

ACID ELECTROLYTIC TREATMENT PROCESS OF SCRAP BATTERY SLUDGE^①

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ABSTRACT The physicochemical problems involved in the process of recovering lead from scrap battery sludge by a new acid electrolytic method have been investigated adopting electrochemical method. The new techniques developed include the utilization of K_2CO_3 as desulphurizer, $FeSO_4-H_2SO_4$ system in reducing-converting, and $PbSiF_6-H_2SiF_6$ as electrolyte in electrowinning. Under experimental conditions, lead greater than 99.99% in purity was obtained with current efficiency greater than 98%, lead direct recovery above 95%, lead total recovery higher than 98%. Research and analysis showed that this process has many advantages, such as strong chemical driving force, stable operation and high lead recovery.

Key words lead battery sludge acid electrolytic treatment

1 INTRODUCTION

The key link in various hydrometallurgical treatments for recovering lead from scrap batteries is to develop and select proper technical method for the treatment of battery sludge^[1]. The solution to the basic theoretical problems of the process is of significance for further research on hydrometallurgical recovery technology^[2, 3]. This paper has further developed a new acid electrolytic method for the treatment of scrap battery sludge, and discussed some physicochemical problems involved.

2 MATERIALS AND PROCEDURES

The lead-containing components of scrap batteries mainly consist of grids and sludge, either of which accounts for 50% their total mass. Generally, the grids are melted, refined and adjusted for later use in making new grids for manufacturing new lead batteries. The sludge is composed of $PbSO_4$, PbO_2 , PbO and fine lead metal. In the new process recommended in this paper, insoluble lead compounds in sludge are converted to soluble lead compounds through

sweetening and reducing-converting, which was followed by electrowinning with $PbSiF_6-H_2SiF_6$ electrolyte to obtain pure lead powder.

3 RESULTS AND DISCUSSION

3.1 Desulphurization

Fig. 1 is plotted according to thermodynamic data which shows thermodynamic stability range of lead compounds in aqueous solution containing carbonate salt^[4].

Under the condition of coexistence of sulfate ions and carbonate ions in reaction system, solid $PbCO_3$ is stable while pH value of the solution is between 6 and 10. However, if pH value goes higher, solid $PbCO_3$ will be converted to basic lead carbonate ($2PbCO_3 \cdot Pb(OH)_2$) or even to soluble plumbate. Therefore, stable solid $PbCO_3$ can be obtained by converting $PbSO_4$ with carbonate salt in a proper pH range.

Much research work had been done as to the application of $(NH_4)_2CO_3$ or Na_2CO_3 as desulphurizer for $PbSO_4$. Instead, K_2CO_3 was used for that purpose in this paper, which is free of volatility and possesses a larger solubility than Na_2CO_3 . The characteristic of this new desulf-

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phurizer was explored by experiment. Eqn. (1) describes the desulphuring reaction for PbSO_4 in sludge.

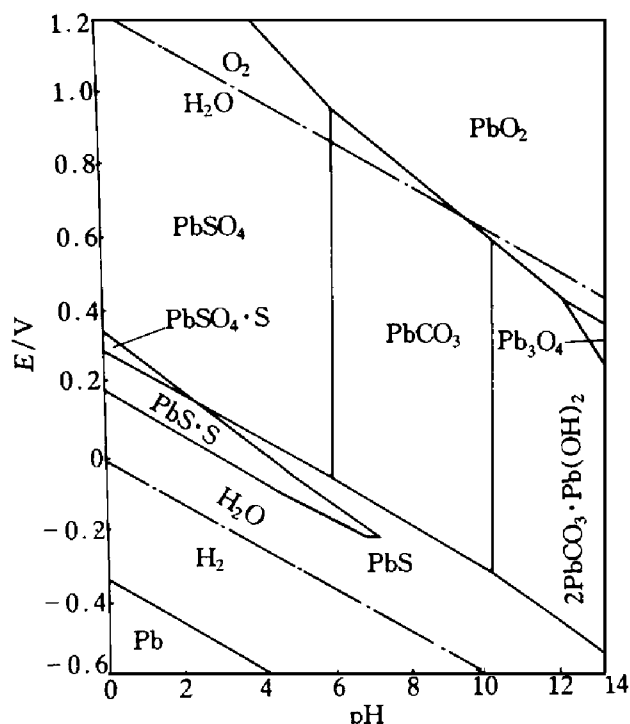


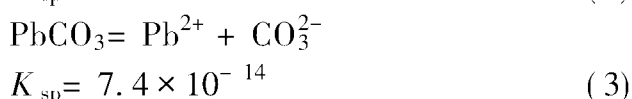
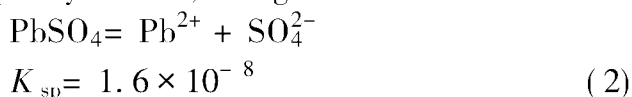
Fig. 1 Stability graph of lead compound in aqueous solution

(25 °C; total sulphur $a = 10^{-1.5} \text{ mol/L}$;
total carbon $a = 10^{-1} \text{ mol/L}$)

Thermodynamic calculation brings out the change in free enthalpy in Eqn. (1) as follows^[5]:

$$\Delta G^\ominus / \text{kJ} = -38.6 < 0$$

So the reaction is a spontaneous process. Solubility products of PbSO_4 and PbCO_3 , both of which are poorly soluble, are given as below^[6].



It is obvious through comparison that the solubility product of PbSO_4 is 10^6 times larger than that of PbCO_3 , which leads to the conclusion that PbCO_3 created in Eqn. (1) is a much more stable solid than PbSO_4 ($\text{pH} = 6 \sim 10$), moreover, the thermodynamic driving force of the related reaction is enormous.

Based on the results of orthogonal experiments, technical conditions for sweetening operation were chosen as follows^[7]:

Parameter	Value selected
$\text{K}_2\text{CO}_3 : \text{PbSO}_4$	1.5: 1 (in mole)
Temperature/ °C	60
Particle size (PbSO_4) / mm	0.125 ~ 0.15
$\text{H}_2\text{O} : [\text{PbSO}_4 + \text{K}_2\text{CO}_3]$	4: 1, (in mass)

It turned out at the end of 1.5 h of reaction that the desulphurization efficiency reached 100%.

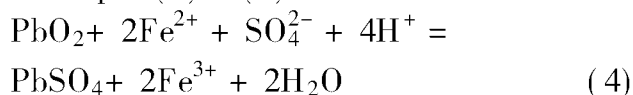
3.2 Reduction conversion

So far as reduction of PbO_2 and conversion of fine lead metal in sludge were concerned in various hydrometallurgical treatments, many methods had been studied, using respectively sulfite, thiosulfate, H_2O_2 , SO_2 , fine lead powder and so on as reductive agents. The common drawbacks of the methods mentioned above involve instability of reducing agent, comparatively low reaction rate and difficulty in separating reductive product from reducing agent^[1, 8]. In this work $\text{FeSO}_4\text{-H}_2\text{SO}_4$ was used as reducing agent. Fig. 2 shows $E\text{-pH}$ graph of $\text{Pb-SO}_4^{2-}\text{-H}_2\text{O}$ and $\text{Fe-H}_2\text{O}$ composite system, which is plotted according to concerned thermodynamic data in literatures^[9, 10].

Lines 1 ~ 14 constitute $\text{Pb-SO}_4^{2-}\text{-H}_2\text{O}$ system and lines 15 ~ 21 constitute $\text{Fe-H}_2\text{O}$ system. Line *a* and line *b* respectively correspond to the upper limit and lower limit on the existence of stable H_2O .

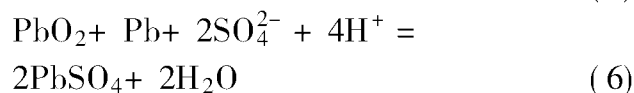
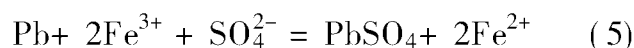
The stable area of PbSO_4 is enclosed by lines 6, 1, 2, 7 and 5. When pH value is lower than 1.617^[10], the $\text{Fe}^{3+} / \text{Fe}^{2+}$ line (i. e. line 18) is below the $\text{PbO}_2 / \text{PbSO}_4$ line (which is composed of lines 5 and 7), and the electric potential gap between them is wide, which indicates, from a thermodynamic point of view, that the driving force for reducing PbO_2 into PbSO_4 by Fe^{2+} is great, and that the formation of $\text{Fe}(\text{OH})_3$ precipitate is unlikely and the separation of Fe^{2+} from PbSO_4 is easy. Similarly, if Pb exists in the system, the $\text{Fe}^{3+} / \text{Fe}^{2+}$ line is above the $\text{PbSO}_4 / \text{Pb}$ line (which is composed of lines 1 and 6),

and the electric potential gap between them is also wide, which indicates, from a thermodynamic point of view, that the driving force for oxidizing Pb with Fe^{3+} into PbSO_4 is great, and Fe^{2+} produced is beneficial to the reduction of PbO_2 . When sulfite is used as reducing agent as in other methods, disproportionated reaction is likely to occur SO_3^{2-} , with the result that solid PbS produced, in which conversion to soluble is very difficult. And then the lead recovery ratio is brought down. The use of FeSO_4 - H_2SO_4 as reducing agent excludes the possibility of the occurrence of disproportionated reaction so that the lead recovery is improved. Reactions involved are given in Eqns. (4) ~ (6).



When fine lead metal exists in sludge, Eqns. (5) and (6) indicate the reactions likely to

occur.



Based on the results of the experiments conducted, technical conditions for reducing-converting operation were chosen as below.

Parameter	Value Selected
FeSO_4 : H_2SO_4 : PbO_2	6: 4: 1, (in mole)
temperature/ $^{\circ}\text{C}$	40 ± 5
testing time/h	3

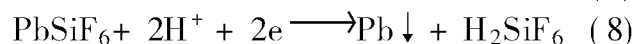
Results: reductive ratio of PbO_2 reached 97.5% with a complete conversion of Pb. Reductive ratio doubled in comparison with that of sulfite reducing experiments^[7].

3.3 Electrowinning

The residue from sweetening operation was leached with H_2SiF_6 to dissolve PbCO_3 and PbO within. After solid-liquid separation, the residue obtained, which mainly contained PbO_2 and fine lead metal, was recycled in reducing converting operation. The PbSiF_6 filtrate would be used as electrolyte in electrowinning.

Cathode process of electrowinning in Pb^{2+} - SiF_6^{2-} electrolytic system was studied by applying dynamic potential method with 217-type calomel electrodes (saturated) as reference electrodes and carbon electrodes as auxiliary electrodes. Fig. 3 presents polarization curves of cathode in simple Pb^{2+} - SiF_6^{2-} system and in Pb^{2+} - SiF_6^{2-} system into which H_3PO_4 was added.

With cathode overpotential going higher, reactions during electrowinning gradually changed from eqn. (7) to eqn. (8).



Curve 2~3 are cathode polarization curves under the condition that 2 g/L and 4 g/L of phosphorus (in phosphate ions) are added respectively, which show much similarity to curve 1. Thus a conclusion is drawn that phosphate ions have minimum effect on cathode reaction^[2]. However, it was observed in technical tests that when electrolyte was free of phosphate ions, e^-

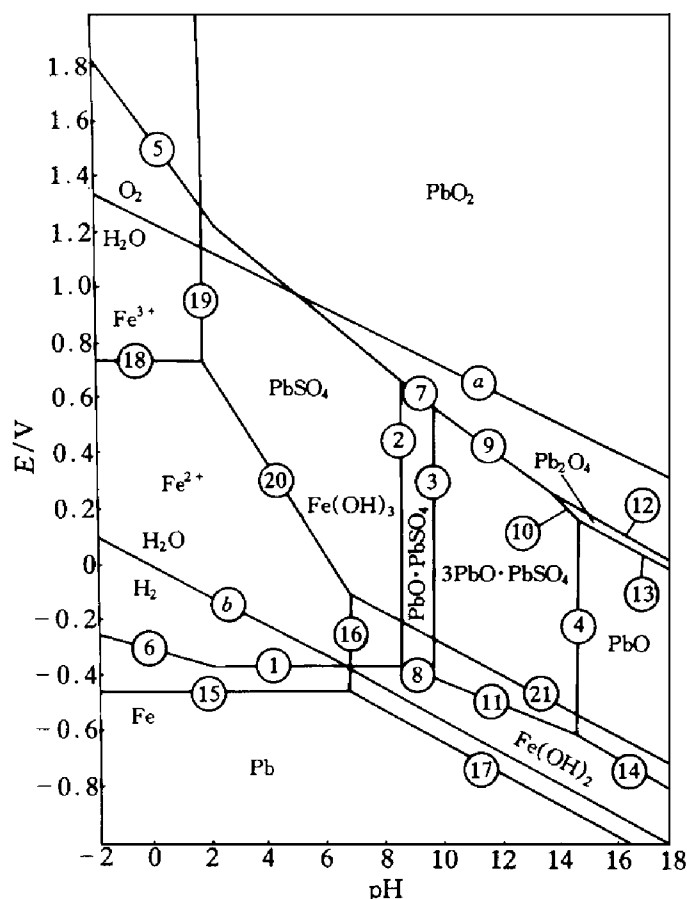


Fig. 2 E -pH graph of Pb-SO_4^{2-} - H_2O and $\text{Fe-H}_2\text{O}$ composite system

(25 $^{\circ}\text{C}$, the value of activity of each material concerned is 1 except H^+)

quimolar PbO_2 was produced on anodes. Conversely, when phosphate in electrolyte was between 1 g/L and 3 g/L, the amount of PbO_2 formed on anodes was less than 1% of the amount of Pb formed on cathodes. These facts show that the addition of phosphate ions primarily benefits anode process^[7].

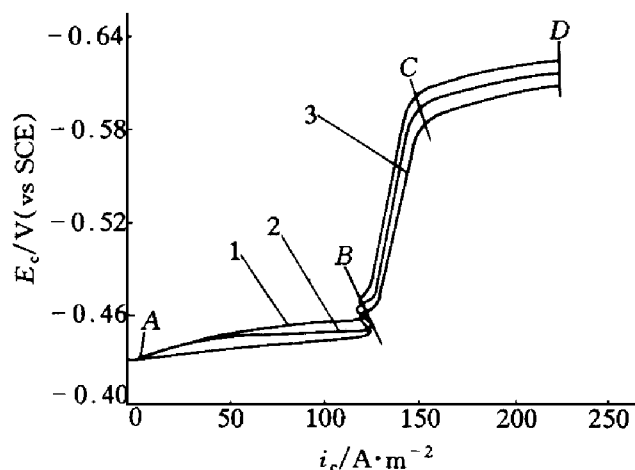


Fig. 3 Effect of H_3PO_4 added to Pb^{2+} – SiF_6^{2-} system on cathode polarization

P content: 1—0g/L, 2—2g/L, 3—4g/L;
Pb content: 40g/L; H_2SiF_6 content: 90g/L

Fig. 4 contains the cathode polarization curves for experiments using electrolyte with varied free H_2SiF_6 concentration and a given lead content. It can be seen from Fig. 4 that the difference in free H_2SiF_6 concentration in electrolyte does not affect balanced electric potential much. The promotion of H_2SiF_6 concentration in electrolyte, on one hand, reduces average free Pb^{2+} concentration, which causes the value of balanced electric potential to become negative; on the other hand, adds to the conductivity of electrolyte and increases free Pb^{2+} content in the part of the solution near the surface of electrodes, which causes the value of balanced electric potential to become positive. The cooperation of these two actions leads to small changes in balanced electric potential. It is advisable for the purpose of reducing power consumption to maintain a certain free H_2SiF_6 concentration in electrolyte which can improve the conductivity of electrolyte and produce a lower cell voltage in case of high current density. Furthermore, it

can prevent hydrolysis of primary salt, caused by deficiency of free acid, which is not favorable for electrowinning. Eqn. (9) illustrates the hydrolytic reaction.

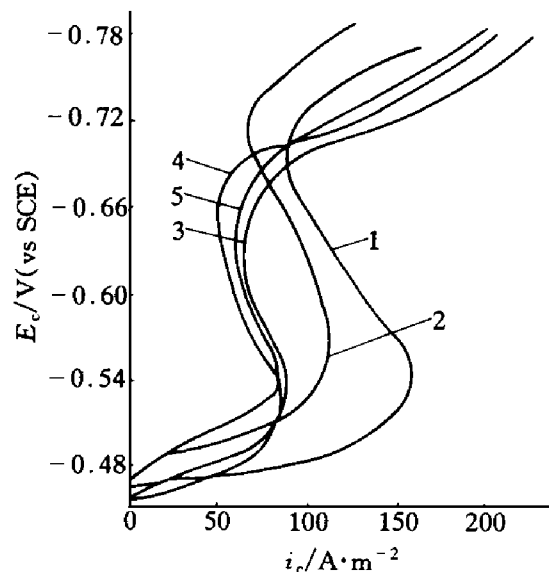
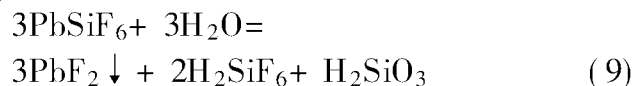


Fig. 4 Effect of free H_2SiF_6 content on cathode polarization

H_2SiF_6 content: 1—30 g/L, 2—60 g/L, 3—90 g/L, 4—120 g/L, 5—150 g/L;
Pb content: 40 g/L; P content: 2 g/L;
lignin sodium sulphonate: 4 g/L

Fig. 5 indicates the cathode polarization curves when lignin sodium sulphonate is added into electrolyte. The addition of sulphonate restrains the occurrence of the reaction followed: $\text{Pb}^{2+} + 2e \longrightarrow \text{Pb} \downarrow$. When 4g/L of the agent is added electrowinning is controlled by electrochemical polarization. The promoted polarizability of cathode prevents crystal grains of lead from going larger during electrowinning and enhances the formation of crystal nuclei, which is conducive to the formation of polycrystalline, fine and sponge-like lead deposit—fine lead metal products of relatively high standard.

On the basis of cathode process and technical experiments of electrowinning, technical conditions for electrolysis were determined as below:

Parameter	Value selected
Pb concentration/ $\text{g} \cdot \text{L}^{-1}$	40~ 120
H_2SiF_6 concentration/ $\text{g} \cdot \text{L}^{-1}$	90~ 120

phosphorus content/ $\text{g} \cdot \text{L}^{-1}$	1~ 3
lignin sodium sulphonate/ $\text{g} \cdot \text{L}^{-1}$	4
current density/ $\text{A} \cdot \text{m}^{-2}$	150~ 250
temperature/ $^{\circ}\text{C}$	40

The outcome of the experiments conducted under the above conditions was as below:

current efficiency/%	99.5
depositing rate of lead/ $\text{g} \cdot \text{h}^{-1} \cdot \text{dm}^{-2}$	8.2
purity of lead obtained/%	> 99.99
PbO_2 to Pb deposit/% (in mass)	< 1

Apparent quality of lead deposit was fine, porous and demand reached.

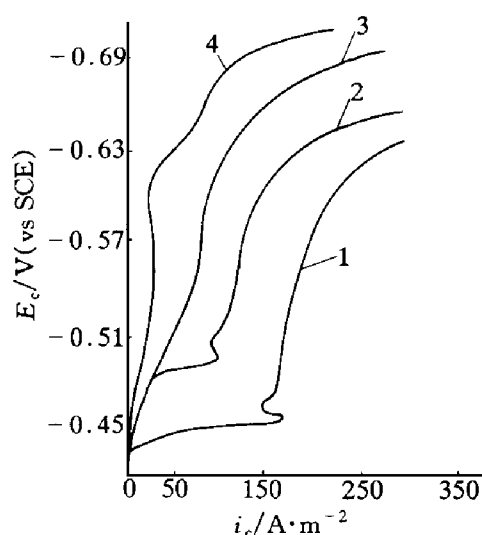


Fig. 5 Effect of lignin sodium sulphonate content on cathode polarization

Lignin sodium sulphonate: 1—0 g/L, 2—2 g/L, 3—4 g/L, 4—6 g/L;
Pb content: 40 g/L; H_2SiF_6 content: 90 g/L;
P content: 2 g/L

4 CONCLUSIONS

(1) The use of carbonate like K_2CO_3 results in strong thermodynamic driving force in reactions occurring during desulfurization process of PbSO_4 in scrap battery sludge. It is demanded, however, that in the course of the process, pH value of solution should be maintained between 6 and 10.

(2) The use of FeSO_4 — H_2SO_4 as reducing agent presents substantial thermodynamic driving power for the reducing PbO_2 in sludge to Pb

SO_4 , this can achieve high efficiency and high speed for reducing and improve lead recovery from sludge.

(3) Desulfurization process should be controlled under neutral or a little basic condition and reducing process should be maintained under acidic condition. The two processes should be separately carried out.

(4) During electrowinning, the depositing of Pb on cathode is chiefly caused by the discharge of PbSiF_6 . The addition of phosphate ions to electrolyte holds back the formation of PbO_2 on anode. Keeping up a certain free H_2SiF_6 concentration improves conductivity of the solution and checks the hydrolysis of PbSiF_6 . The principal function of lignin sodium sulphonate is to enhance polarizability of cathodes and to improve apparent quality of lead deposits.

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