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RESEARCH PROGRESS OF DESULPHURIZATION METHODS FOR SCRAP LEAD PASTE

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ABSTRACT
Different desulphurization methods for scrap lead paste have been introduced. At this stage, the major methods are pyrometallurgy and hydrometallurgy. The first one is the general used method to recovery scrap lead acid batteries. It shows faster reaction speed, great handing capacity, higher production efficiency and well adapt for raw material, but products secondary pollutants of lead dust and sulfur dioxide on these processes. The second one shows favorable environmental benefit for lower pollution, higher controllability, greater security and higher metal recovery rate, but it exists the problem of higher requirement for production equipment, higher energy consumption and longer technological processes.

Keywords: Desulphurization, Scrap lead paste, Hydrometallurgy, Pyrometallurgy, Lead acid batteries, Recovery.

Contribution/ Originality
The paper's primary contribution is introducing the major desulphurization methods for scrap lead paste.

1. INTRODUCTION
At present, lead acid battery is one kind of widespread used second batteries for the advantages of simple construction, reliable performance, lower price, easy get of raw materials and convenient to use [1, 2]. It is major used as power source for automobile start and as auxiliary power supply for illumination, mintype electric vehicle and UPS [3-5]. Lead acid battery is the primary consumption product all over the world, however, it also become the major lead renewable resources. Lead is a kind of highly toxic heavy metal, therefore, recycling and reusing of lead from scrap lead acid battery is very important in the environmental view. When charging, the cathode material of lead acid battery turns into PbO_2 and anode material turns into

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Pb. While discharge, the cathode and anode electrode active materials all turn into $PbSO_4$. The reaction of materials while discharge as follows,

Cathode reaction, $PbO_2 + HSO_4^- + 3H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$

Anode reaction, $Pb + HSO_4^- \longrightarrow PbSO_4 + H^+ + 2e^-$

Overall reaction, $Pb + PbO_2 + 2H_2SO_4 \longrightarrow PbSO_4 + 2H_2O$

The manufacturing processes of lead acid battery main contain exploit and transformation of resource, preparation of materials for batteries and assemble of batteries. Among the process of preparation of materials for batteries and assemble of batteries, in especially among the process of preparation of electrodes, plenty of lead pastes will fall off as scrap lead pastes. Cyclic utilization of them is a significance measure which should reduce the batteries production fee and environmental pollution by heavy metal lead. The scrap lead pastes mainly contain $PbSO_4$ and PbO_2; therefore, desulphurization methods for scrap lead pastes are very important among cyclic utilization of scrap lead pastes. At this stage, the major methods are pyrometallurgy and hydrometallurgy.

2. PYROMETALLURGY METHOD

Pyrometallurgy method [6, 7] by adding reductive agent such as carbon powder, iron scrap and $Na_2C_2O_4$, using professional furnace type such as reverberatory, rotary furnace and blast furnace to smelt then get pure lead.

This method shows the advantages of follows: the process is simple and operation is easy. But it also shows the disadvantage, the temperature among these desulphurization processes is higher than 1000 °C because the smelt temperature of $PbSO_4$ is higher than this, therefore, energy consumption is higher while use this method. These processes like as fig 1.

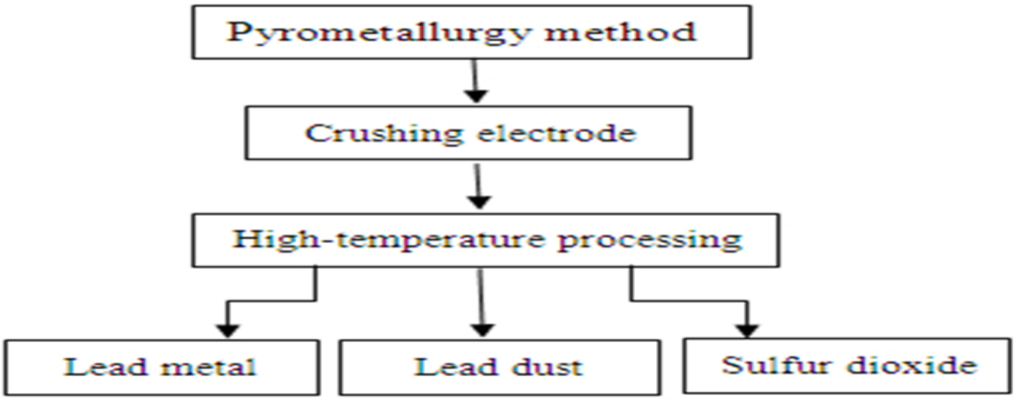

Fig-1. Pyrometallurgies processing to desulphurization for scrap lead paste

3. HYDROMETALLURGY METHOD

This technology usually uses desulfurization agent (such as Na_2CO_3, $(NH_4)_2CO_3$ [8], $NaHCO_3$, NH_4HCO_3, NaOH, sodium citrate, citric acid, acetic acid, sodium acetic and so on) make $PbSO_4$ transform to $PbCO_3$, lead citrate or lead acetic, Then with high temperature (300 °C~500 °C) to get PbO or leaching to get Pb. At the first step, SO_4^{2-} from $PbSO_4$ will turn to $(NH_4)_2SO_4$ or Na_2SO_4, not contain SO_2, and $(NH_4)_2SO_4$ should be used as a chemical fertilizer. These processes like as fig 2.

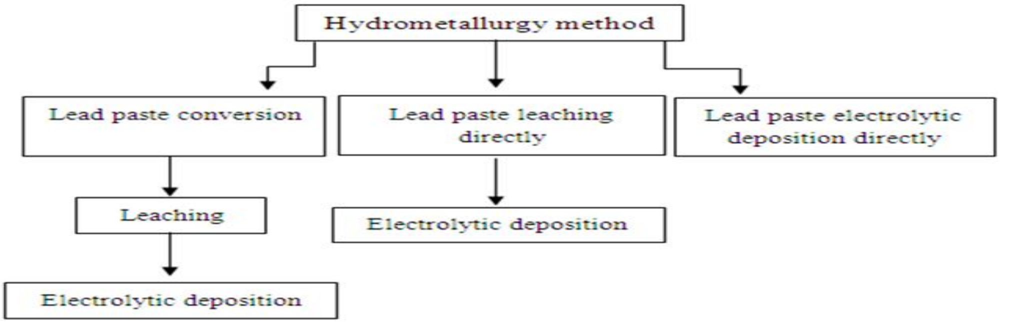

Fig-2. Hydrometallurgies processing to desulphurization for scrap lead paste

3.1. Carbonate as Desulfurization Agent

Carbonate is a kind of usually used desulfurization agent [9, 10] to dispose with scrap lead paste. RSR [11, 12] and USBM [13] technologies use $(NH_4)_2CO_3$ as desulfurization agent, CX-EW [14] technology uses Na_2CO_3 as desulfurization agent. When this kind of desulfurization agent be used, lead sulfate ($PbSO_4$) will translate into lead carbonate ($PbCO_3$), sodium sulfate (Na_2SO_4) or ammonium sulfate ($(NH_4)_2SO_4$). Na_2SO_4 or $(NH_4)_2SO_4$ should be solute in aqueous solution, but $PbCO_3$ not be solute in aqueous solution, SO_4^{2-} and Pb^{2+} will be isolated then get the aim of desulfurization. Na_2SO_4 or $(NH_4)_2SO_4$ should be recycled after evaporative crystallization as chemical products; $PbCO_3$ should be translated into lead (Pb) or lead oxide (PbO) after be leached or heated. These processes like as fig 3. When electrolytic 24 h at the current density of $180 A \cdot m^{-2}$, the current rate is 97%, energy consumption is lower than $700 kWh \cdot t^{-1} Pb$.

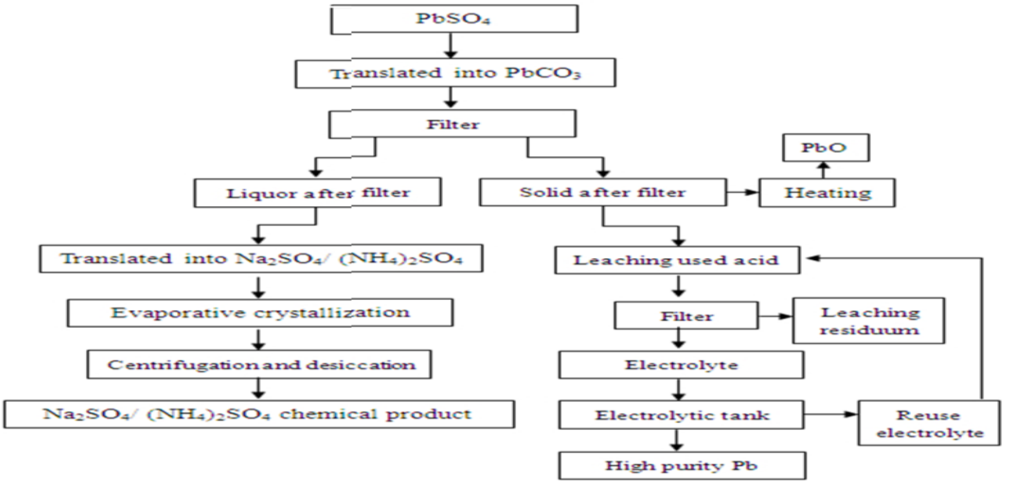

Fig-3. Hydrometallurgies processing used carbonate as desulfurization agent

3.2. NaOH as Desulfurization Agent

$NaOH-KNaC_4H_4O_6$ technology [15, 16] uses NaOH as desulfurization agent. When this kind of desulfurization agent be used, lead sulfate ($PbSO_4$) will translate into lead oxide (PbO) and sodium sulfate (Na_2SO_4). Na_2SO_4 should solute in aqueous solution, but PbO not solute in aqueous solution, SO_4^{2-} and Pb^{2+} will be isolated and get the aim of desulfurization. Na_2SO_4 should be recycled after evaporative crystallization as chemical product; PbO should be translated into lead (Pb) after used NaOH-$KNaC_4H_4O_6$ dissolve and then electrolyze. These processes like as fig 4. Lead powder with purity of 99.99% should be get and current efficient is attained 98% used this method.

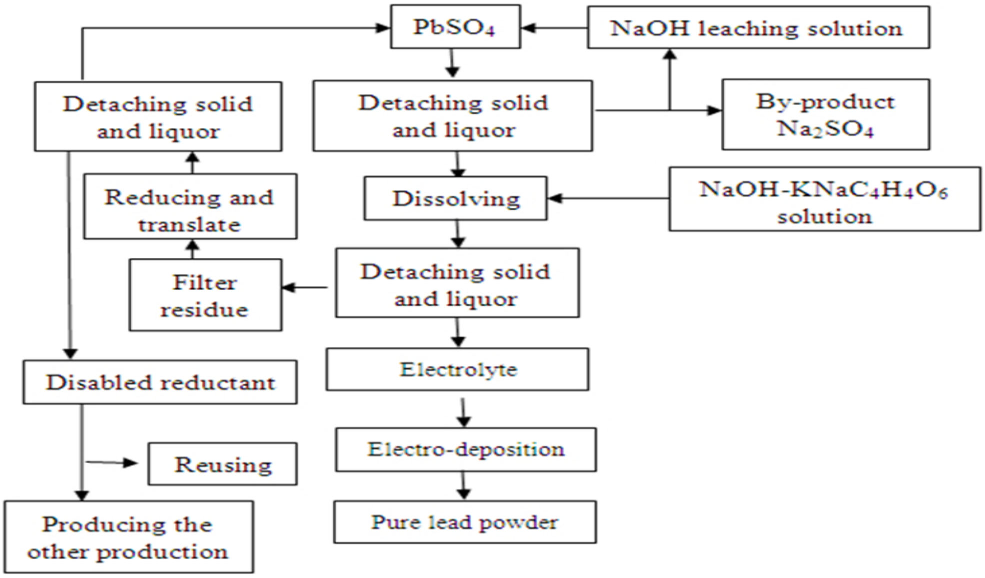

Fig-4. Hydrometallurgies processing used NaOH as desulfurization agent

3.3. NaCl-HCl as Desulfurization Agent

NaCl-HCl is used as desulfurization agent in placid technology [17]; lead sulfate ($PbSO_4$) will be translated into lead chloride (PbCl) and sodium sulfate (Na_2SO_4). PbCl should be translated into lead (Pb) after electro-deposition; Na_2SO_4 should be recycled after evaporative crystallization as chemical product. This method shows easy operation, clean production and high efficiency during these processes, but meantime shows higher energy consumption (1300 $kWh\cdot t^{-1}$Pb).

3.4. Citric Acid-Sodium Citrate as Desulfurization Agent

When used citric acid-sodium citrate ($C_6H_8O_7\cdot H_2O$-$Na_3C_6H_5O_7\cdot H_2O$) as desulfurization agent [18-22], lead sulfate ($PbSO_4$) will be translated into lead citrate ($Pb_3\ (C_6H_5O_7)_2\cdot H_2O$) and sodium sulfate ($Na_2SO_4$). $Pb_3\ (C_6H_5O_7)_2\cdot H_2O$ should be translated into lead oxide (PbO) after calcinations at 300-400 °C; Na_2SO_4 should be recycled after evaporative crystallization as chemical product. These processes like as fig 5 and the reaction as follows,

$$3PbSO_4 + 2Na_3C_6H_5O_7\cdot H_2O \longrightarrow Pb_3\ (C_6H_5O_7)_2\cdot H_2O + 3\ Na_2SO_4 + H_2O$$

$$Pb_3\ (C_6H_5O_7)_2\cdot H_2O + 9\ O_2 \longrightarrow 3PbO + 12\ CO_2\uparrow + 6H_2O$$

The recycle rate of lead is more than 95% during this desulfurization method, SO_2 will not be produced and among these processes the calcinations temperature just at 300-400 °C, lower than the temperature of pyrometallurgy method (higher than 1000 °C), energy consumption is lower. Therefore, this desulfurization method is an environmental and economical method for recycling scrap lead paste.

3.5. Sulfate-Reducing Bacteria as Desulfurization Agent

CX-EWS technology [23] uses sulfate-reducing bacteria as desulfurization agent. When use this kind of desulfurization agent, lead sulfate ($PbSO_4$) will be translated into lead sulfide (PbS), then Fe $(BF_4)_3$ will be used as oxidizing and leaching agent to oxidize S^{2-} into simple substance sulfur (S) and lead solution should be translated into lead (Pb) by electro-deposition. These processes like as fig 6. In these processes, for $PbSO_4$, in the condition of 19 kg $PbSO_4$ $m^{-3}\cdot d$, $PbSO_4$ almost be translated completely. In the generated crystal lead phase, the concentrate of PbS is more than 98%.

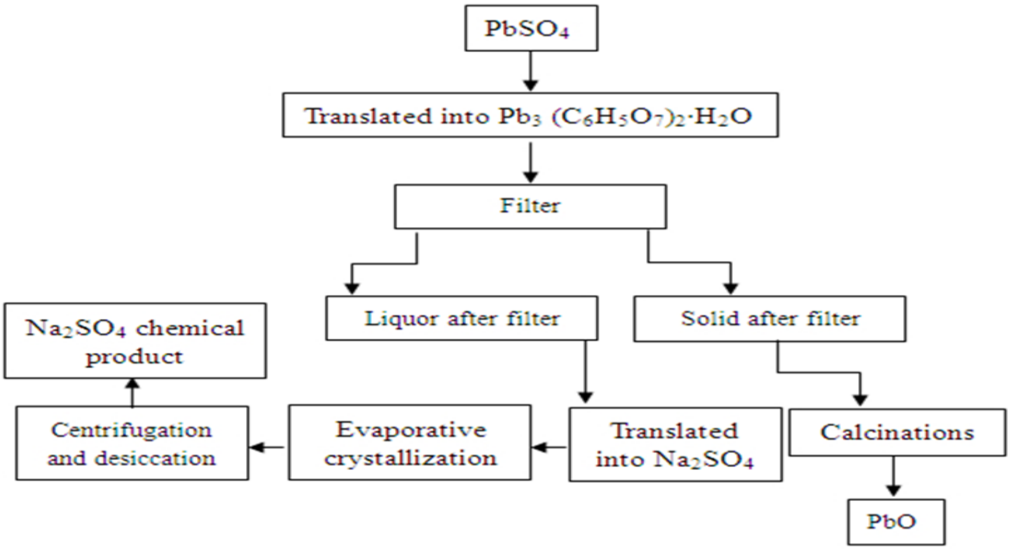

Fig-5. Hydrometallurgies processing used $C_6H_8O_7\cdot H_2O$-$Na_3C_6H_5O_7\cdot H_2O$ as desulfurization agent

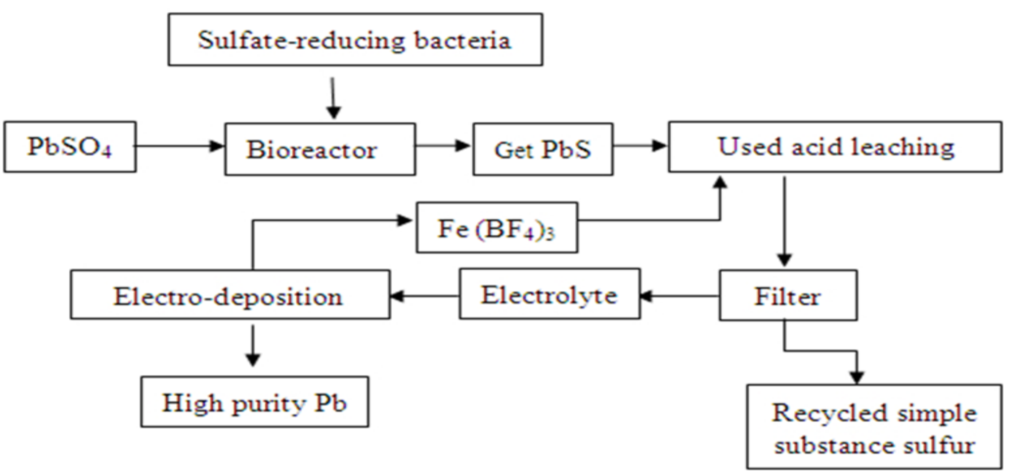

Fig-6. Hydrometallurgies processing used sulfate-reducing bacteria as desulfurization agent

4. CONCLUSIONS

Desulphurization methods for scrap lead paste are important among cyclic utilization of scrap lead paste. Desulphurization methods major contain pyrometallurgy method and hydrometallurgy method. Energy consumption is higher and the gas of SO_2 will produce during pyrometallurgy processes. Therefore, pyrometallurgy method is not environmental. Hydrometallurgy technology usually used different desulfurization agents to translate $PbSO_4$ to

$PbCO_3$, lead citrate, lead acetic, Then with high temperature (300 °C~500 °C) to get PbO or leaching to get Pb. This technology not product SO_2, Therefore, it is environmental.

5. ACKNOWLEDGEMENTS

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