[Article ID] 1003- 6326(2002)02- 0344- 05

Technological condition in slurry electrolysis of high-silver galena concentrate①

CHEN Ling(陈 凌)[1], YANG Xian-wan(杨显万)[1],
SI Yun-sen(司云森)[2], ZHANG Yin-jie(张英杰)[2]
(1. Faculty of Material and Metallurgy Engineering,
Kunming University of Science and Technology, Kunming 650093, China;
2. Faculty of Science, Kunming University of Science and Technology,
Kunming 650093, China)

[Abstract] Effects of various technological conditions such as $\rho(Cl^-)$, $\rho(Fe)_T$, pH value and temperature on the cell voltage, lead leaching rate and the cathodic current efficiency of the slurry electrolysis of high-silver galena concentrate were studied, and the behavior regularity of lead and silver was investigated. As a result, the suitable condition was determined as: $\rho(Cl^-)$ 230 g/L, $\rho(Fe)_T$ 15 g/L, pH 1, temperature 70 ℃, electrolysis time 6 h. Under such condition, adopting the cathodic current density of 150 A/m^2 and the liquid-solid ratio of 15:1, lead powder with a purity degree of 91.18% was got. At the same time, leaching rate of lead, leaching rate of silver and cathodic current efficiency amounted to 96.88%, 70.88% and 75.68% respectively.

[Key words] slurry electrolysis; technological condition; galena
[CLC number] TD923 **[Document code]** A

1 INTRODUCTION

Traditional lead metallurgy mainly gives priority to pyrometallurgy all the time. But lead pyrometallurgy has the inherent drawback of severely polluting the environment, e.g. lead's poisoning over operator may exceed the corresponding standard limit; and it's hard for SO_2 to avoid contaminating[1]. Since the 1970's, many countries have had more and more strict demand over the environment. For instance, in September 1978, State Bureau of Environmental Protection of U.S.A. promulgated the atmosphere standard of lead, stipulating that the allowable volume of lead in atmosphere was 150 μg/m^3, which is far more exacting compared to its universally accepted counterpart in industry —500 μg/m^3[2].

Since P. R. Kruesi, an American, submitted a patent thus declared the emerging of Slurry Electrolysis in 1971, this new technology of hydrometallurgy has raised many times of research upsurge all over the world including China. So called Slurry Electrolysis means combining the processes of leaching, purification and electrodeposition in the same device, then adding well-ground ore into the device and taking products from it directly. Slurry Electrolysis has such features as short process, low energy consumption and excellent ecology environment etc[3~4]. In view of some successfully industrialized examples such as in Shizhuyuan, Hunan Province, P. R. China and Yuangyang, Yunnan Province, P. R. China, Slurry Electrolysis has the possibility of overcoming the drawback of lead pyrometallurgy[5~8]. It can deal with various complex lead ores or waste lead materials. It transforms sulphur in materials into S^0 directly, not only preventing SO_2 from polluting atmosphere but also avoiding the inconvenience of transport and store of sulphuric acid[9, 10].

This paper mainly studies the technological conditions in the Slurry Electrolysis of the high-silver galena concentrate.

2 EXPERIMENTAL

2.1 Samples

High silver galena concentrate from Menzhi, Yunnan Province, P. R. China was used as samples in experiments. Its chemical composition are given in Table 1. Lead in the concentrate is mainly come from galena.

Table 1 Chemical composition of Menzhi galena concentrate

Element	Mass fraction/%	Element	Mass fraction/%
Pb	49.49	Sb	1.83
Cu	0.32	S	21.23
Fe	11.40	Ag(g/t)	2126.6
Zn	5.77	Au(g/t)	< 0.7

① [Received date] 2001- 05- 31; [Accepted date] 2001- 09- 20

2.2 Experimental device

Experiments were processed in a specially made electrolyser, which differs from ordinary one in that there is a percolating diaphragm to separate the electrolyser into anodic zone and cathodic zone. Anode and cathode were made of graphite and lead respectively, both with an exposed area of 8 cm × 8 cm. Slurry, composed of Cl^- and galena concentrate, was placed in anodic zone and then was agitated with the JJ-1 type electric agitator to make the ore grain uniformly suspended in it. Metallic ore was leached in anodic zone, then metallic ions percolated through the diaphragm into the cathodic zone, where they were deposited.

The cell was maintained in an HH-2 type water bath to keep the temperature being constant (±1 ℃). Voltage stabilizing D. C. was produced by WYJ-15 type commutator, and cell voltage was measured by DG-168 type multimeter.

2.3 Examined index

Suitable technological conditions were determined by three indexes of cell voltage, leaching rate of lead and cathodic current efficiency.

3 RESULTS AND DISCUSSION

3.1 Effect of Cl^- concentration in slurry

Cl^- was added with $CaCl_2$, not NaCl. It is because that Cl accounts for more proportion in $CaCl_2$ than in NaCl and $CaCl_2$ dissolves more easy in water than NaCl under the same condition.

Effect of concentration of Cl^- in slurry on every index of galena slurry electrolysis is shown in Table 2 and Fig. 1.

Table 2 Leaching rates and current efficiencies under various concentration of Cl^- in slurry

$\rho(Cl^-)$ /(g·L^{-1})	Galena leaching rate /%	Current efficiency in cathode /%
100	43.22	35.51
200	51.39	43.22
230	56.36	45.12
260	56.93	46.23
300	57.16	45.99

(Other Conditions: $\rho(Fe)_{Total}$ 6 g/L, θ 60 ℃, pH 1, D_k 150 A/m^2, time 6 h)

When Cl^- concentration in slurry is below 200 g/L, cell voltage is relatively high. With it increasing, cell voltage decreases accordingly. But when Cl^- concentration is more than 200 g/L, the decrease amount of cell voltage is very limited, which is reflected in Fig. 2 in that after passing the point of 200 g/L, slopes of the curves tend to be gentle.

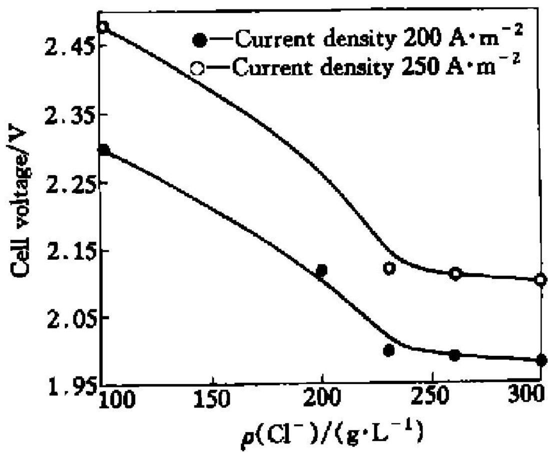

Fig. 1 Effect of Cl^- concentration on cell voltage of Slurry Electrolysis
(Other conditions: $\rho(Fe)_T$ 6 g/L, θ 60 ℃, pH 1)

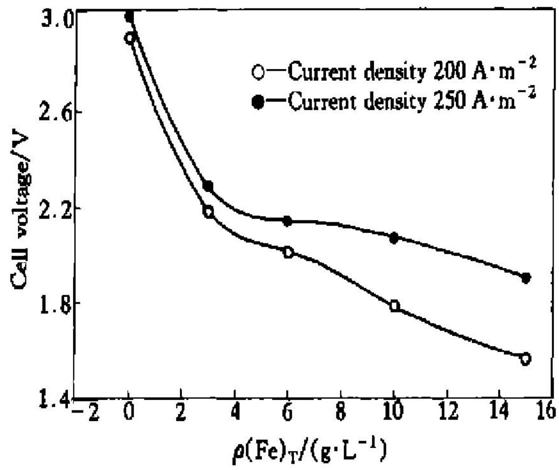

Fig. 2 Effect of Fe (total) concentration on cell voltage of Slurry Electrolysis
(Other conditions: $\rho(Cl^-)$ 230 g/L. θ 60 ℃, pH 1)

Moreover, it can be told from Table 3 that either leaching rate of lead or cathodic current efficiency has no distinct difference under three conditions. Economically concerned, $\rho(Cl^-) = 230$ g/L is appropriate.

3.2 Effect of Fe (total) concentration in slurry

Table 3 Leaching rates and current efficiencies under various concentration of Fe (total) in slurry

$\rho(Fe)_{Total}$ /(g·L^{-1})	Galena leaching rate /%	Current efficiency in cathode/%
0	23.64	7.5
3	36.28	35.66
6	56.36	45.12
10	74.32	63.26
15	97.36	70.35

(Other Conditions: $\rho(Cl^-)$ 230 g/L, θ 60 ℃, pH 1, D_k 150 A/m^2, time 6 h)

It can be seen that the concentration of Fe (total) in slurry has a great effect on three indexes.

Document[4] pointed out from five different points of view that non-electrode process, not anodic oxidation, is the main leaching way of Pb in Slurry Electrolysis. Non-electrode process embodies two respects, those are chemical dissolution and chemical oxidation. Fe exactly has a great contribution to both of them. In chemical oxidation, Fe(Ⅲ) is an excellent oxidant which can oxidate and leach sulphide as following:

$$MeS + 2Fe(III) = Me^{2+} + 2Fe(II) + S^0$$

At the same time, Fe(Ⅲ) can be regenerated by Fe(Ⅱ) being oxidized in anode, having the effect of electron conveying.

On the other hand, because Fe(Ⅱ) in solution can be continuously oxidized in anode into Fe(Ⅲ), the concentration of Fe(Ⅲ) is fairy high in solution which causes the H_2S produced from acid dissolution of sulphides to be oxidized into S^0 quickly:

$$H_2S + 2Fe(III) = 2H^+ + 2Fe(II) + S^0$$

so that the H_2S concentration in slurry is very low which facilities the dissolution of sulphide.

Above-mentioned two respects explain why the leaching rate of slurry electrolysis is much higher than that of common oxidizing leaching. The effect of Fe is self-evident. $\rho(Fe)_{Total} = 15$ g/L is the optimal condition.

3.3 pH value of slurry

Effect of pH value of slurry on every index of galena slurry electrolysis is shown in Table 4 and Fig. 3.

Table 4 Leaching rates and current efficiencies under various pH value

pH	Galena leaching rate / %	Current efficiency in cathode / %
< 0.5	97.66	63.26
1	97.36	70.35
2~3	93.77	66.82

(Other Conditions: $\rho(Cl^-)$ 230 g/L, $\rho(Fe)_{Total}$ 15 g/L, θ 60 ℃, D_k 150 A/m^2, time 6 h)

In Fig. 3, two U-I curves of pH< 0.5 and pH 1 are overlapping mainly, and as is seen from Table 4 the leaching rates of lead are about the same under the two conditions, but the cathodic current efficiency of pH< 0.5 is much lower than that of pH 1, which indicates that high HCl concentration not only is unnecessary but also can intensify the separating out of H_2 in cathode, thus lowering the cathodic current efficiency and increasing the energy consumption effectively.

But excessively low acidity doesn't work as well. It is the minimum demand of slurry acidity to

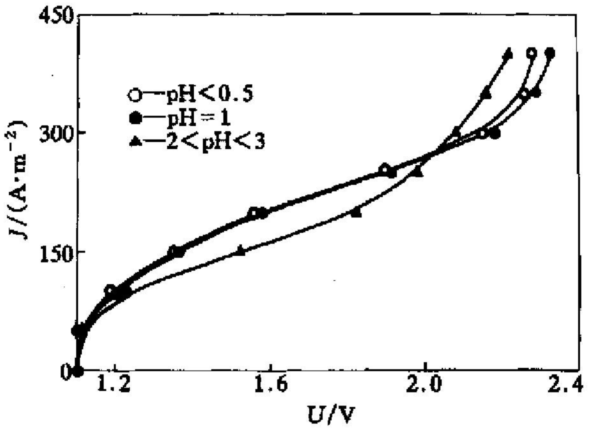

Fig. 3 *U-J* curves of different pH value
(Other conditions: $\rho(Cl^-)$ 230 g/L, $\rho(Fe)_T$ 15 g/L, θ 60 ℃)

avoid the occurrence of hydrolysis of various metallic ions such as Fe^{2+} and alkaline earth metal, the hydrolyzing pH values of which are 2.0 and 4.0 respectively. Comprehensively considering, pH value of 1.0 is the best.

3.4 Temperature

As is seen from Table 5 and Fig. 4, the higher the temperature of slurry electrolysis, the lower its cell voltage, and the higher the leaching rates of lead as well. Comparing the two electrolysis temperature

Table 5 Leaching rates and current efficiencies under various electrolysis temperature

θ / ℃	Galena leaching rate / %	Current efficiency in cathode / %
60	97.36	70.35
70	97.92	75.35
80	98.88	65.88

(Other Conditions: $\rho(Cl^-)$ 230 g/L, $\rho(Fe)_{Total}$ 15 g/L, D_k 150 A/m^2, pH 1, time 6 h)

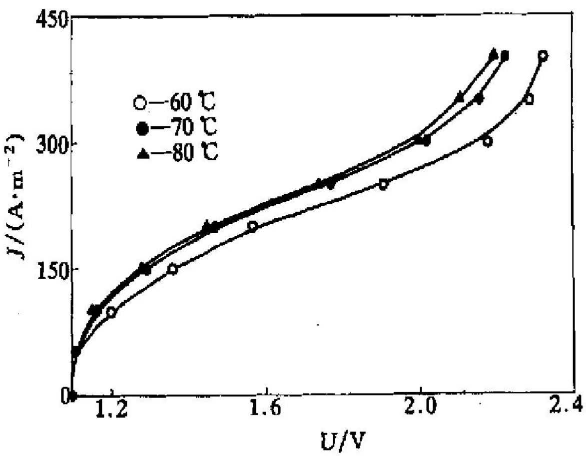

Fig. 4 *U-J* curves of different pH value
(Other conditions: $\rho(Cl^-)$ 230 g/L, $\rho(Fe)_{Total}$ 15 g/L, pH 1)

of 70 ℃ and 60 ℃, the lead leaching rate of the former is slightly higher than that of the latter, but the cathodic current efficiency of the former is far higher than that of the latter. It can be concluded that higher slurry electrolysis temperature not only helps lower cell voltage and increase the leaching rate of lead, but also is beneficial to the increase of cathodic current efficiency. On the other hand, lead leaching rate of 80 ℃ is higher than that of 60 ℃ and 70 ℃, while its cathodic current efficiency is comparatively low instead. Maybe it is because of lead powder's backward dissolution in excessively high temperature. Moreover, excessively high temperature causes electorlyte to evaporate seriously, which lowers the stability of electrolyte, results in the difficulty of practical operation, increases energy consumption and worsens work condition as well. Electrolysis temperature of 70 ℃ is suitable.

3.5 Effect of electrolysis time

In order to determine suitable electrolysis time, the behavior regularity of lead and silver during slurry electrolysis was examined.

Behavior of lead is shown in Fig. 5. Galena rapidly dissolves when solution condition is: $\rho(Cl^-)$ 230 g/L, $\rho(Fe)_{Total}$ 15 g/L, pH 1 and θ 70 ℃. The leaching rate of galena reaches 93.52% only in two hours. Because chemical dissolution is in progress along with chemical oxidation, leaching rate of Pb in anodic zone is far faster than its deposition rate in cathode. Thus Pb concentration in solution rises rapidly, which reaches the maximum value in about half an hour. After that, leaching rate of galena slows down. Because the deposition rate of Pb in cathode is basically invariable under constant current density, Pb concentration in solution descends continuously, while deposition amount of Pb in cathode ascends steadily. Pb being basically leached out must not mark the end of slurry electrolysis, for, as is seen in Fig. 5, Pb leaching rate achieves 96.11% in three hours but Pb concentration in solution is as high as 19.76 g/L at the same time and it is very easy to separate out $PbCl_2$ crystal which will block up the diaphragm. On the other hand, after 6 h of electrolysis time, variation of galena leaching rate, Pb concentration in solution and Pb deposition rate in cathode are not very distinct. This characteristic can also be reflected in Fig. 6, which shows the behavior regularity of silver, in that slopes of three curves tend to be gentle during the electrolysis time from 6 h to 10 h. Comprehensively concerned, 6 h of electrolysis time is appropriate.

Up to this moment, the suitable condition is determined as: $\rho(Cl^-)$ 230 g/L, $\rho(Fe)_{Total}$ 15 g/L, pH 1, temperature 70 ℃, electrolysis time 6 h. Under such condition, adopting the cathodic current density of 150 A/m^2, the liquid-solid ratio of 15∶1, several experiments have been processed to verify the reappearance. The average results of them are respectively purity degree of lead powder 91.18%, and the leaching rate of lead, leaching rate of silver and cathodic current efficiency as well 96.88%, 70.88% and 75.68%.

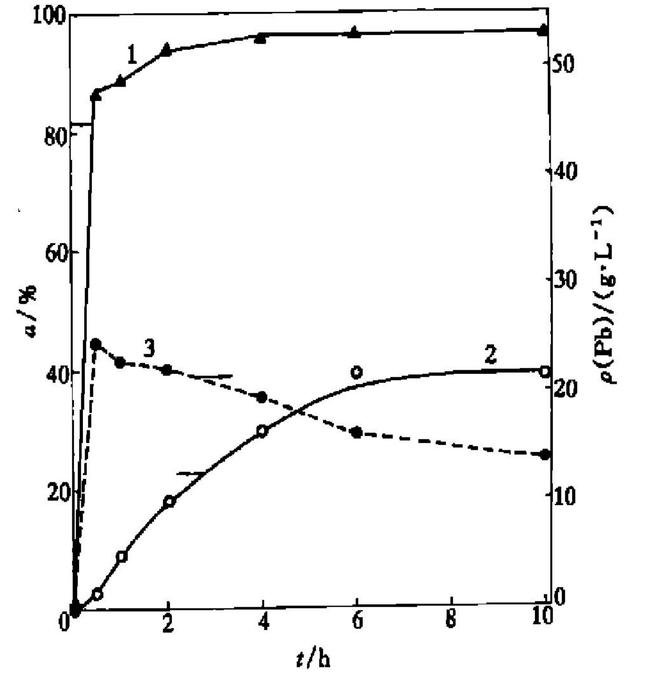

Fig. 5 Behavior of lead during slurry electrolysis
1 —Leaching rate of Pb; 2 —Pb depositing rate in cathode; 3 —Concentration of Pb in slurry ($\rho(Cl^-)$ 230 g/L, $\rho(Fe)_{Total}$ 15 g/L, pH 1, D_K150 A/cm^2, θ 70 ℃)

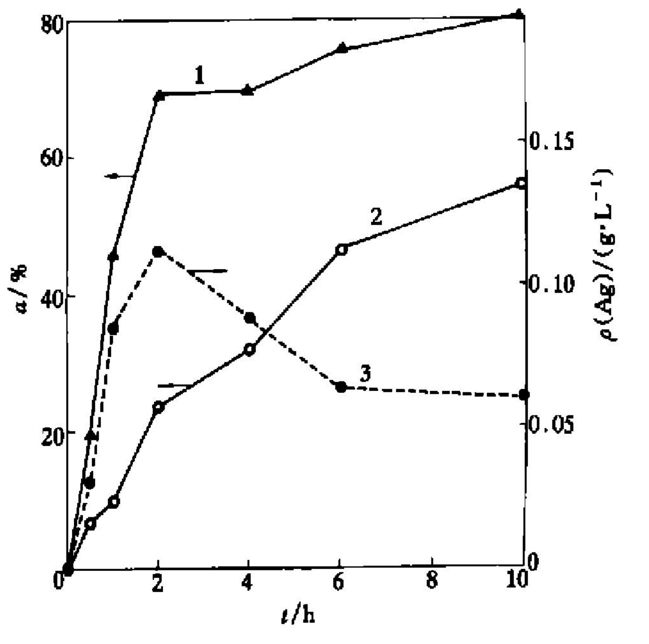

Fig. 6 Behavior of silver during slurry electrolysis
1 —Leaching rate of Ag; 2 —Ag depositing rate in cathode; 3 —Concentration of Ag in slurry($\rho(Cl^-)$ 230 g/L, $\rho(Fe)_{Total}$ 15 g/L, pH 1, D_K150 A/cm^2, θ 70 ℃)

4 CONCLUSIONS

Through investigating its cell voltage, lead leaching rate, cathodic current efficiency and studying the behavior regularity of lead and silver, meanwhile, considering practical operation, the suitable conditions in the slurry electrolysis of high-silver galena are determined as: $\rho(Cl^-)$ 230 g/L, $\rho(Fe)_{Total}$ 15 g/L, pH 1, temperature 70 ℃, electrolysis time 6 h. Under such conditions, adopting the cathodic current density of 150 A/m^2 and the liquid-solid ratio of 15∶1 as well, lead powder with a purity degree of 91.18% have got. At the same time, leaching rate of lead, leaching rate of silver and cathodic current efficiency amount to 96.88%, 70.88% and 75.68% respectively.

[REFERENCES]

[1] QIU Ding-fan. Slurry Electrolysis, (in Chinese) [M]. Beijing: Metallurgical Industry Press, 1999.

[2] ZHAO Tian-cong. Nonferrous Metallurgy Without Pollution [M]. Beijing: Science Press, 1992.

[3] YANG Xian-wan, QIU Ding-fan. Hydrometallurgy, (in Chinese) [M]. Beijing: Metallurgical Industry Press, 1998.

[4] YANG Xian-wan, Zhang Yin-jie. Theory of Slurry Electrolysis, (in Chinese) [M]. Beijing: Metallurgical Industry Press, 2000.

[5] WAN Chen-yan, Qiu Ding-fan, ZHANG Yin-shen, et al. Research on the slurry electrolysis of bismuthinite [J]. Nonferrous Metallurgy, 1995, 2: 50.

[6] ZHANG Yan-shen, JIANG Pei-hai. Slurry Electrolysis of the complex lead concentrate [J]. Nonferrous Metallurgy, 1991, 5: 11.

[7] ZHANG Ying-jie, YANG Xian-wan, DENG Lun-hao, et al. Leaching mechanism of sulfide ores in slurry electrolysis[J]. Transactions of Nonferrous Metal Society of China, 2000, 10: 105.

[8] ZHANG Ying-jie, YANG Xian-wan, DENG Lun-hao, et al. Thermodynamic of the slurry electrolysis of the galena[J]. Nonferrous Metallurgy, 1998, 50(3): 71-75.

[9] QIU Ding-fan. Recovery copper and zinc from scrap material by electroslurry-solvent extraction process [A]. ICHM' 88 [C]. Beijing: Metallurgical Industry Press, 1988, 251.

[10] QIU Ding-fan. Recovery of metals from secondary material by slurry electrolysis [A]. Proceeding 4th International Symposium on East Asian Resource Recycling Technology [C]. Kunming: Yunnan Science and Technology Press, 1997, 93.

(Edited by ZHU Zhong-guo)