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COMMUNICATION

Electroreductive Stripping of Silver in the $(C_6H_5)_3P$–$Na_2S_2O_3$ Two-Phase System

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INTRODUCTION

The increasing application of hydrometallurgical alternatives for the treatment of complex ore materials has caused remarkable development in solvent extraction processes (1). The success of solvent extraction for the purification of metals depends both on the efficiency and selectivity of the chosen solvent, as well as on the suitability of the stripping solution. Electrolysis of this latter aqueous phase is then necessary to produce the metal in its final form (2).

The recovery of precious metals from different sources is of economic interest, and several solvent extraction studies, either from a technological (3) or from a scientific point of view (5), have appeared. A detailed survey on this subject indicates an effective affinity of this class of metals for sulfur- and/or phosphorous-containing extractants (4–6).

The aim of this work is to emphasize the viability of the direct production of a metal, namely silver, by a two-phase electrolysis. The conventional operations of metal stripping and subsequent electrowinning are, in this way, replaced by a one-step technique (7).

EXPERIMENTAL

An 0.8-M solution of triphenylphosphine (98%) in dichloromethane p.a. was used in all the extraction experiments. An aqueous solution of silver

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nitrate (99.5%) with a 0.5-M concentration was performed by dissolution of the salt in 0.7 M nitric acid. A 2-M sodium thiosulfate solution in distilled water was also prepared.

Extraction experiments were carried out using equal volumes of the silver feed and organic solution, which were mixed by a magnetic stirrer for 15 minutes. Metal contents in the organic phase were calculated by the difference between the silver concentration before and after extraction using atomic absorption spectroscopy (SP9 Pye-Unicam model).

Conventional stripping essays were similarly performed by equilibration of the loaded solvent and the thiosulfate solution for 1 hour.

Density measurements were carried out by using the pycnometer method.

Determinations of conductivity were performed in the required organic and aqueous phases by a Metrohm Conductometer model 644.

Two-phase electrolysis was carried out in a cell consisting of a silver wire cathode and a graphite bar anode. Equal volumes of the loaded organic phase and the thiosulfate solution were then mixed by mechanical stirring.

The circuit consisted of a Unilab Power Supply (2.5 V; 8.5 A), a Fluke 75 Multimeter to control the current intensity, and an Univolt DT-777 Multimeter to measure the potential of the cell. All operations were at constant current, the average current density and cell potential being 37 $mA \cdot cm^{-2}$ and 2.4 V, respectively.

Cathode deposits were analyzed by scanning electronic microscopy using a JEOL JSM-T300 Scanning Microscope associated with an EDS model TRACOR Northem TX 1/50-6618.

RESULTS AND DISCUSSION

The solvent extraction of silver from a nitric medium was carried out by the use of triphenylphosphine as the extractant (8, 9) and sodium thiosulfate for the stripping solution (4). The results obtained are presented in Table 1.

TABLE 1

Extraction and Stripping Efficiencies. Efficiency of Silver Extraction from Nitric Medium and Stripping Yield ($[Ag^+] = 0.5$ M, $[HNO_3] = 0.7$ M, $[(C_6H_5)_3P] = 0.8$ M in Dichloromethane, $[Na_2S_2O_3] = 2$ M

	Extraction	Stripping
Efficiency (%)	98	62
Equilibration time (minutes)	15	60

TABLE 2
Selectivity of $(C_6H_5)_3P$. Extraction Efficiencies of $(C_6H_5)_3P$ for Silver and Copper in Two Different Ion Ratios

	η_{ext} (%)	
$Ag^+:Cu^{2+}$	Ag^+	Cu^{2+}
1:1	100	0
1:450	100	3

As would be expected, triphenylphosphine proved to be an efficient extractant for silver, also denoting good selectivity for this metal in the presence of an excess of copper, as shown by the results presented in Table 2.

Although the reasonable results obtained for conventional stripping led to a preliminary choice of a similar solution for the two-phase electrolysis process, some other parameters had to be adjusted, mainly the densities of the loaded organic and stripping phases and the related conductivities (7).

In combination with the shaking speed of the mixture, the density ratio of two immiscible liquids is determinant when a good intrinsic mixture is to be achieved (7). Therefore, the densities of a silver–triphenylphosphine–dichloromethane solvent and a 2-M sodium thiosulfate solution were measured, giving values of 1.4 and 1.2, respectively. The nearer the densities of the two phases, the higher the degree of mixing attained, thus the results obtained were close enough to allow good mixing.

Some problems could have arisen in the adjustment of a suitable conductivity for the mixture because the conductivity values for organic solvents are usually low (10). Among the carriers available, dichloromethane is the best in enhancing the electric conductivities of the organic phase, and this result is in agreement with data presented previously (7).

An 0.8-M solution of triphenylphosphine in dichloromethane was then submitted to contact with a 0.7-M solution of HNO_3 in order to determine its conductivity after equilibration with a 2-M sodium thiosulfate solution as a function of different times of shaking, Fig. 1. It can be seen from the figure that the conductivity increased to about 0.8 $mS \cdot m^{-1}$ for 15 minutes of equilibration, and that value remained practically constant after that time. A first evaluation of these results suggested that the electric conductivity was quite low for an electrolysis to be carried out. However, the conductivity cell immersed in the mixture of organic and aqueous stripping phases showed values of about 2.4×10^3 $mS \cdot m^{-1}$, which are more appro-

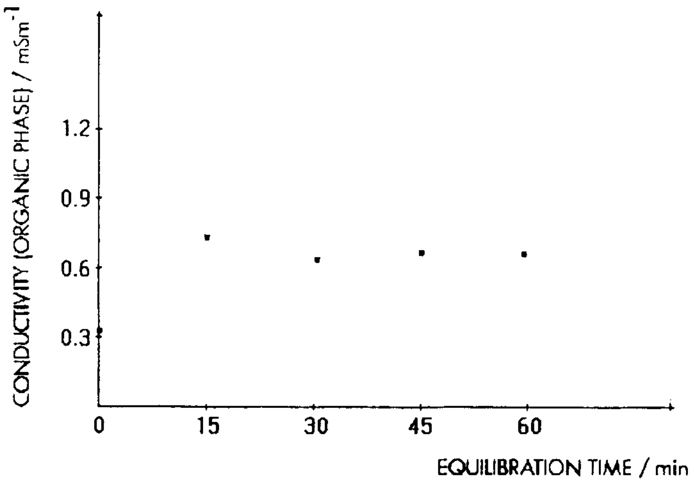

FIG. 1 Conductivity of an organic phase after different times of contact with a 2-M thiosulfate stripping solution (aqueous:organic = 1).

priate for the electrolytic process. Moreover, the presence of silver ion certainly increases this parameter.

Equal volumes of $Ag^+-(C_6H_5)_3P-CH_2Cl_2$ and $Na_2S_2O_3$ solutions were mixed by mechanical stirring in the electrolytic cell. Metallic silver was always obtained with a current efficiency greater than 90% for at least 1 hour of electrolysis. For instance, 2 hours of electrolysis resulted in a current efficiency of 98% and a yield of stripping for silver (given by the sum of the deposit and the stripping solution silver content) of about 88%.

For comparison with conventional stripping, a two-phase electrolysis was carried out for 1 hour. The results are summarized in Table 3.

To confirm the viability of this two-phase system electrolysis, experiments testing the performance in a second electrolysis of already used organic and stripping solutions were carried out. Current efficiencies of

TABLE 3
Conventional and Electroreductive Stripping Efficiencies. Comparison of the Efficiencies Presented by the Conventional and Electroreductive Stripping of Silver

Stripping	Efficiencies (%)
Conventional	62
Electroreductive	79 (ρ_I = 99%)

93 and 95% were obtained, respectively, for the first and second electroreductive processes. These results showed that the organic solvent maintains a reasonable stability and has a high extractive power after having suffered an application of electric current.

Furthermore, analysis of the cathode deposits resulting from two successive two-phase electrolysis runs showed comparable values, Table 4.

In addition to the main reactions taking place in the electrodes:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \tag{1}$$

$$Ag^+ + e \rightarrow Ag^0 \tag{2}$$

the decomposition of $S_2O_3^{2-}$ to SO_3^{2-} in the anode is also possible:

$$S_2O_3^{2-} + 6OH^- \rightarrow 2SO_3^{2-} + 3H_2O + 4e \tag{3}$$

The presence of sulfur in both deposits can be explained by a reductive process involving the S atom of thiosulfate in combination with silver ion and protons:

$$S_2O_3^{2-} + 4Ag^+ + 6H^+ + 8e \rightarrow 2Ag_2S + 3H_2O \tag{4}$$

It can be assumed that Reaction (4) occurred to a greater extent during the second electrolysis. One reason for this is the decrease of pH in the stripping solution after the first passage of current.

Phosphorous in the cathode deposits may be considered to arise by another competitive reaction taking place in the cathode:

$$(C_6H_5)_3P + 3H^+ + 3e \rightarrow 3C_6H_6 + P^0 \tag{5}$$

The decrease in phosphorous content verified in the second deposit is probably caused by the lower availability of the extractant after the first two-phase electrolysis.

TABLE 4
Metallic Silver Analysis. Analysis of the Cathode Deposits before and after the Reutilization of Phases by SEM-EDS

	Appearance (%, w/w)	
Element	1st electrolysis	2nd electrolysis
Ag	88.6	87.8
P	7.9	0.3
S	3.5	9.1
Na	—	2.8
	$\rho_I = 93\%$	$\rho_I = 95\%$

In spite of the contaminations referred to in Table 4, the purity of silver in both deposits is acceptable.

CONCLUSIONS

The results presented in this work demonstrate that the electroreductive stripping of silver from a loaded organic solvent containing triphenylphosphine is possible.

An average current efficiency greater than 90%, a reasonable electrical energy consumption (0.63 kW/kg of Ag), a good silver content in the cathode deposits, and the possibility of phase reutilization are encouraging features for the optimization and implementation of this alternative process.

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