BASIC ELECTROLYTIC METHOD FOR RECOVERY OF LEAD FROM SCRAP BATTERIES①

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ABSTRACT A new basic electrolytic method for recovering lead from scrap batteries was proposed, with NaOH as sulphur-eliminating agent and self-made I# as reducing-converting agent. Lead powder of 99.99% Pb was obtained by electrowinning with NaOH solution, to which $KNaC_4H_4O_6$ was added as electrolyte, and the current efficiency > 98%. The direct recovery efficiency of Pb from the battery scrap is higher than 95% and total Pb recovery efficiency higher than 98%. The technological process is stable without environmental pollution.

Key words battery sludge lead recovery electrowinning

1 INTRODUCTION

Current basic electrolytic method for recovering Pb from scrap batteries is represented by direct slurry electrolytic method, which has the disadvantages of low current efficiency (roughly 75%~80%), unpurified electrolyte, inevitable refining and purifying operation for obtained lead sponge. In addition, its by-product Na_2SO_4 from enriched electrolyte contains lots of lead compounds to be removed[1]. In this paper, a new basic electrolytic method was proposed, and its process was studied.

2 PROCESS FLOW

Table 1 gives typical composition of lead-containing waste materials from a sort of scrap batteries[2]. The principal process of the basic electrowinning for recovery of lead from scrap batteries is outlined in Fig. 1.

3 EXPERIMENT AND DISCUSSION

All of the reagents are of C. P. or A. R. grade. Measured precisions are given below: weight 0.001 g, temperature ±1 ℃, chemical analysis 0.01%.

3.1 Sweetening experiment

Equation 1 indicates the reaction occurring during the sweetening process.

$$PbSO_4 + 2NaOH = PbO\downarrow + Na_2SO_4 + H_2O \quad (1)$$

When NaOH is excessive and highly

Table 1 Typical composition of lead-containing materials from a sort of scrap batteries

Materials	Content/%						Visual color
	Total Pb	Metallic Pb	PbO	PbO_2	$PbSO_4$	Sb	
Lead grid	92~95	92~95	TA	–	TA	3~6	grey
Anode sludge	76.28	0	8.59	44.75	31.82	0.54	reddish brown
Cathode sludge	78.55	18.95	29.39	0	21.45	0.50	grey
Mixed sludge	81.90	17.22	16.92	26.80	31.50	–	brown

Note: TA—trace amount.

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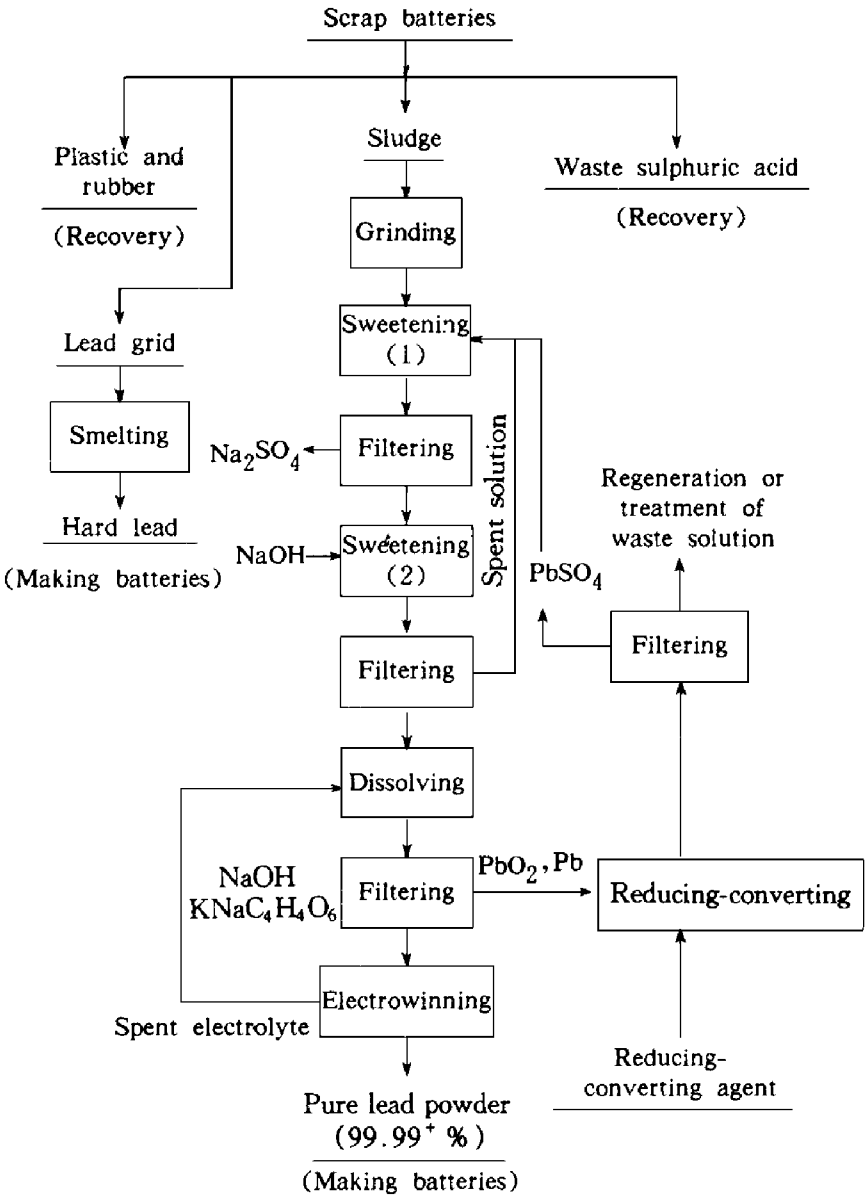

Fig. 1 Flow diagram of basic electrolytic method for scrap batteries

concentrated, the reaction occurs according to equation 2.

$$PbSO_4 + 3NaOH = NaHPbO_2 + Na_2SO_4 + H_2O \quad (2)$$

Desulfurization efficiency is chosen as assessment index. The projects of sweetening experiment are given in Table 2.

The results of desulfurization experiments are presented in Table 3. According to the results, the importance of various factors can be arranged as follows: liquid-solid ratio> temperature> particle size> time> mixed ratio. The preferential conditions are E_3, A_4, D_1, B_4, C_1.

Liquid-solid ratio indirectly indicates the amount of solution and NaOH concentration. Small ratio means small amount of solution and SO_4^{2-} concentration will increase at a high rate,

Table 2 Orthogonal experimental projects of desulfurization

Level	Factors				
	A θ/ ℃	B t/ min	C r_m [1]	D d_p [2] / mesh	E r_{ls} [3]
1	20	10	2∶1	− 16~ + 40	2∶1
2	40	20	3∶1	− 80~ + 100	6∶1
3	60	40	4∶1	− 160~ + 180	10∶1
4	80	80	5∶1	− 280~ + 300	14∶1

Notes: 1) r_m —mixed molar ratio of NaOH to $PbSO_4$;
2) d_p —particle size;
3) r_{ls} —liquid-solid ratio: weight ratio of H_2O to solids of both $PbSO_4$ and NaOH;
The stirring rate: 1 000 r/ min.

thus SO_4^{2-} is likely to reach its saturation point soon in the solution. On the contrary, when the ratio is excessively large, NaOH concentration will notably decline. Either case is not favorable to the reaction. High temperature ensures high reaction rate and high Na_2SO_4 solubility, thus helps improve the desulfurization efficiency. Experiment in this field has revealed that in the case of extremely fine particles of raw materials, it occurred after some time of reaction that the feed-stock would agglomerate and stick to the inner surface of the container, which would weaken the stirring effect. Therefore, extremely fine particles of the raw material might cause the drop in apparent desulfurization efficiency. So the proper size of the raw material should be comprehensively considered. Mixed ratio under the condition of such experiment has little effect on desulfurization efficiency. As a result, the feed-in amount of NaOH needs to be slightly larger than the calculation value from Eq. 1.

According to the discussion above, proper technical conditions can be determined as follows:

Parameters	Selected values
Mixed ratio	2.5∶1
Liquid-solid ratio	10∶1
Temperature, ℃	80
Particle size, mesh	-80~+100
Desulfurization efficiency, %	99.6 (after 80 min of reaction)

3.2 Reducing-converting experiment

The cationic reducing-converting agent (abbr. $I^{\#}$ reducing agent) made by the authors is a solution containing both reducing and converting components in a fixed ratio. Eq. 3 indicates the reaction occurring during the reduction operation.

$$PbO_2 + I^{\#} \longrightarrow PbSO_4 \quad (3)$$

The existence of lead powder in the stuffing benefits the reduction, as is indicated in Eq. 4:

$$PbO_2 + Pb + I^{\#} \longrightarrow PbSO_4 \quad (4)$$

Single factor testing method was employed to determine the proper technical parameters. The results of the reducing-converting experiment are given in Fig. 2.

According to the results in Fig. 2, proper technical parameters can be determined as follows. The ready amount of the reducing-converting agent for reaction is three times as much as that theoretically calculated according to the reducing component for PbO_2 in this agent. The temperature is 40 ± 5 ℃. The weight of H_2O should be 20 times as much as that of PbO_2. The reaction time is from 2.5 to 3.0 h. Under the conditions above, the reduction efficiency is almost twice as much as that of the well-recommended Rolla method (U.S.A) using

Table 3 Average desulfurization efficiency from orthogonal experiment (%)

Level	Factors				
	A	B	C	D	E
1	53.66	45.24	62.18	70.65	37.46
2	56.20	56.44	61.49	62.04	61.26
3	50.07	67.85	54.71	60.94	72.71
4	78.62	69.03	60.18	44.93	67.14
Range	28.55	23.80	7.47	25.72	35.25

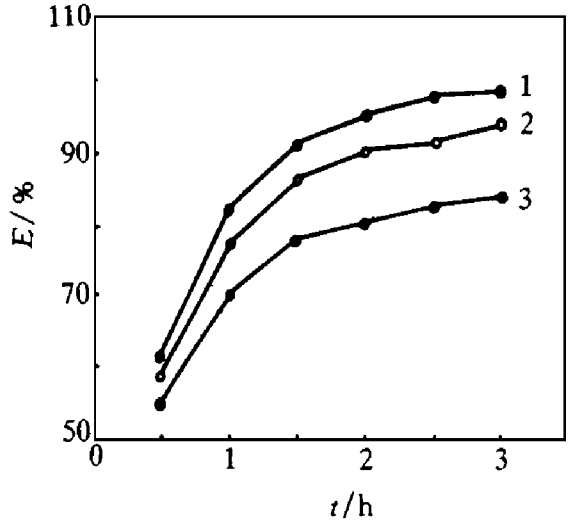

Fig. 2 Effect of $I^{\#}$ reducing agent

(E —reduction efficiency; ①The mixed ratio of reducing components is three times as much as that calculated from Eq. 3; ②The mixed ratio of converting components is twice as much as that calculated from Eq. 3 or 4; ③The ratio of H_2O to PbO_2 in weight is 20; ④Curve 1: under the same conditions as ①~③, some lead powder weighing as much as 15% of PbO_2 is added; ⑤The stirring rate is 1 000 r/min)

1, 2—40 ℃; 3—80 ℃

NH_4HSO_3.

3.3 Dissolving experiment

The electrolyte is made by leaching PbO with NaOH-$KNaC_4H_4O_6$ solution. During leaching operation, the reactions occur as follows:

$$2PbO + 2KNaC_4H_4O_6 + 2H_2O = Pb_2(C_4H_4O_6)_2 + 2KOH + 2NaOH \quad (5)$$

$$2PbO + 3KNaC_4H_4O_6 + 2H_2O = KNaPb_2(C_4H_4O_6)_3 + 2KOH + 2NaOH \quad (6)$$

$$PbO + NaOH = NaHPbO_2 \quad (7)$$

$$PbO + 2NaOH = Na_2PbO_2 + H_2O \quad (8)$$

When the amounts of both NaOH and $KNaC_4H_4O_6$ are sufficient, total Pb in the solution would run to 150 g/L or even higher, favorable to the electrodepositing operation. It is also testified that, without $KNaC_4H_4O_6$, total Pb in the solution can only reach 20 g/L or so. In this case, the current efficiency is extremely low in lead electrodepositing operation, since the electrolyte contains too little Pb.

3.4 Electrowinning experiment

Cathodic reactions:

$$Pb^{2+} + 2e \rightarrow Pb\downarrow \quad (9)$$

$$2H_2O + 2e \rightarrow H_2\uparrow + 2OH^- \quad (10)$$

Anodic reactions:

$$4OH^- - 4e \rightarrow O_2\uparrow + 2H_2O \quad (11)$$

$$Pb^{2+} + 4OH^- - 2e \rightarrow PbO_2\downarrow + 2H_2O \quad (12)$$

Orthogonal experiment method was applied to determine the technical parameters. Selected assessment indexes include current efficiency, quality of lead at the cathode and anode state. The quality of lead falls into 5 grades. Sponge Pb, which is easy to be ground, is of the best quality, and thus is marked Grade 1. Compact or coarse-grained Pb, which is hard to be ground, is of the worst quality, and is therefore marked Grade 5. Generally Pb of or above Grade 2 is acceptable. Anode state falls into 5 grades as well according to the amount of PbO_2 formed at the anode. If there is only trace amount of PbO_2, the anode state is of the best quality and thus is marked Grade 1. Otherwise, if there is a large quantity of compact PbO_2 (roughly 50% of the lead formed at the cathode), the anode state is of the worst quality, and therefore marked Grade 5. It is demanded that the amount of PbO_2 formed at the anode should be as little as possible. Details see Table 4 and Table 5.

As is shown in Table 5, according to their respective effects on current efficiency, the factors can be arranged in order of importance as below: gelatin > $KNaC_4H_4O_6$ > current density > NaOH > Pb content. The favourable conditions are D_3, C_4, E_3, B_1, A_3. Experiment showed that certain amount of gelatin and $C_4H_4O_6^{2-}$ can prevent the release of H_2 to some extent, thus beneficial to the increase of current efficiency.

According to their respective effects on the quality of lead, the factors can be arranged in order of importance as the following: gelatin>

Table 4 Projects of the orthogonal experiment of electrowinning

Level	Factors				
	A C(Pb) /g·L^{-1}	B C(NaOH) /g·L^{-1}	C r_w	D C(gelatin) /g·L^{-1}	E J_c /A·m^{-2}
1	28	80	1.0	0	50
2	56	150	1.5	0.05	100
3	80	200	2.0	0.2	200
4	112	250	2.5	0.5	300

Notes: r_w —the weight ratio of $KNaC_4H_4O_6 \cdot 4H_2O$ to PbO; J_c —cathode current density.

Table 5 Results of the orthogonal experiment of electrodepositing

	Test	A	B	C	D	E
Current efficiency /%	$\overline{\text{I}}$	97.21	98.70	96.17	95.97	97.35
	$\overline{\text{II}}$	97.74	97.88	97.46	98.45	97.81
	$\overline{\text{III}}$	98.15	96.88	98.20	98.46	98.59
	$\overline{\text{IV}}$	97.25	96.89	98.52	97.47	96.65
	Range	0.94	1.81	2.35	2.49	1.94
Quality of lead powder (grade)	$\overline{\text{I}}$	3.0	3.25	3.25	5	3.5
	$\overline{\text{II}}$	3.25	3.5	3.5	3.75	3.0
	$\overline{\text{III}}$	3.5	3.25	3.25	3.0	3.5
	$\overline{\text{IV}}$	3.5	3.25	3.25	1.5	3.25
	Range	0.5	0.25	0.25	3.5	0.5
Anode state (grade)	$\overline{\text{I}}$	3.38	3.25	3.38	2.63	2.50
	$\overline{\text{II}}$	2.13	1.63	3.13	2.75	2.50
	$\overline{\text{III}}$	2.0	2.50	1.0	2.13	2.50
	$\overline{\text{IV}}$	2.13	2.25	1.75	2.13	2.13
	Range	1.38	1.62	2.38	0.62	0.37

Pb content, current density > NaOH > $KNaC_4H_4O_6$. The fairly good conditions determined are D_4, A_1, E_2, B_1(B_3, B_4), C_1(C_3, C_4). It is indicated that the addition of certain amount of gelatin to the electrolyte is the key to the improvement of the quality of lead powder.

According to their respective effects on the formation of PbO_2 at the anode, the factors can be arranged in order of importance as below: $KNaC_4H_4O_6$ > NaOH > Pb content > gelatin > current density. The fairly good conditions determined are C_3, B_2, A_3, D_3(D_4), E_4. Experiment indicated that the comprehensive action of $KNaC_4H_4O_6$, NaOH and Pb content has relatively great effect on the formation of PbO_2 at the anode, maintaining a fixed Pb content and OH^- concentration in the electrolyte, which reduces the releasing potential of O_2, the cell voltage, and the free Pb^{2+} concentration simultaneously. Consequently, the formation of PbO_2 at the anode is controlled.

Under comprehensive considerations, the technical conditions are chosen as below:

Parameters	Selected values
Pb content, g/L	40~ 100
NaOH, g/L	150
$KNaC_4H_4O_6 \cdot 4H_2O$, g/L	150
Gelatin, g/L	0.5
Current density, A/m^2	150~ 250
Temperature, ℃	room temperature

Results of the experiment under above conditions are given as below: current efficiency ≥ 98%, deposit velocity of Pb= 5.7~ 9.5 g/h·dm^2, purity of lead powder ≥99.99%, weight of PbO_2 formed at the anode< 1% of the cathodic Pb weight. Coat of deposited Pb at the cathode is sponge-like and fine-grained, meeting the quality requirements.

4 BATTERY SCRAP TESTS

Mixed sludge from scrap batteries was applied to the experiment, which contains 70.93% Pb as a whole, 40.41% $PbSO_4$, 32.96% PbO_2, 5.56% Pb and 13.50% PbO. The results in average from three parallel tests are given below: desulfurization rate 95%, reduction rate 8.8%, current efficiency 99%, purity of lead powder ≥ 99.99%. In addition, it was observed that in all the tests, metallic Pb in the sludge was totally converted, lead coat at the cathode was loose-surfaced and fine-grained, and PbO_2 formed at the anode was less than 1% of the Pb deposit at the cathode. After calculation, it turned out that direct and total recovery rates of Pb are above 95% and 98%, respectively.

5 CONCLUSION

The new basic electrolytic method differs from all the previous ones in three points: (1) Its desulfurization and electrolysis processes are separately carried out, avoiding the loss of Pb and NaOH during the elimination of Na_2SO_4 from electrolyte. (2) Its by-product Na_2SO_4 is obtained in high purity during desulfurization process. (3) The addition of tartrate greatly increases Pb content in the electrolyte, which is favorable to improving the electrodepositing efficiency.

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