of waste lead paste, lead carbonate products, and lead oxide products were determined by scanning electron microscope (Tescan Vega 3 SBHEDS, Czech Republic). Meanwhile, the metal impurities in waste lead paste and PbO powder were detected with an inductively coupled plasma atomic emission spectrometry (ICP-OES, Thermo Scientific iCAP 7400, USA).

III. RESULTS AND DISCUSSION

A. Direct roasting of SPL without Na₂CO₃ and NaNO₃

From the XRD pattern of raw SLP in Figure 1, it is identified that the main chemical compositions of SLP are PbSO₄, PbO₂, PbO and metal Pb substances. The content of above substance is determined to be 46.0%, 26.6%, 18.7% and 1.5%, respectively, with a small amount of impurity (Table 1) via titration method.

Table 1 The detailed content of Pb species in SPL

Chemical composition	PbO ₂	PbSO ₄	PbO	Pb	Other impurities
Content(wt.%)	46.0	26.6	18.4	1.5	7.2

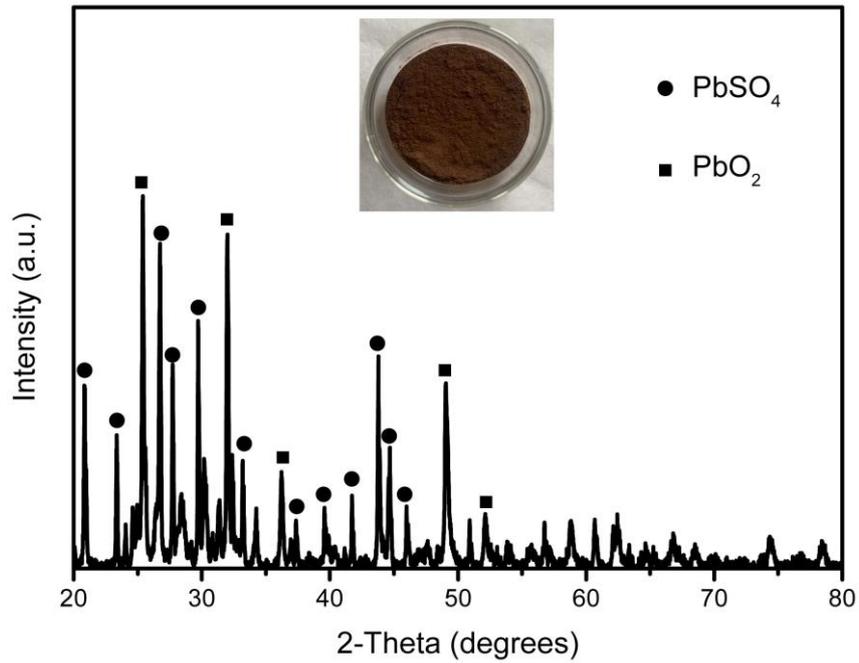


Figure 1 The appearance and XRD pattern of SLP

The feasibility of single roasting conversion of Pb-containing substances in SLP without Na_2CO_3 and NaNO_3 is validated, as presented in Figure 2. The possible reactions during direct roasting of SPL are described in below.[18]



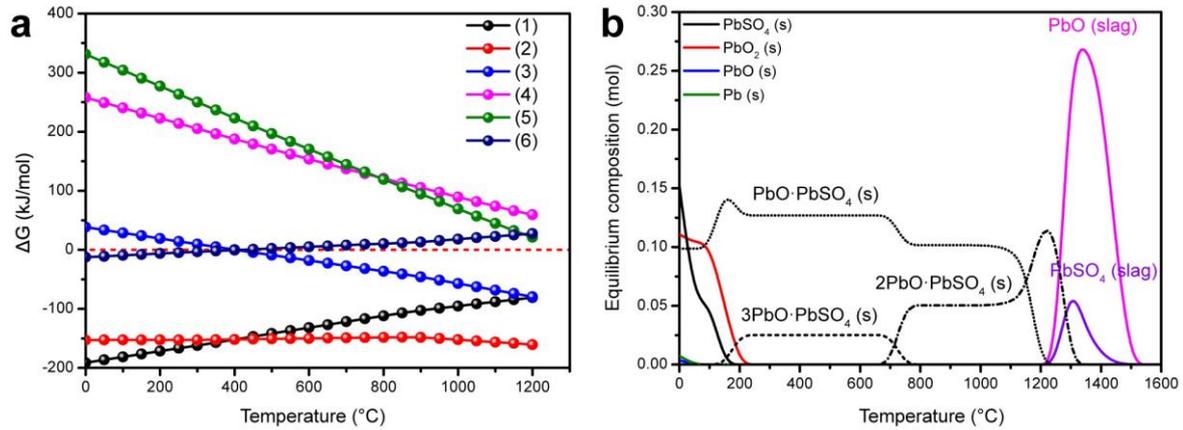


Figure 2 (a) Free Gibbs energy change of various reactions, (b) equilibrium composition of SLP during direct smelting

The Gibbs free energy values (ΔG) of lead substances in SLP during direct roasting in Figure 2a are calculated to clarify the thermodynamic process and preliminarily judge the potential thermodynamic pathways of lead substances. As observed, the oxidation of metallic Pb and decomposition of PbO_2 into PbO will perform spontaneously at temperatures higher than 300 °C. As the temperature below 500 °C, the conversion of PbO to Pb_3O_4 would occur. Meanwhile, the decomposition of $PbSO_4$ is hard to spontaneously proceed when the temperature is lower than 1200 °C. As the emission of SO_x gas would occur during the direct roasting of $PbSO_4$ phase under high temperatures, hence, the fixation of sulfur in $PbSO_4$ without SO_x gas emission should be considered particularly during the direct smelting.

The TG curve of SLP demonstrates a multi-stage behaviour during smelting (Figure 3). Based on the TG profile of single phase in SPL, the stages include the decomposition of PbO_2 into PbO, volatilization of PbO and decomposition of $PbSO_4$, which is consistent with the stability diagram of SLP (Figure 2b).[19]

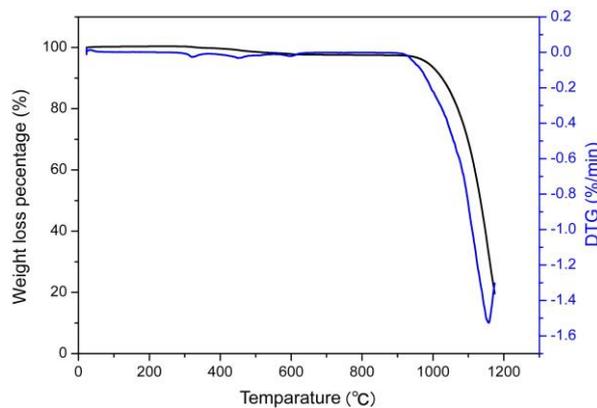


Figure 3 TG curve of SPL

During the thermal treatment of SLP, the converted $xPbO \cdot PbSO_4$ phases would appear, which could be confirmed by the XRD patterns of SLP roasted under various temperatures (Figure 4a). In fact, it should be noted that the existence of PbO is related to the original and converted PbO in SPL, not the thermal decomposition of $PbSO_4$, which could be demonstrated by the XRD patterns of pure $PbSO_4$ after thermal treatment (Figure 4b). Meanwhile, high temperature is conducive to the growth of $PbO \cdot PbSO_4$ phase in SLP. In addition, the

experimental results indicate that only 1.6% desulfurization rate is achieved at high temperature 900 °C despite obtaining 58.6% PbO recovery ratio for SLP, which could be ascribed due to the conversion of PbO₂ and metal Pb, as described in Figure 4c. It is concluded that efficient desulfurization could not be realized via single direct smelting of PbSO₄ or SLP. That is, high temperature above 1000 °C is required to decompose PbSO₄ phase accompanied by toxic SO_x emission during single direct smelting of PbSO₄ or SLP (Figure 5), which could be indicated by the TG curve of PbSO₄ (Figure 6).

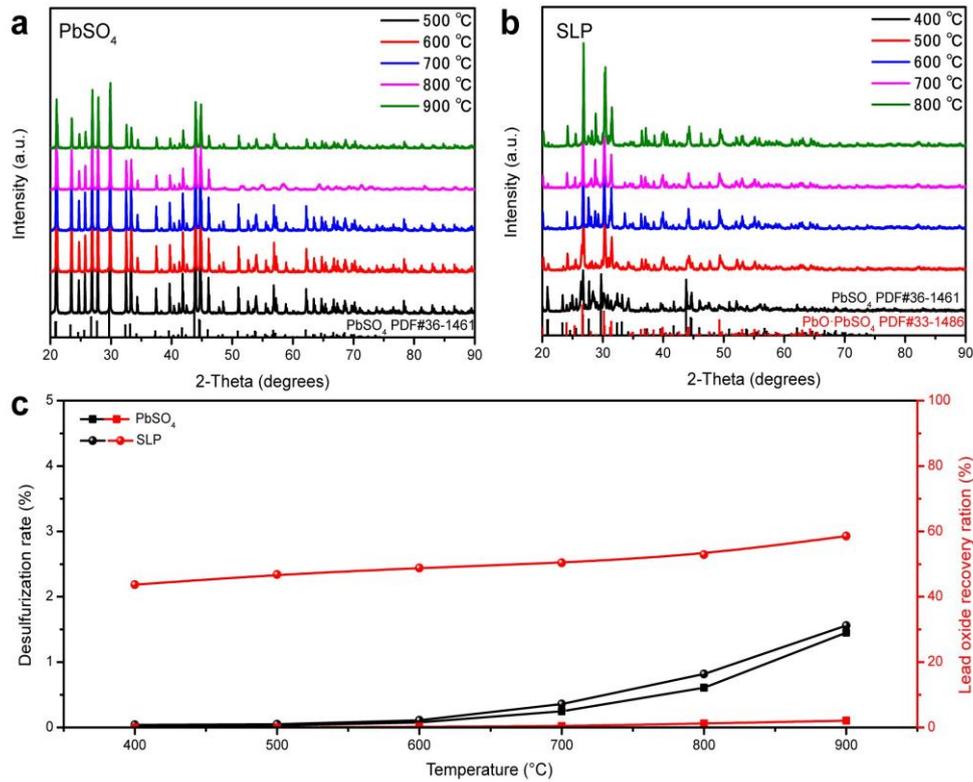


Figure 4 (a, b) XRD patterns of desulfurized samples, (c) the lead oxide recovery and desulfurization ratio under different temperatures

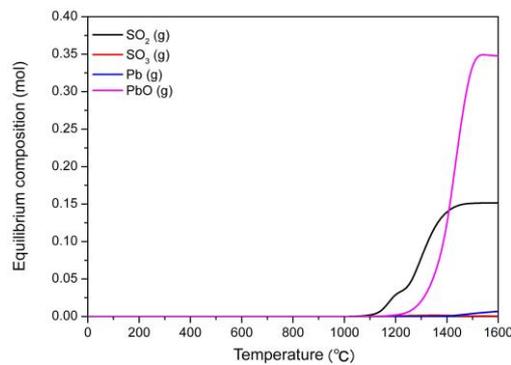


Figure 5 The gas equilibrium composition of SLP during direct smelting

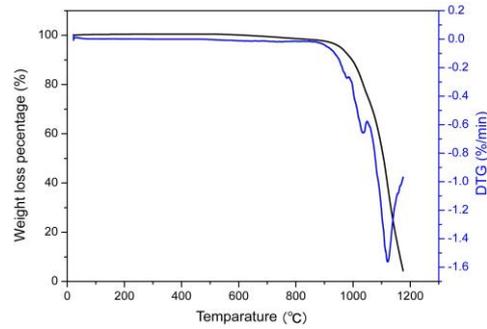


Figure 6 TG curve of pure PbSO₄

B. Direct roasting of SPL-Na₂CO₃ system without NaNO₃

The Gibbs free energy could be employed to analyse possible thermodynamic behaviours in presence of Na₂CO₃ desulphurisation agent. When Na₂CO₃ is introduced into SPL or PbSO₄ as the desulphurisation reagent, PbSO₄ phases are preferentially converted to PbCO₃, which would be further converted to generate PbO under roasting, simultaneously (Figure 7a).

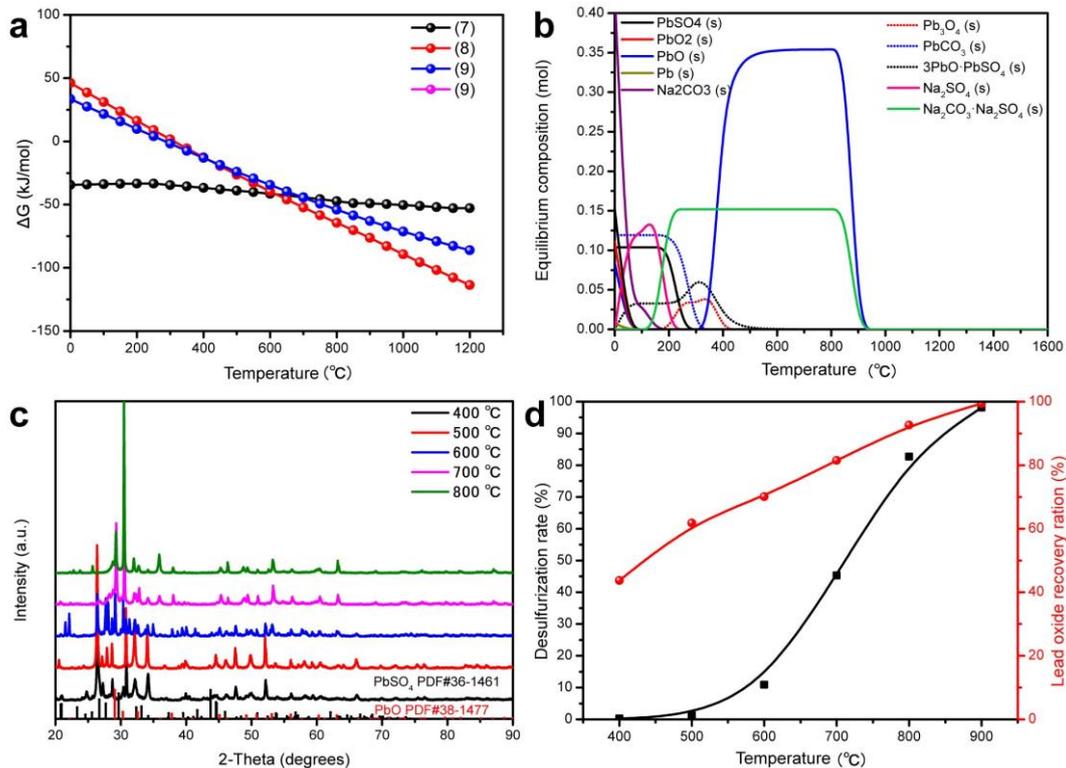
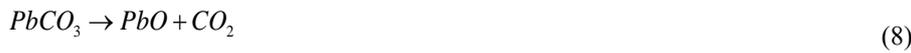


Figure 7 (a) Gibbs energy change of various reactions when containing Na₂CO₃, (b) equilibrium composition of the SLP-Na₂CO₃ system, (c) XRD patterns of desulfurized samples, (d) the lead oxide recovery and desulfurization ratio under different temperatures.

The theoretical analysis and equilibrium composition (Figure 7b) verify the thermodynamically favorable of SLP- Na_2CO_3 system to obtain PbO . [20] From the TG curve of SLP- Na_2CO_3 system (Figure 8), the introduction would not intrinsically determine the decomposition of lead species.

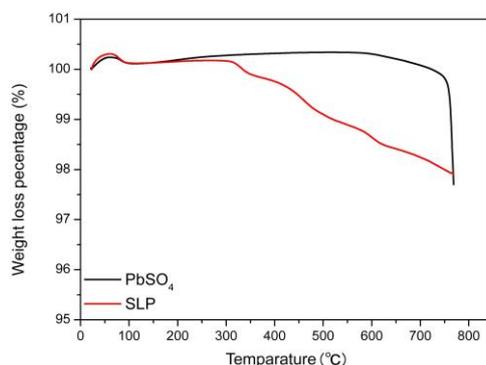


Figure 8 TG curve of SPL and PbSO_4 containing Na_2CO_3

The XRD patterns of the calcined products of SLP and PbSO_4 under different temperatures are shown in Figure 7c. At roasting temperatures below 700 °C, obvious peaks of PbSO_4 can be still detected for pure PbSO_4 , revealing low-temperature would not allow the decomposition of PbSO_4 - Na_2CO_3 mixture (Figure 9).

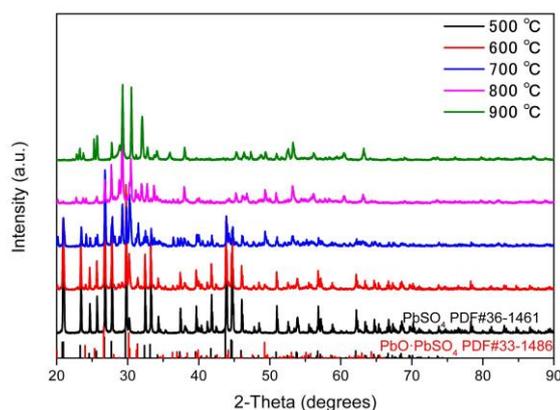


Figure 9 XRD patterns of pure PbSO_4 samples containing Na_2CO_3

As for SLP, the generation of PbO_x substances occurs from the conversion of PbO_2 , PbO and metal Pb in SLP. The desulfurized samples exhibit the characteristic diffraction peaks of $x\text{PbO}\cdot\text{PbSO}_4$ at 700 °C. The peaks of β - PbO (PDF#38-1477) and α - PbO (PDF#35-1482) could be observed above 800 °C. The increase of roasting temperature would be conducive to the lead oxide recovery ratio and desulfurization rate, where high smelting temperature strengthens thermal motion between solid particles. However, it should be noted that the desulfurization rate is raised from 2.3% to 45.3%, and the lead oxide recovery ratio is only increased from 61.8% to 81.5% as roasting temperature is boosted from 500 °C to 700°C. As roasting temperature continues to be raised from 800 °C to 900 °C, the desulfurization rate is increased to 98.1% from 82.7% (Figure 7d). In addition, SO_x emission is not detected in the range of 500–900 °C when containing Na_2CO_3 desulphurisation reagent (Figure 10).

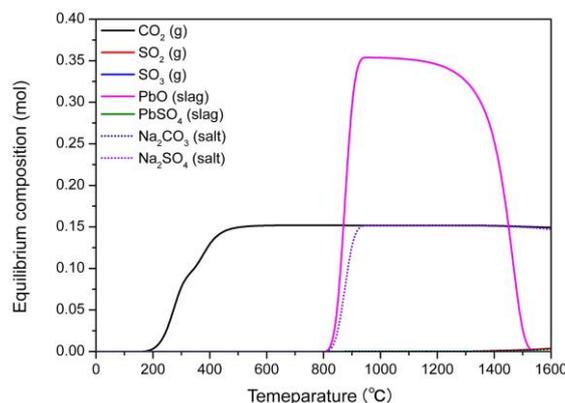


Figure 10 The gas equilibrium composition of SLP- Na_2CO_3 during direct smelting

Hence, it is possible to one-step obtain PbO powder by melting a mixture of SLP or PbSO_4 with Na_2CO_3 while fixing sulfur successfully and avoiding the generation of harmful SO_x gas. However, as observed, the direct roasting of SLP- Na_2CO_3 system still requires relatively high temperature above 900 °C to realize relatively high desulfurization efficiency. So, the employment of Na_2CO_3 alone introduced into SLP or PbSO_4 is not economical for the desulphurisation as high temperatures and high energy consumption are still necessary.

As proved, the experimental results mismatch with theoretical results in Figure 7a, where the introduction of Na_2CO_3 desulfurizer is feasible for desulfurization. The reasons can be as follows. Firstly, the reaction between PbSO_4 and Na_2CO_3 leaching solution to produce PbCO_3 is considered during conventional hydrometallurgical processes, where Na_2CO_3 exists as Na^+ and CO_3^{2-} ion in aqueous solution. The decomposition temperature of the obtained PbCO_3 is lower than that of PbSO_4 , and PbCO_3 could be readily pyrolyzed to generate PbO powder at a comparatively low temperature of ~500 °C. Here, free contact between the CO_3^{2-} ions in aqueous solution and PbSO_4 particles can be guaranteed. In fact, as for the direct roasting process, the solid-solid contact between PbSO_4 and Na_2CO_3 solid particles leads to weak interaction and reaction possibility.[21] That is, in the real experimental conditions, the whole perfectly conversion of SLP or PbSO_4 to lead oxide after the introduction of Na_2CO_3 would not be easy to occur as it sounds in theory or should take enough time and high temperature to complete the reaction.

C. Molten salt mediated roasting of SLP- Na_2CO_3 system

Based on the phase diagram of NaNO_3 - Na_2CO_3 (Figure 11), the introduced NaNO_3 would be converted into liquid phase molten salt at 307 °C. The introduction of NaNO_3 into SLP- Na_2CO_3 would not affect the whole reaction paths as NaNO_3 would not react with Pb substances in SLP or Na_2CO_3 . Yet, the molten salt would promote the interfacial reaction between lead species (especially PbSO_4) and Na_2CO_3 solid particles, resulting into effective displacement reaction and desulphurisation behaviour[22], as presented in the TGA curves of SLP- Na_2CO_3 - NaNO_3 system (Figure 12).

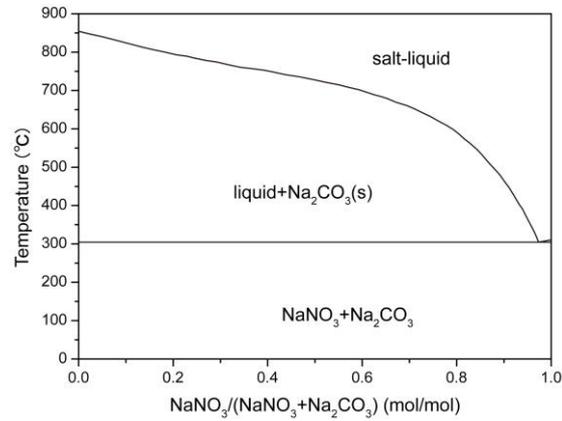


Figure 11 Phase diagram of NaNO₃-Na₂CO₃ system

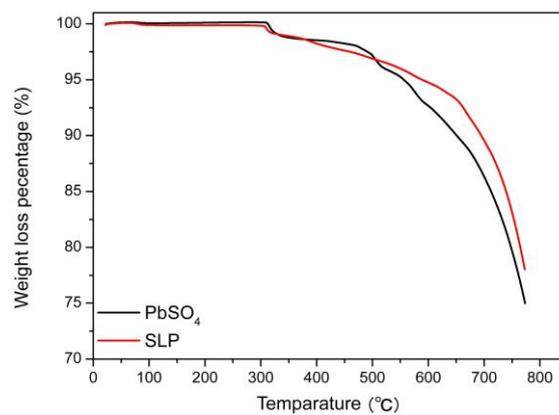


Figure 12 TG curves of SPL and PbSO₄ containing Na₂CO₃ and NaNO₃

From the XRD patterns of desulfurized SLP samples at various temperatures (Figure 13a), apparent characteristic peaks of crystalline phase Pb₃O₄ could be detected at low temperature 400-500 °C, revealing the remarkable role of molten salt in promoting the chemical transformation of PbSO₄. The purity of the Pb₃O₄ product from the calcination at low temperature of 500 °C is determined to be 96.5% with no significant impurities is observed. When high temperature exceeds 600-700 °C, β-PbO phase is generated due to the thermal conversion of Pb₃O₄ and high oxidation capacity of NaNO₃. As for pure PbSO₄ raw material, α-PbO is the main phase at below 600 °C (Figure 14). The conversion from α-PbO to β-PbO phase occurs when high temperature exceeds 700 °C. As a result, β-PbO or Pb₃O₄ is the final roasting product from lead species in SLP at low-temperature process. The simple recycling method exhibits a vigorous impact on the recovery of PbO_x from the secondary SLP.

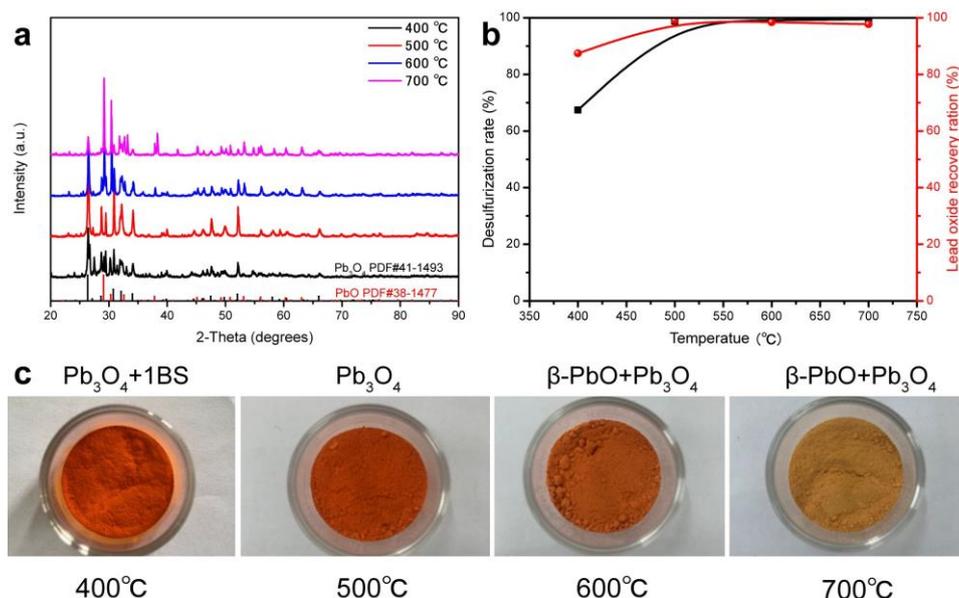


Figure 13 (a) XRD patterns of desulfurized samples, (b) the lead oxide recovery and desulfurization ratio under different temperatures, (c) digital photographs and main phases of SPL under different roasting temperatures

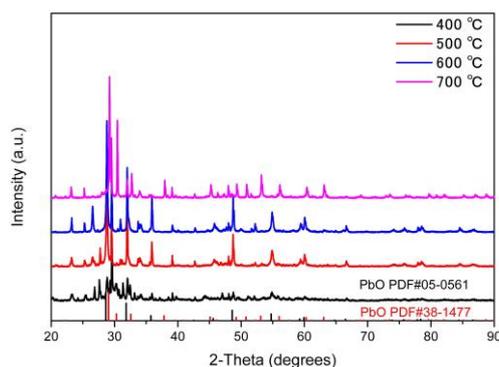


Figure 14 XRD patterns of pure PbSO₄ samples containing Na₂CO₃ and NaNO₃

It is obvious that the lead oxide recovery ratio and desulfurization rate raise gradually with the increase of roasting temperature. The desulfurization rate remains above 98.7% when the temperature exceeds 500 °C, and the lead oxide recovery ratio reaches the maximum of 99.2%. The slightly decrease of PbO recovery ratio could be attributed to the volatilization of PbO at high temperatures (Figure 13b). It should be noted the decomposition reaction of NaNO₃ would occur at above 600 °C, as confirmed by the TGA profile of NaNO₃. Hence, the roasting temperature of the molten salt mediated approach is optimized at ~500 °C.

The effect of the addition quantity of Na₂CO₃, NaNO₃ and reaction time is explored (Figure 15-16). The results indicate that Na₂CO₃ and NaNO₃ exert a considerable influence on the recovery efficiency and desulfurization ratio. Raising the dosage of Na₂CO₃ contributes to the desulfurization conversion, and the dosage of Na₂CO₃ should exceed the theoretical ratio 1:1 to ensure total conversion of PbSO₄. (Figure 15a)[23] High NaNO₃ content increases the volume of the molten salt and accelerates the conversion (Figure 15b-15c). The presence of Pb₃O₄ could be ascribed to the intensified oxidization capacity under high NaNO₃ content.[24] Finally, the content of Na₂CO₃ should be determined to be 1.1 times of the molar amount of PbSO₄ in SPL with the NaNO₃/Na₂CO₃ molar ratio of 1.0 and roasting time of 3 h. After the introduction of NaNO₃, the original solid-

solid reaction of SLP- Na_2CO_3 system is changed to solid-liquid-solid contact mediated by molten salt intermediate medium. As the activation energy of the particle movement increases, molten salt is in full contact with Pb substances and Na_2CO_3 desulphurisation agent.[25] Meanwhile, with the increase of roasting temperature, the diffusion and solubility of Na_2CO_3 in molten salt would increase. As a result, more reaction probability between Na_2CO_3 and PbSO_4 results into high PbO recovery ratio and desulfurization rate at relatively low temperature.

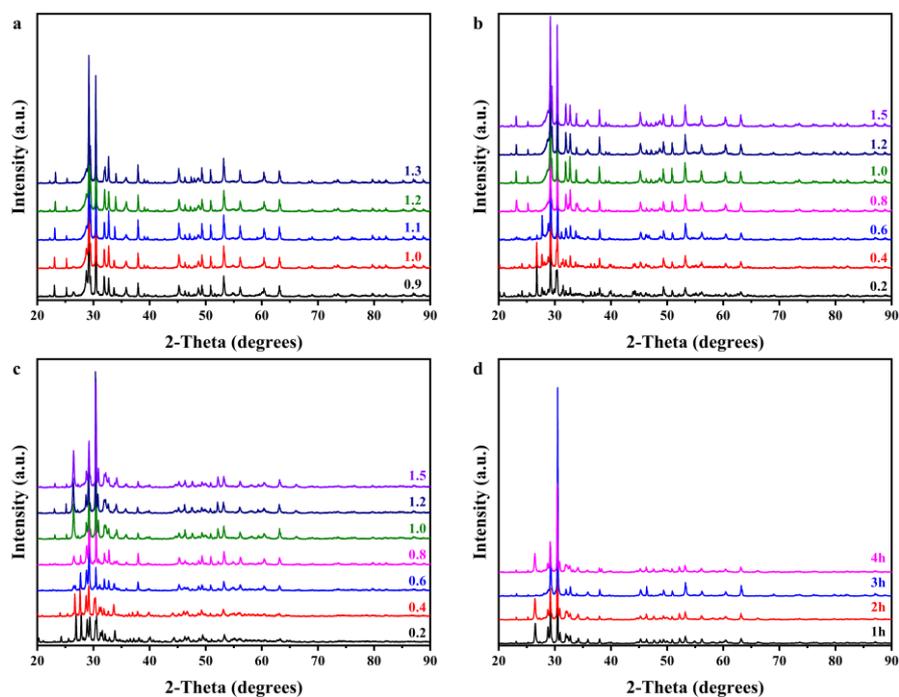


Figure 15 (a) XRD patterns of $\text{PbSO}_4\text{-Na}_2\text{CO}_3\text{-NaNO}_3$ system under different $\text{Na}_2\text{CO}_3/\text{PbSO}_4$ molar ratios, (b) XRD patterns of $\text{PbSO}_4\text{-Na}_2\text{CO}_3\text{-NaNO}_3$ system under different $\text{NaNO}_3/\text{Na}_2\text{CO}_3$ molar ratios, (c) XRD patterns of $\text{SPL-Na}_2\text{CO}_3\text{-NaNO}_3$ system under different $\text{NaNO}_3/\text{Na}_2\text{CO}_3$ molar ratios, (d) XRD patterns of $\text{SPL-Na}_2\text{CO}_3\text{-NaNO}_3$ system under different roasting time

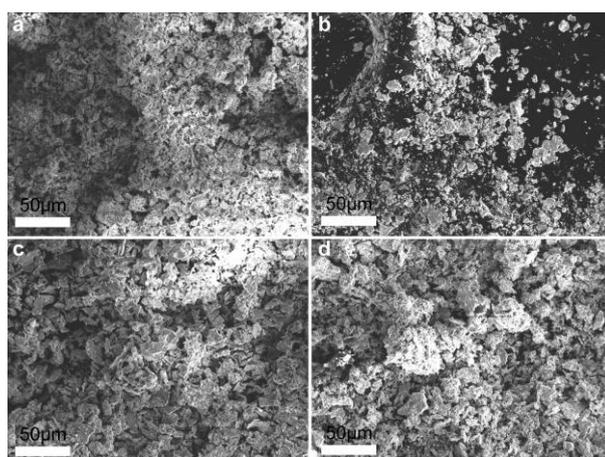


Figure 16 SEM images of the obtained PbO_x product under different roasting time, (a) 1h, (b) 2h, (c) 3h, (d) 4h

D. Economical analysis

The treatment of 1.0 t SLP as an example based on the laboratory scale is economically evaluated. Overall,

the whole roasting consists of energy input, raw materials (SLP, Na₂CO₃, water, and NaNO₃), product output (PbO_x) containing secondary Na₂SO₄ product output and benefits (Table 2).[26] It is noteworthy that the recycling of NaNO₃ would also reduce the cost of chemical reagents. As calculated, the total profit of the molten salt mediated low-temperature direct smelting for 1.0 t SLP recovery is \$378.2. The economic analysis in Figure 17 reveals the economically feasible and benefits of the proposed molten salt mediated low-temperature direct smelting of SLP, which is feasible to be applied in industrial applications.

Table 2 The economic analysis of the molten salt mediated low-temperature direct roasting of spent lead paste

Item	Item	Unit	Amount	Unit price	Cost
Power consumption					
Energy input	Electricity for mixing	kWh	40 kWh	\$0.1/kWh	\$4.0
	Electricity for heating	kWh	90 kWh	\$0.1/kWh	\$9.0
	Electricity for water evaporation	kWh	121 kWh	\$0.1/kWh	\$12.0
Raw material input	Spent lead paste	kg	1000 kg	\$1400/t	\$1400
	Na ₂ CO ₃	kg	192.9 kg	\$500/t	\$96.5
	NaNO ₃	kg	154.7 kg	\$305/t	\$47.2
	Water	kg	3460 kg	\$0.5/t	\$1.7
Product output	Lead oxide	kg	790.8 kg	\$2360/t	\$1866.3
	NaNO ₃	kg	154.7 kg	\$305/t	\$47.2
	Na ₂ SO ₄	kg	215.5 kg	\$70/t	\$15.1
Direct air emissions					
gas	O ₂	kg	12.2 kg		
gas	CO ₂	kg	66.9 kg		

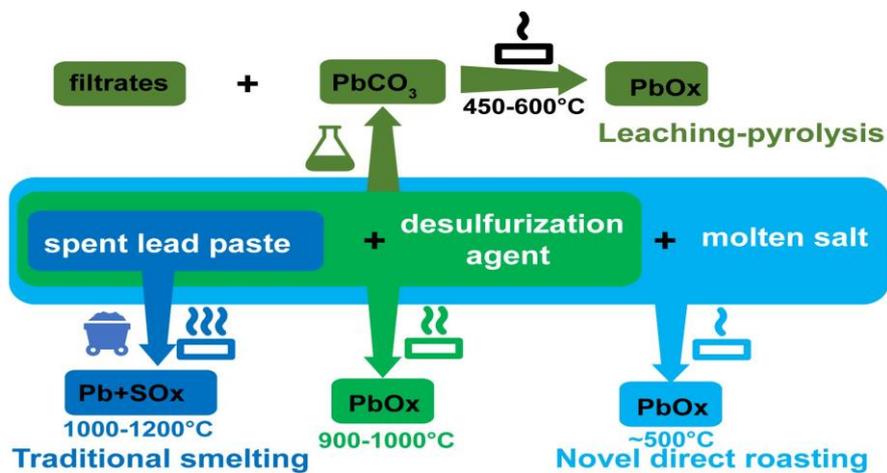


Figure 17 The comparison of the molten salt mediated low-temperature direct roasting of spent lead paste with traditional pyrometallurgy and hydrometallurgy techniques.

The proposed molten salt mediated roasting approach could realize the high-purity PbO recovery and

efficient sulphur fixation at low reaction temperature of only 500 °C. The approach delivers a pronounced technological benefit over traditional pyrometallurgy, which is commonly operated above 1000 °C while accompanied with emissions of SO_x and lead dusts. Compared to inorganic/organic acids in hydrometallurgy, the employed chemical reagents Na₂CO₃ and NaNO₃ exhibit the features of environmental-friendly, no potential secondary risks and hazards.

IV. CONCLUSION

In summary, a molten salt mediated low-temperature direct roasting of spent lead paste for simultaneous sulfur fixation and lead oxide recovery was developed with Na₂CO₃ and NaNO₃ as reagents. The molten salt intermediate medium provides effective solid-liquid-solid contact and more reaction probability between Na₂CO₃ and PbSO₄ phase. The proposed novel pyrometallurgy approach eliminated the emission of harmful SO_x from PbSO₄ phase and releases of lead containing wastewater. The approach offers a low roasting temperature of only 500 °C, while 98.7% desulfurization rate could be realized. A profit of \$378.2 per ton spent lead paste could be achieved from the economically evaluations. The approach provides a robust lead oxide recovery substitute from secondary lead resources while possesses remarkable environmental and economic benefits.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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