An efficient and environmentally friendly route for PbS crystal recovery from lead ash generated in tin removal section (LATR) via high-speed leaching and recrystallization method

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Abbreviation/acronym/symbol full form

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|----------------------|-----------------------------------|
| LATR                 | Lead ash generated in Tin removal section |
| Pb\(_{\text{in the LATR}}\) | The Pb element in original LATR used in the leaching process |
| Pb\(_{\text{in the filtrate}}\) | The Pb ions in the filtrate after leaching process |

\textbf{Abstract:} This paper mainly investigated on synthesis of a high purity PbS crystal directly from lead ash which was collected from Tin ash removal process (LATR). The LATR was firstly disposed by nitric acid leaching system to generate the lead nitrate solution. The PbS crystal would be prepared by mixing the lead nitrate solution with the sodium sulfide at the room temperature (25 °C). The effects of molar ratio of HNO\(_3\) to Pb\(_{\text{in the LATR}}\) on Pb leaching efficiency was investigated, demonstrating that the Pb leaching efficiency could attain to 82.9 % at molar ratio of 3. The leaching ratio of As, Cu, Fe, and Al generally increased with increasing molar ratio of HNO\(_3\) to Pb\(_{\text{in the LATR}}\), while 99.99 wt% of Sn was still left in the residue. In the process of generating PbS crystal from the leaching solution, the yield of PbS crystal was increased with increasing molar ratio of Na\(_2\)S to Pb\(_{\text{in the filtrate}}\). The yield of PbS crystal could up to 93.1%
at a molar ratio of 1.5. Overall, this method proved to be an efficient and environmental friendly route for synthesis of high quality PbS crystal directly from the common lead containing waste from the lead ore or secondary smelting factory.

**Keywords:** Lead ash; PbS crystal; Leaching; Recrystallization; Recovery; Environmentally friendly

1 Introduction

China is producing and consuming a large quantity of lead in the world every year, and more attention has also been paid to the lead pollution. In the lead smelting enterprise, many lead alloys would be refined and generated every day with huge amount, including tin-lead alloy, antinomy-lead alloy, nickel-lead, cobalt-lead, zinc-lead alloy, and calcium-lead alloy [1][5]. Most of lead element would be refined (at a higher temperature) and finally entering into the lead alloy product [6][7]. However, we should not ignore that a large quantity of by-products would be generated in the smelting process. The typical by-products were mainly including lead ash and lead slag. The lead ash was usually generated and emitted into the factory dust collector, and the lead slag was generated during the smelting-cooling process of the lead compounds [8][10]. The lead ash was quite common in the lead smelting enterprise with a relatively large quantity [11][14]. As reported, the annual production of lead ash would reach up to nearly 50,000 tons [15].

Currently, most of lead ash would be directly cycled into the melting process (in the furnace). This smelting process would usually be conducted at a higher temperature, that would easily emit large amount of lead particles [16]. Besides the smelting process, a hydro-electrometallurgy route was also applied in the recycling of fly ash generated in spent lead acid battery smelting process [17]. In the hydro-electrometallurgy route, the chemical reagents e.g. HNO₃ or NaOH were used to leach the fly ash, and then the pregnant leach solution after leaching was electrodeposited to get lead dioxide and metallic lead on the anode and cathode, respectively. The above hydro-electrometallurgy approach was beneficial to produce high purity lead product, but its higher energy consumption in this process should not be ignored. The composition of lead fly ash is similar to the spent lead paste, for their main compositions were lead oxide or lead sulfate. Thus, the method for recycling spent lead paste should also be a reference to the treatment of lead fly ash, such as the reagent dissolution-electrowinning method, the leaching by citric acid solution method, and the desulfurization-dissolution-electrowinning method et al [18][20].

It would be quite attractive to explore an efficient and feasible method for recycling the lead ash. For different sections where the lead ash was produced in the lead ore or secondary, the composition of lead ash would also be different. Besides the Pb element, the lead fly ash was also consisting of other metal compound e.g. antinomy, nickel, cobalt, iron, copper, and aluminum, et al. The lead compound in the fly ash was usually lead, lead oxide, lead sulfide, lead sulfate, and oxysulfates (PbO-PbSO₄ or (PbO)₂·PbSO₄) [21][22]. Currently, more attention was paid to recycle spent lead waste (including spent lead paste, lead sludge, and lead fly ash) to generate lead oxide products. However, the lead oxide product should not be the single choice for generating Pb product, other lead compound (such as PbS and PbCl₂) should also be an ideal choice [23][24]. Consider the special composition of LATR, the PbS could also an alternative product (generated from LART) for it could simplify the recycling process. It’s obvious that, the simpler recycling process could reduce the emission of lead containing particles into outside environment.

Here, the proposed schematic diagram of this study could be illustrated by Fig. 1. As shown, this study mainly focuses on two key issues. Firstly, the LATR was leached
by the nitric acid, where the lead element would be entered into the filtrate (Pb in the filtrate), while the majority of impurity element would be left in the filter cake due to their attachment between the impurity compound and the residue. Secondly, the generated filtrate would be mixed and reacted with sodium sulfide to generate PbS crystal (namely the crystallization process). This study would have a positive significance to recovery of LATR recovery and preparation of high purity lead sulfide crystal.

Fig. 1. Proposed schematic diagram for this study.

2 Material and Methods
2.1 Raw materials and Reactants

The LATR used in this experiment was collected from the tin element removing section (an essential process to refine the tin - lead alloy), applied by Hubei Jinyang Metallurgical Co., Ltd. The concentrations of main elements including Pb, Sn, As, Fe, Cu, and Al were determined and shown in Fig. 2(b), the detailed process for determination of the main elements was presented in Supporting Information. It was obvious that the major elements in the original LATR were Pb (81.4%) and Sn (7.2%), also with small amount of As, Fe, Cu, and Al. The XRD pattern of original LATR was shown in Fig. 2 (c), also illustrating the main crystal composition in the LATR was PbO and SnO<sub>2</sub>. From the appearance (Fig. 2(a)) of the original LATR, the collected LATR was yellow powder, mainly attributing to the existence of PbO crystal. As shown in the SEM image (Fig. 2(d)), the LATR was with irregular sphere and rough porous surface.
Fig. 2. The characterization of the original LATR: (a) the appearance of LATR packed in the test tube; (b) the concentration of main metal elements in LATR samples; (c) The XRD pattern of original LATR; (d) The SEM image of LATR with Mag of 1 kX.

The nitric acid used in this study was of analytical purity, supplied by Yantai Shuangshuang Chemical Co., Ltd. The sodium sulfide was also of analytical purity, purchased by Tianjin Damao Chemical Reagent Co., Ltd. The standard solution of Al, Fe, and Cu was supplied by National Nonferrous Metals Research Institute.

2.2 Leaching of LATR

To study the leaching efficiency of LATR in nitric acid system, various concentrations of nitric acid (0.6, 0.8, 1.0, and 1.2 mol/L, in Table S1) were separately mixed up with 50 g of LATR in 1L beaker at 25 °C with a stirring speed of 400 rpm (Figure S1).

During the leaching process, the solution sample (10 mL) was quickly withdrawn from the mixed solution in the beaker at setting leaching time of 0, 10, 20, 30, 60, 90, and 120 minutes, respectively. The withdrawn solution samples were then directly filtrated through the microporous membrane (0.45μm pore size). The concentration of lead in the filtrate was measured by the EDTA-2Na Testing Method (explained in S1). The concentrations of Sn, As, Cu, Fe, and Al were determined by ICP-OES 5100 (Keysight Technologies).

At the terminal of leaching time (120 minutes), the left mixed slurry was filtered to get the filtrate for further the next step. The residual filter cake was continuously washed with deionized water until the pH of washing water was near to 7, followed by dried in the oven under 55 °C for 24 hours. The concentrations of Pb, Sn, As, Cu, Fe, and Al in the filtrate and residual filter cake were measured to analyze the flow of main elements during the leaching process.

The leaching efficiency of lead and other elements were calculated by using Eq. (1).

\[
\text{Leaching efficiency (wt\%) } = \frac{v_1 \times m_1}{(g_1 \times w_1)} \times 100\%
\]

Here, \(v_1\) stands for total volume of leaching experiment (L); \(m_1\) stands for mass concentrations of metal ions (g/L); \(g_1\) stands for the weight of LATR (g); \(w_1\) stands for the percentage of metal element in LATR (wt%).

2.3 Synthesis of PbS crystal

Various mass of sodium sulfide reagents was separately added into the stored filtrate solution in 250 mL tall beaker under 25 °C for 30 minutes (as shown in Figure S1). The added amount of sodium sulfide reagents was calculated according to various molar ratio of Na2S to Pb in the filtrate as 0.75, 1, 1.25 and 1.5, respectively (as shown in Table S2).

At the reaction terminal of 30 minutes, the solution after reaction was quickly filtered, then the solid filter cake was washed by deionized water, finally dried in the oven under 55 °C. The conversion rate of Pb (wt%) at various molar ratio of Na2S to Pb in the filtrate could be calculated by using Eq. (2).

\[
\text{The conversion rate of lead (wt\%) } = \frac{g_2 \times w_2}{(m_2 \times v_2)} \times 100\%
\]

In the Eq. (2), \(g_2\) is representing the mass of the synthesis product (g); \(w_2\) is representing the content of lead in the synthesized product (wt%); \(m_2\) is representing the concentration of lead in the stored filtrate solution (g/L); \(v_2\) is representing the volume of the stored filtrate solution (L).

2.4 Characterization of Original LATR and PbS crystal products

The original LATR and synthesized PbS crystal were both investigated by X-ray Powder Diffraction method (Philips, PANalytical B.V., Holland) with Cu Kα radiation

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[Note: The table and detailed data are not provided here due to text format limitations.]
(λ = 1.54 Å), while the XRD patterns were calculated through the X'pert Highscore Software.

The micromorphology for original LATR and prepared PbS crystal was investigated throughFocused Ion Beam Scanning Electron Microscopy (Zeiss/Auriga FIB SEM).

2.5 Thermodynamics analysis of lead and other metal elements in the solution

The Potential-pH phase diagram and Fraction diagram for Pb, Sn, As, Cu, Fe, and Al were calculated by the MEDUSA software, which has been commonly used in thermodynamics analysis [25][27].

3 Results and Discussion

3.1 Leaching of LATR

The leaching efficiency of lead from the LART with varying molar ratio of HNO$_3$ to Pb in the LART was presented in Fig. 3. As shown in Fig. 3, the leaching efficiency of lead was increased quickly at leaching time ranging from beginning to 20 minutes. After the beginning 20 minutes, the leaching efficiency would slightly increase. This result was mainly attributed to it that the lead-containing components (mainly PbO in this study) would be easy to react with nitric acid in the mixed solution. Especially, the surface part of PbO would be firstly reacted with HNO$_3$, and then the inner PbO be exposed and consumed by the HNO$_3$ in the solution.

We could also know that more lead ion would be leached with increasing molar ratio of HNO$_3$ to Pb in the LART (Fig. 3). When the molar ratio was 1.5, the leaching efficiency of Pb at 120 min was only 67.5%, this results was mainly attributed to it that the added HNO$_3$ (at the molar ratio of 1.5) could not entirely consume the whole PbO in the LART for the theoretical reaction molar ratio was 2. The leaching efficiency of lead was measured to be 76.7% and 82.9% at leaching time of 60 minutes, when the molar ratio was 2.5 and 3, respectively. The more nitric acid in the solution would be beneficial to react with PbO from the LART, for the easier contact between the solution and LART particles.

![Fig. 3. Effect of molar ratios of HNO$_3$ to Pb in the LART on leaching efficiency of Pb from LART (Conditions: stirring speed of 400 rpm, 25 °C).](image)

The Eh-pH and Fraction phase diagrams for lead in the leaching system were shown in Fig. 4. As shown, the pH and potential of the leaching system would influence the dominant phase of lead compound in the solution. When the pH was less than 4, and the E$_{SHE}$ was above -0.2V, the Pb$^{2+}$ was obviously dominated in the solution. With increasing pH, the dominated phase would be mainly transferred into Pb(OH)$_2$. From this above analysis result, it was easy to find that it was not essential to add oxidant or
reducing agent into the leaching system, for the Pb\(^{2+}\) was dominated at a relatively large potential ranging from -0.2V to 7V. It could also be seen that the lead in the leaching system mainly existed in the dissolved state, further confirming the majority of lead was entering into the leaching solution.

However, it should be clear that small amount of lead would still be left in the residual filter cake after leaching and filtration procedure. The distribution of Pb in the stored filtrate and residual filter cake was shown in Fig. 5(a). As shown in Fig. 5(a), the proportion of lead (wt%) in the filtrate was generally decreased with increasing molar ratio of HNO\(_3\) to Pb in the LART, that was attributed to it that more lead ions would be leached into the filtrate with increasing dosage of nitric acid. The sum percentage of lead in the filtrate and residual filter cake would all reach more than 88% under various molar ratios, indicating that our measurement for the distribution of lead during the leaching process should be relatively accurate. This leaching process should also be illustrated by Fig. 5(b).

The leaching efficiency of other metal impurities including As, Cu, Fe, and Al at various molar ratio of HNO\(_3\) to Pb in the LART was presented in Fig.6. The ratio of metal impurity entering into the filtrate at different molar ratio of HNO\(_3\) to Pb in the LART at the terminal time of 120 min was shown in Table. S4. From Table. S4, the most abundant element - Sn would be hardly reacted with the nitric acid, for its leaching efficiency was only 0.0001% at molar ratio of 1.5 and 2. Thus, the leaching efficiency of Sn was not further studied in Fig.6. As shown in Fig. 6, the ratio of As entering into the filtrate was relatively higher, which would reach up to 16% at 120 minutes at the molar ratio

Fig. 4. Potential-pH phase diagram (a) and Fraction phase diagram (b) of Pb-HNO\(_3\) leaching system (Conditions: 25 °C, Designed with MEDUSA software).

Fig. 4. (a) The molar ratio of HNO\(_3\) to Pb in the LART influence on the distribution of lead in the filtrate and residual filter cake. (b) Based on the lead distribution, the schematic of lead flow during the leaching process was proposed (b). (Here, the Residue and Filtrate was representing the lead leached into the filter and the lead left in the filter cake, respectively).
of 3. The leaching efficiencies of As at the molar ratio of 2.5 and 3 were relatively kept constant. At a smaller molar ratio of 1.5 and 2, the ratios of As entering into the filtrate generally were decreased with increasing leaching time. The ratio of Cu entering into the filtrate generally decreased rapidly with leaching time ranging from leaching beginning to 120 min. The ratio of Cu entering into the filtrate was around 0.05~0.2% at leaching time after 20 min. The leaching efficiency of Fe generally increased with leaching time ranging from reaction beginning to 120 min, while the ratio of Fe entering into the filtrate was around 0.5~0.7% at terminal of leaching process. The leaching efficiency of Al would fluctuate between 0.6~1.3% during the leaching process. Under higher molar ratio of 3, the ratio of Al in the filtrate would be highest, indicating that more Al containing compound would be reacted with more nitric acid in the leaching system.

Fig. 5. Leaching efficiency of impurity elements with leaching time at different molar ratio of HNO$_3$ to Pb in the LATR (Conditions: stirring speed of 400 rpm at 25 °C): (a) As, (b) Cu, (c) Fe, and (d) Al.

The Potential-pH diagram of typical impurity element including Sn, As, Fe, and Al in the leaching system could be revealed in Fig. S2. As shown in Fig. S2(a), the dominant phase for Sn element was mainly SnO$_2$ at pH ranging from 1 to 12 at potential of more than 0V, indicating that the Sn was merely measured in the filtrate (Table. S2). This result demonstrated that the SnO$_2$ would be left in the residue after leaching process. The dominant phase of As in the leaching system was more complicated, for the dominant phase of As would easy to be varied at varying potential. The dominant phase of Fe would be transferred from Fe$^{2+}$ ions into Fe$_2$O$_3$ (solid) with pH ranging from 1 to 12 at potential of 0V. This Potential-pH diagram result would illustrate that the ratio of Fe entering into the filtrate would increase with increasing molar ratio of HNO$_3$ to Pb in the LATR (Fig. 6). It was obvious that the dominate phase of Al was mainly Al$^{3+}$ ion in the solution, while the solid Al(OH)$_3$ was dominant phase at pH of larger
than 4.6. Thus, with more molar ratio of HNO$_3$ to Pb in the LATR in the leaching system, the pH would decrease, which would result in more Al$^{3+}$ measured in the filtrate. The XRD patterns and appearance of filter residue was shown in in Figure S3. The XRD patterns at various molar ratios were illustrating that the PbO and SnO$_2$ were main composition of the filter residue. This XRD analysis results were accordance with the Sn in the filtrate result (Fig. 6), for part of SnO$_2$ was left in the residue. The appearance of the filter residue gradually changed from yellow into light yellow with increasing molar ratio of HNO$_3$ to Pb in the LATR, which was attributed from that less PbO was left in the residue with increasing dosage of HNO$_3$ in the leaching system. The weight of filter residue after leaching and filtration was shown in Tab. S3, indicating that the weight of filter residue decreased with the increasing molar ratio of HNO$_3$ to Pb in the LATR. The decreasing of the filter residue was mainly resulting from that more PbO and element impurity in LATR have been reacted with more added HNO$_3$.

### 3.2. Synthesis of PbS crystal

The conversion rate of lead in the store filtrate solution (wt%) under various molar ratio of Na$_2$S to Pb in the filtrate was presented in Fig. 7(a). As shown, the conversion rate of lead was increased with increasing molar ratio of Na$_2$S to Pb in the filtrate ranging from 0.75 to 1.5. The reaction between the sodium sulfide and the lead nitrate in the filtrate was presented by Eq. 3, indicating that the theoretical molar ratio of sodium sulfide to lead nitrate was 1:1. With more added sodium sulfide, the lead ions in the stored filtrate would be easier to contact and react with the sulfur ion in the system, while more amount of PbS crystal would be generated, as illustrated by Fig. 7(b). The appearance of the synthetic PbS crystal product was shown in Fig. 7(I–IV), while the prepared PbS crystal products were all black powders, further confirming to the existence of PbS. From the appearance of products, not obvious appearance difference for PbS crystal was observed at different molar ratios.

$$\text{Pb(NO}_3\text{)}_2 + \text{Na}_2\text{S} \rightarrow \text{PbS} + 2\text{NaNO}_3$$

![Fig. 7](image-url)

Fig. 7. The conversion of lead in the filtrate to the PbS crystal (Conditions: stirring speed of 300 rpm, and temperature of 25 °C): (a) the conversion rate of lead at different molar ratio of Na$_2$S to Pb in the filtrate; (b) Proposed model for the synthesis of PbS crystal; (I–IV) the appearances of the products for the synthesis procedure at molar ratio of 0.75, 1, 1.25 and 1.5, respectively.

The XRD patterns of the generated PbS crystal at various molar ratios of Na$_2$S to
Pb in the filtrate was shown in the Fig. 8(a). The XRD results were indicating that all of the generated powders were pure PbS crystal (PDF: 03-0614) at various molar ratios, indicating that the prepared PbS crystal was with high purity. The SEM images of PbS crystal synthesized at molar ratio of 0.75 and 1.5 were shown in Fig. 8(b1)-(b4). As shown, not obvious difference was observed between the products at different molar ratio of Na$_2$S to Pb in the filtrate. The prepared PbS crystal was mainly rendering square blocks with varying dimension ranging among 20 and 100 nm, indicating the prepared PbS powders were mainly nano-sized materials. The crystallization process would be beneficial to the separation of other element from the lead containing crystal, due to their different crystallization performance as shown in Fig. 8(c) [28][29].

Fig. 8. The material characterization of the prepared crystal products (Conditions: stirring speed of 300 rpm, temperature at 25°C): (a) the XRD patterns; (b) the SEM diagrams ((b1, b2) the molar ratio of Na$_2$S to Pb in the filtrate=0.75, (b3, b4) the molar ratio of Na$_2$S to Pb in the filtrate=1.5); (c) the proposed model for the separation of Pb ions from the impurities

It could be revealed that most part of lead was transferred into the PbS crystal product, while only a smart part of lead was left in the filtrate. The lead distribution in the PbS crystal and filtrate was shown in Fig.S4. As shown in Fig.S4, the amount of lead in the synthetic product generally increased with an increasing molar ratio of Na$_2$S to Pb in the filtrate, which was attributed from that more lead ions would contact and react with sufficient sulfur ions with the increasing dosage of sodium sulfide reagent. The percentage of lead in the synthetic product and filtrate would be summed for more than 88% under various molar ratios as presented in Fig.S4. The sum percentage of lead was maximum at molar ratio of Na$_2$S to Pb in the filtrate was 1.5, which could attain to 94.5%.

4. Conclusion

The PbS crystal was successfully synthesized through this high-speed leaching and recrystallization method. The leaching efficiency of lead increased with an increasing molar ratio of HNO$_3$ to Pb in the LATR, which would reach up to 82.9% at the molar ratio of 3. The main metal impurities in the leaching process was Sn, As, Cu, Fe, and Al. The ratio of As, Cu, Fe, and Al entering into the filtrate increased when the
molar ratio of HNO₃ to Pb in the LATR increasing from 1.5 to 3, while the ratio of Sn entering into the filtrate was only 0.002% at the molar ratio of 3. The yield of PbS crystal would increase with increasing molar ratio of Na₂S to Pb in the filtrate, which could reach up to 93.1% at the molar ratio of Na₂S to Pb in the filtrate as 1.5. As shown in the XRD patterns of the product, the product was relatively pure crystal of PbS. The method could provide a green route for the efficient recovery of lead from waste lead ash at room temperature, which would not generate lead particles and high energy consumption. In the future recycling process, the recovery of Sn and other precious metals should be further considered.

Acknowledgments

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[28] Meng W, Yuan W, Wu Z, et al., Powder. Technol., 347 (2019) 130-135.
(1) Fig. 1. Proposed schematic diagram of the entire study.

(2) Fig. 2. The characterization of the original LATR: (a) The appearance of LATR packed in the test tube; (b) The concentration of main metal elements in LATR samples; (c) The XRD pattern of original LATR; (d) The SEM image of LATR, Mag of 1 kX.

(3) Fig. 3. Effect of molar ratios of HNO₃ to Pb in LART on leaching efficiency of Pb from LART. Conditions: stirring speed of 400 rpm, at 25 °C.

(4) Fig. 4. Potential-pH phase diagram (a) and Fraction phase diagram (b) of Pb-HNO₃ leaching system. Conditions: 25 °C. Designed with MEDUSA software.

(5) Fig. 5. The molar ratio of HNO₃ to Pb in the LART influence on the distribution of lead in the filtrate and residual filter cake (a). Based on the lead distribution, the schematic of lead flow during the leaching process was proposed (b). Here, the Residue and Filtrate was representing the lead leached into the filter and the lead left in the filter cake, respectively.

(6) Fig. 6. Leaching efficiency of impurity elements with leaching time at different molar ratio of HNO₃ to Pb in the LART: (a) As, (b) Cu, (c) Fe, and (d) Al. Conditions: stirring speed of 400 rpm at 25 °C.

(7) Fig. 7. The conversion rate of lead at different molar ratio of Na₂S to Pb in the filtrate for the synthesis procedure (a); Proposed model for the synthesis of PbS crystal (b); the appearances of the products for the synthesis procedure at molar ratio of 0.75, 1, 1.25 and 1.5 (I–IV), respectively. Conditions: stirring speed of 300 rpm, temperature at 25 °C.

(8) Fig. 8. The XRD patterns of the synthesized products with disparate Na₂S to Pb in the filtrate molar ratios (a); Synthesis products SEM diagrams (The molar ratio of Na₂S to Pb in the filtrate=0.75 (b₁, b₂), The molar ratio of Na₂S to Pb in the filtrate=1.5 (b₃, b₄)), (b₁ and b₃ was with Mag of 2 kX, while b₂ and b₄ was with Mag of 1 kX.). Conditions: stirring speed of 300 rpm, temperature at 25°C.
Supplementary File

An Efficient and Environmental Friendly Route for PbS Crystal Recovery from Lead Ash Generated in Tin Removal Section (LATR) via High-speed Leaching and Recrystallization method

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Tab. S1. Leaching experimental material dosing scheme.

| No. | Mass (g) | Mole (mol) | Mole of HNO$_3$ to Pb in the LATR | Mole of HNO$_3$ (mol) | Adjusted concentration of HNO$_3$ (mol/L) | Volume of HNO$_3$ (mL) |
|-----|----------|------------|----------------------------------|------------------------|------------------------------------------|------------------------|
| 1   | 50       | 0.1824     | 1.5                              | 0.2736                 | 0.6                                      |                        |
| 2   | 50       | 0.1824     | 2                                | 0.3648                 | 0.8                                      | 456                    |
| 3   | 2.5      | 0.456      | 2.5                              | 0.456                  | 1.0                                      |                        |
| 4   | 3        | 0.5472     | 3                                | 0.5472                 | 1.2                                      |                        |
| NO. | Leaching filtrate | Dosage of sodium sulfide |
|-----|------------------|--------------------------|
|     | Volume (mL)      | Mole of Pb in the filtrate (mol) | Mass of Pb in the filtrate (g) | Molar ratio of Na₂S/Pb in the filtrate | Mole (mol) | Mass (g) |
| I   | 50               | 0.0179                    | 3.6967                          | 0.75                                     | 0.0134     | 3.2244    |
| II  | 50               | 1.00                       |                                  | 1.00                                     | 0.0179     | 4.2992    |
| III | 50               | 0.0179                    | 3.6967                          | 1.25                                     | 0.0224     | 5.3739    |
| IV  | 50               | 1.00                       |                                  | 1.50                                     | 0.0269     | 6.4535    |
| Molar ratio of HNO₃/Pb in the LATR | 1.5 | 2  | 2.5 | 3  |
|-----------------------------------|-----|----|-----|----|
| Filter residue weight (g)         | 20.88 | 17.07 | 15.75 | 14.85 |
| Percentage of filter residue/LATR (wt%) | 41.76 | 34.14 | 31.50 | 29.70 |
Tab. S4. Ratio of metal impurity entering into the filtrate under different molar ratio of HNO$_3$ to Pb in the LATR at leaching terminal of 120 min.

| Metal impurity | Initial mass of metal impurity in 50 g of LART (mg) | Leaching process: various molar ratio of HNO$_3$ to Pb in the LATR | Amount of metal impurity entering into the filtrate (mg) | Ratio of metal impurity entering into the filtrate (wt%) |
|----------------|-----------------------------------------------|---------------------------------------------------------------|-------------------------------------------------|-----------------------------------------------|
| Sn             | 3619.25                                       | 1.5                                                          | 0.0036                                         | 0.0001                                         |
|                |                                               | 2                                                            | 0.0036                                         | 0.0001                                         |
|                |                                               | 2.5                                                          | 0.0072                                         | 0.0002                                         |
|                |                                               | 3                                                            | 0.0072                                         | 0.0002                                         |
| As             | 654.5                                         | 1.5                                                          | 0.91644                                        | 0.14                                           |
|                |                                               | 2                                                            | 34.6938                                        | 5.30                                           |
|                |                                               | 2.5                                                          | 101.20                                         | 15.46                                          |
|                |                                               | 3                                                            | 104.87                                         | 16.02                                          |
| Fe             | 34.95                                         | 1.5                                                          | 0.2586                                         | 0.74                                           |
|                |                                               | 2                                                            | 0.2062                                         | 0.59                                           |
|                |                                               | 2.5                                                          | 0.2447                                         | 0.70                                           |
|                |                                               | 3                                                            | 0.2447                                         | 0.70                                           |
| Cu             | 11.6                                          | 1.5                                                          | 0.0046                                         | 0.04                                           |
|                |                                               | 2                                                            | 0.0046                                         | 0.04                                           |
|                |                                               | 2.5                                                          | 0.0092                                         | 0.08                                           |
|                |                                               | 3                                                            | 0.0184                                         | 0.16                                           |
| Al             | 6.4                                           | 1.5                                                          | 0.0365                                         | 0.57                                           |
|                |                                               | 2                                                            | 0.0410                                         | 0.64                                           |
|                |                                               | 2.5                                                          | 0.0550                                         | 0.86                                           |
|                |                                               | 3                                                            | 0.0819                                         | 1.28                                           |
Fig. S1. Experimental process diagram of LATR leaching and PbS crystal synthesis.
Fig. S2. Potential-pH phase diagrams for main metal impurities in the presence of nitric acid in leaching system: (a) Sn; (b) As; (c) Fe; (d) Al, at 25 °C. Designed with MEDUSA software.
Fig. S3. XRD patterns, real picture of leaching residues and post-reaction solution with various molar ratio of HNO$_3$ to Pb in the LATR: (a) Molar ratio of 1.5; (b) Molar ratio of 2.0; (c) Molar ratio of 2.5; (d) Molar ratio of 3.0.
Fig. S4. The molar ratio of Na$_2$S to Pb in the filtrate influence on the percent of lead (wt%) in the product and filtrate. Here, the Filter and Product was representing the lead left in the filter and transferred into the product, respectively.
EDTA-2Na Testing Method.

Pipette 3 mL of filtrate into a 250 mL erlenmeyer flask and dilute with water to about 90 mL. The pH of the solution was adjusted to 5 ~ 6 with 1 : 1 ammonia water, while 5 mL of 20% sodium acetate solution and 5 mL of 20% hexamethylenetetramine were used as buffer solutions to stabilize the pH. Add 3 drops of 0.5% xylene orange indicator and shake well. At this time, the solution is purple-red. Titrate with the 0.05 mol/L EDTA-2Na standard solution after calibration until the solution changes from purple-red to bright yellow. Record the amount of EDTA-2Na standard solution as \( v_{4E} \), then the lead ion concentration was shown as Eq. (S1):

\[
m_4 = c_4 \times v_{4E} \times m_r / v_4
\]

(S1)

Where \( m_4 \) is the concentration of the lead ion, g/L; \( c_4 \) is the concentration of the EDTA-2Na, mol/L; \( v_{4E} \) stands the dosage of EDTA-2Na, mL; \( m_r \) is the relative molecular weight of lead, g/mol, 207.1; \( v_4 \) is the filtrate volume, mL, take 3 mL at this experiment.

Determination of the impurity elements in the LATR.

LATR materias (0.2 g) was placed in a beaker (50 mL), then adding 15.0 mL of aqua regia into the beaker. The slurry containing LATR materias and aqua regia was heated at 200 °C until no obvious particle solid was observed in the slurry. The dilute nitric acid solution (3% wt) was added into the slurry until the volume reaching up to 30 mL, then cooling down to room temperature. The slurry was finally filtered through microporous filter membrane and diluted into a 50 mL colorimetric tube. The concentration of impurities in the filtrate was eventually determined by ICP-OES 5100 (Keysight Technologies).