

电化学法从废料中回收金银和铅的工艺研究

梁晓琪 徐扣珍 陈世琯 曹雪琴 张仲燕

(上海大学化工学院, 上海 200072)

摘要 研究从含 Au、Ag 和 Pb 废料中综合回收 Au、Ag 和 Pb 的电化学分离过程. 在实验确定的最佳工艺条件(电极组成: 70 g/L Pb²⁺、100 g/L $\sum(\text{SiF}_6^{2-})$, 电解温度 40℃, 电流密度 100 A/m², β -萘酚、骨胶浓度分别为 0.002 g/L 和 0.5 g/L)下制得了纯度为 99% Pb 的平滑致密阴极铅沉淀物, 铅电流效率大于 98%, 比电能消耗 117 kW·h/tPb, Au、Ag 进入阳极泥的回收率分别高于 99% 和 98%.

关键词 金银回收, 电化学分离, 废料处理, 铅回收, 电解精炼.

含金银废料一般 Au、Ag 含量不高, 而 Cu、Pb、Bi 含量往往是 Au、Ag 的几 10 倍. 本研究以数量较多、目前尚无经济合理处理工艺的含金抛灰和银铅电容边框为研究对象, 将 2 种废料混合进行还原熔炼制取贵铅, 然后用电化学法分离回收金银和铅^[1]. 本课题以还原熔炼所得贵铅为阳极, 研究阴阳极过程及影响因素, 从而确定合适的电解条件以获得优质铅沉积物和良好的技术经济指标, 并使 Au、Ag 最大限度富集于阳极泥中以达到综合回收 Au、Ag 和 Pb 的目的. 贵铅电解的电极化过程已经报道^[2], 本文主要探讨电解工艺及电能消耗等技术经济指标.

1 贵铅电解过程电能消耗及降低的途径

为了降低金属电解过程直流电耗, 应设法提高电流效率和降低槽电压. 在电解设备绝缘良好的条件下, 为了取得高的电流效率, 主要应选择适当的电解技术条件, 特别是添加剂, 获得平整致密阴极沉积物以避免阴、阳极间短路. 铅电解精炼电流效率一般可达 95%—98%, 故为了降低能耗, 关键在于如何降低槽电压. 为此就要选择适当的溶液组成和温度, 在保证足够高的极化值以获得平整致密阴极铅沉积物的条件下, 力求降低电解液比电阻.

1.1 铅电解液比电阻测定方法和装置

文献[3]指出, 在微小电流密度下测量阴、阳极极化电位及其间的电压降, 即可计算求得高导电率溶液的比电阻. 本研究采用了如图 1 所示的测定装置^[4]. 所用阴、阳极面积均为 16 cm², 极距 5 cm. 在电流强度 5—50 mA 范围内测定不同铅电解液的比电阻.

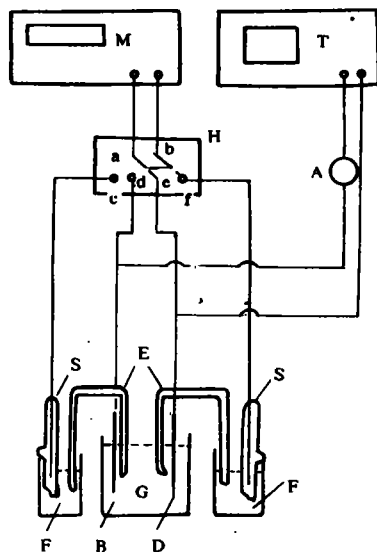


图1 测定比电阻装置示意图

A. 毫安表 B. 铅阳极 D. 铅阴极 E. 盐桥
F. KCl 饱和溶液 G. 电解池 H. 转换开关
M. 数字式电压表 S. 饱和甘汞参比电极 T. 恒电位仪

1.2 测定结果与讨论

(1) 铅离子浓度对电解液比电阻的影响

实验结果见图 2. 在总酸度 110 g/L 不变的情况下, 电解液的比电阻随铅离子浓度升高而增大, 这主要是由于铅离子浓度增加, 电解液中游离硅氟酸浓度下降所致; 同时随着铅离子浓度增加, 离子间相互作用增强, 使离子运动速度下降而比电阻上升.

从图 2 可见, $[Pb^{2+}]$ 在 30—50 g/L 时, 比电阻随浓度增大而缓慢增加, 50—70 g/L 内比电阻增加较快, 而当 $[Pb^{2+}]$ 为 70 g/L 以上时, 比电阻随浓度增加而剧烈升高. 为此仅从节电考虑, $[Pb^{2+}]$ 应选择 50 g/L 以下, 但为兼顾阴极沉积物质量, 则以 70 g/L 为宜.

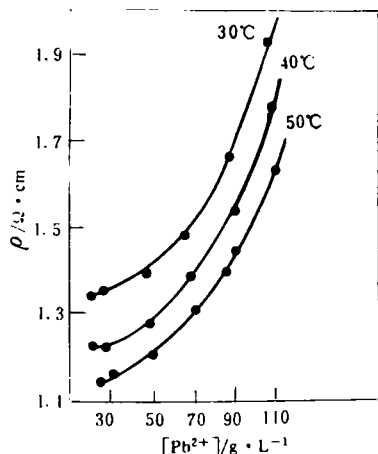


图 2 电解液比电阻随铅离子浓度变化曲线

(2) 硅氟酸浓度的影响 在 $[Pb^{2+}]$ 70 g/L 条件下, 电解液比电阻随硅氟酸总浓度升高而降低(见图 3). 这是由于硅氟酸总浓度升高, 电解液中游离酸含量增加, 从而导致电解液比电阻的下降. 这种趋势在总酸度为 60—80 g/L 时尤为明显. 因此从节能角度考虑, 提高电解液硅氟酸总浓度是有利的, 实践证明这还有利于改善阴极质量和提高电流效率. 但是酸度过高, 则对降低比电阻的作用减弱, 且酸的挥发损失增加, 还会污染周围环境, 同时电铅成本增加, 故当 $[Pb^{2+}]$ 浓度为 70 g/L 时, 总酸度定为 100 g/L 是合适的.

(3) 温度的影响 由图 2 和 3 可见, 当电解液成分一定时, 其比电阻随温度升高而降低, 有利于降低电耗. 但温度太高, 硅氟酸分解加快, 电解液蒸发损失增加; 而且阴极极化会过分降低, 将恶化电解铅质量, 故温度控制在 40℃ 比较合适.

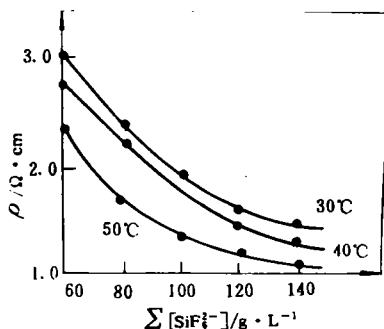


图 3 电解液比电阻随硅氟酸总浓度变化曲线

(4) 添加剂 在铅电解精炼中, 添加剂对电解液比电阻的影响往往由于加入量少而被忽视, 事实上少量添加剂的加入对电解液粘度等一些物理、化学性质将产生不同程度影响. 随着电解时间的增长, 添加剂及其分解产物在电解液中积累的影响更不可忽视.

当 $[Pb^{2+}]$ 为 70 g/L, 总酸度 100 g/L, 温度 40℃. 不含添加剂的比电阻 $\rho_0 = 1.78 \Omega \cdot \text{cm}$, 加入添加剂后的比电阻与 ρ_0 之比值即为相对电阻率. 借此定量表示添加剂对电解液比电阻的影响.

测定结果表明, 电解液的相对电阻率随表面活性剂添加量的增加而升高. 其中胶的影响最大, 木质磺酸钠添加量小于 3 g/L 时影响不大, 超过 3 g/L 则急剧上升. 但 β -萘酚由于添加量少, 对比电阻影响很小, 在一定范围内加入量增加时, 比电阻还略有下降, 这可能是它在溶液中呈酸性的缘故.

当 β -萘酚与骨胶联合添加时, 其影响并不是它们单一添加时效果的总和, 但随用量增加比电阻略有上升, 而用量低时影响不大. 表 1 列举 β -萘酚-骨胶联合添加时对比电阻的影响.

2 金银与铅分离的电解条件试验

由铅电极极化和电解液比电阻研究初步得出最佳的铅离子浓度、总酸度、温度以及添加剂种类和数量。为了获得良好的阴极铅和较高的金银回收率,按表 2 条件进行连续电解实验。

表 1 β -萘酚-骨胶添加量对比电阻的影响

添加量/ $\text{g} \cdot \text{L}^{-1}$	0.001/0.5	0.002/0.5	0.003/0.5
$\rho/\Omega \cdot \text{cm}$	1.948	2.096	2.730
相对电阻率	1.094	1.177	1.220

表 2 连续电解试验条件

项 目	基准条件	变化范围
$\text{Pb}^{2+}/\text{g} \cdot \text{L}^{-1}$	70	30—130
总酸度/ $\text{g} \cdot \text{L}^{-1}$	100	60—160
温度/ $^{\circ}\text{C}$	40	30—50
阴极电流密度/ $\text{A} \cdot \text{m}^{-2}$	100	80—160
β -萘酚-骨胶/ $\text{g} \cdot \text{L}^{-1}$	0.002(0.5) ¹⁾	0.001(0.5) —0.003(0.5)

1) 括号内为骨胶浓度

2.1 铅离子浓度的影响

其它因素采用基准条件,铅离子浓度对电解各项指标的影响如图 4 所示。

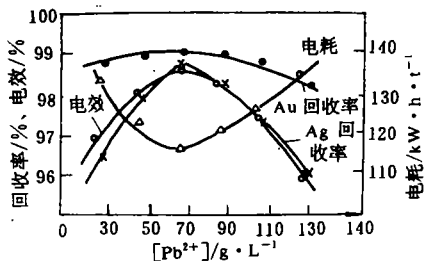


图 4 $[\text{Pb}^{2+}]$ 变化对金银回收率, 电流效率及电能消耗的影响

实验结果表明, $[\text{Pb}^{2+}]$ 为 70 g/L 时, 阴极铅光滑致密, 电流效率可达 98.71%, 阴极铅纯度 99.27%, Au、Ag 回收率分别为 99.12% 和 98.86%, 电能消耗只有 116.91 $\text{kW} \cdot \text{h/t Pb}$ 。当 $[\text{Pb}^{2+}]$ 过低时, 阴极铅质量恶化而导致阴极中 Au、Ag 含量上升, 致使进入阳极泥中的 Au、Ag 回收率降低, 同时电流效率下降、电耗升高。但 $[\text{Pb}^{2+}]$ 过高时, 阴极铅结晶颗粒变粗, 容易把溶液中包括 Au、Ag 在内的杂质机械夹带到阴极上, 同样各项指标均降低。选定 $[\text{Pb}^{2+}]$ 70 g/L 左右是合适的。

2.2 总酸度的影响

其它因素采用基准条件, $\sum(\text{SiF}_6^{2-})$ 在 60—160 g/L 范围内对电解各项指标的影响见图 5。

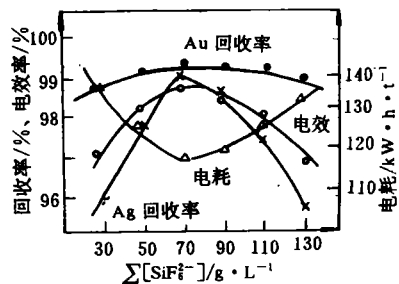


图 5 总酸度变化对金银回收率, 电流效率及电能消耗的影响

由图 5 可见, 总酸度为 100 g/L 时各项指标最佳。在一定范围内增加电解液中硅氟酸浓度可提高电解液的导电率、降低槽电压、减少电耗, 对电流效率的增加和改善阴极铅质量有利, 但过高的酸度也是不利的。因此选定 100 g/L 比较合适。

2.3 温度的影响

温度对各项指标的影响见图 6。温度升高溶液比电阻下降、电耗降低、电流效率增加、金银回收率也较高, 阴极铅质量亦好。但温度较高, 阴极铅结晶粗大, 各项指标下降; 而且高温也增大电解液的蒸发损失, 使劳动环境恶化也是不可取的, 因此温度选定 40 $^{\circ}\text{C}$ 是合适的。

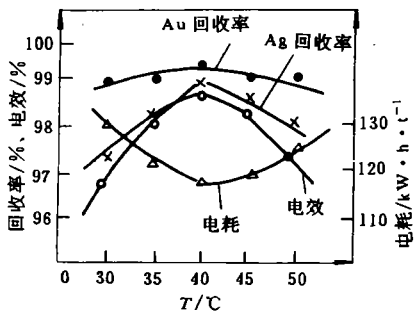


图 6 温度变化对金银回收率, 电流效率及电能消耗的影响

2.4 电流密度的影响

其它因素为基准条件, 电流密度对各项指标的影响见图 7。

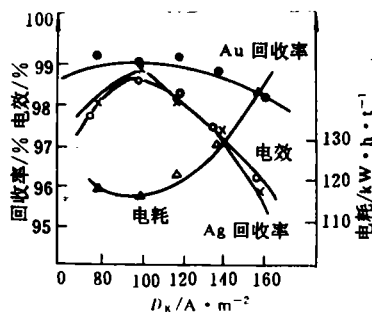


图7 电流密度变化对金银回收率, 电流效率及电能消耗的影响

电流密度较低时, 阴极极化不高, 较难形成光滑致密的阴极铅, 也会增加金银的机械损失和降低电流效率。但电流密度过高时, 阴极极化过于强烈, 阴极附近铅离子浓度显著降低, 致使阴极铅结晶不佳。同时阳极极化的增加会使某些杂质在阳极溶解和随后阴极析出, 甚至引起阳极钝化。从图7可见最佳阴极电流密度为 100 A/m^2 。

2.5 添加剂的影响

β -萘酚-骨胶联合添加剂可显著改善阴极铅结晶状况。若添加量太少, 则阴极极化过低, 而使阴极铅沉积物结构恶化; 但过多又会增大电解液比电阻而使电耗升高。由图8可见添加 0.002 g/L 萘酚和 0.5 g/L 骨胶时效果最好。

3 结论

(1) 本研究贵铅电解分离过程最佳工艺条

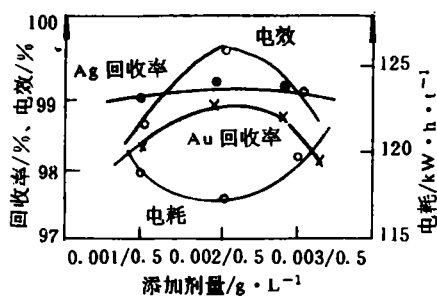


图8 β -萘酚-骨胶联合添加剂对金银回收率、电流效率及电能消耗的影响

件为: $[\text{Pb}^{2+}] 70 \text{ g/L}$; $\sum[\text{SiF}_6^{2-}] 100 \text{ g/L}$; 40°C ; β -萘酚-骨胶联合添加剂浓度, 其中 β -萘酚 0.002 g/L , 骨胶 0.5 g/L ; 阴极电流密度 100 A/m^2 。

(2) 在最佳工艺条件下电解时, 金银回收率分别在 99% 和 98% 以上, 电流效率 98.7% , 比电耗 $117 \text{ kW} \cdot \text{h/t Pb}$ 。

(3) 还原熔炼-电化学分离工艺适合处理含 Au、Ag 低同时存在 Pb(或 Cu) 或其氧化物之废料。回收金银和铅的工艺可获得较好的经济及环境效益。

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敬 告 作 者

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creasing with reaction time under conditions of 0.85 MPa and 900°C, and the conversion rate is in range of 23.5% to 42% at 120 minutes. The conversion rate is drastically growing with temperature under conditions of 1.15 MPa and 750–950°C at 120 minutes. The conversion rate was slowly and linearly increasing with pressure under condition of 860°C. Finally, the reaction mechanism was discussed.

Key words: pressurized thermogravimetric analysis, limestone, dolomite, desulfurization.

Study on the Regeneration of NaHSO_3 in the Recovery of SO_2 from Flue Gas by Bipolar Membrane Electrodialysis. Yu Lixin et al. (Department of Chemical Engineering, Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 40–42

Bipolar membrane electrodialysis is adopted in the regeneration of NaHSO_3 , which is used as absorbent of SO_2 from flue gas. When cation-exchange membrane is supplemented with , both homogeneous and heterogeneous bipolar membranes which are made in our lab and by Shanghai Chemical Factory, respectively, can produce satisfactory conversion ratio (higher than 80%) in the regeneration process. The decrease of current efficiency (from approximately 80% to approximately 20%) is resulted from the increase of the concentration of proton in acid chamber. The existence of small amount of Na_2SO_4 in NaHSO_3 solution doesn't cause much effect on regeneration process. The short membrane lifetime hinders the process from getting into practical application.

Key words: bipolar membrane electrodialysis, recovery of SO_2 from flue gas, regeneration of NaHSO_3 .

Study on Characterization of Adsorption of Zinc onto five types of soil in Beijing Area. Zhou Wei and Li Jiyun (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 43–45

The results of study on adsorption of zinc onto five types of soil in Beijing area showed that the capacity of five types of soil adsorbing zinc presents positive correlation with pH value of the soil solution, contents of organism and CaCO_3 etc in soil. The adsorption data could be fitted to the Freundlich-type equation.

Key words: adsorption, zinc, soil, Beijing area.

A Study on Acclimation Technique of Activated sludge and Biological Treatment of High Consistence Cheni-thermomechanical Pulp Wastewater. Chen Min (Guangdong University of Technology, Environment & Resource Engineering Department, Guangzhou, 510090), Sung-Nien Lo and H-Claude Lavallée (Université du Québec à Trois-Rivières, Québec, Canada, G9A 5H7); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 46–49

The treatment of high consistence Cheni-thermomechanical Pulp (CTMP) pulping wastewater using activated sludge method was studied in this paper. The effect of improving technique in activated sludge acclimation on the sludge settleability and removal efficiencies was discussed. The Experiments showed that the improved technique i. e

combination of batch and continous feed in sludge acclimation process can remarkably improve the sludge settleability and removal efficiencies. The sludge volume after 30 minutes of settling was 290–320 ml/L, sludge volume index was 48–55 ml/g, the removal of COD reached to 77%–85%, removal of BOD_5 was 90%–95%, removal of TSS was 75%–89%.

Key words: batch feed, continous feed, activated sludge, acclimation technique, CTMP wastewater.

Test of Tar Emulsified Liquid as Dust Suppressant for Dirt Roads. Wu Chao et al. (Dept. of Resources Exploitation Engineering, Central South University of Technology, Changsha 410083); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 50–52

In order to control the dust raising on the dirt roads efficiently, the tar emulsified liquid with low concentration was taken as the dust suppressant. Based on a great number of experiments in laboratory, the optimum compositions of surfactants and the prepared condition for emulsifying tar were achieved, tar is 3%–6%, surfactants is 0.5% and water is 93.5%–96.5 Wt. %. The prepared temperature is greater than 70°C. Depended on a lot of tests both in laboratory and field, the results showed that the liquid is very efficient for binding dust and maintaining the dirt roads. The active time can reach more than 10 days, when the liquid is sprinkled on the road in 2.2 kg/m². A rational profit can also be achieved after it is used for years.

Key words: dust suppressant for roadway, tar emulsified liquid, field test.

Electrochemical Separation Process for Recovery of Gold, Silver and Lead from Scrap. Liang Huqi et al. (Dept. of Chem. Eng., Shanghai University, 200072); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 53–56

The electrochemical separation process for comprehensive recovery of gold, silver and lead from Au, Ag-containing scrap was investigated. The smooth and dense cathodic deposit with purity of 99% Pb was prepared by electrochemical separation process under the optimum technological conditions (electrolyte composition: 70 g/L Pb^{2+} , 100 g/L total SiF_6^{2-} ; solution temperature: 40°C. current density: 100 A/m²; concentration of β -naphthol to bone glue: 0.002 g/L and 0.5 g/L) experimentally. The current efficiency of lead was higher than 98%, the specific electric energy consumption was 117 kW · h/tPb. The recovery of Au and Ag in the anode slime were as high as 99% and 98% respectively.

Key words: recovery of Au and Ag, electrochemical separation, treatment of scrap.

Effects of Low pH Value and Aluminum on Uptake of ^{45}Ca by *Misgurnus anguillicaudatus*. Kong Fanxiang et al. (Dept. of Environ. Sci. and Eng., Nanjing University, Nanjing 210093); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 57–59

The effects of low pH value and with or without the addition of aluminum on the uptake of ^{45}Ca by *Misgurnus anguillicaudatus* were studied. The results showed that