Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Bart, H. J. , Marr, R. and Prior, A.(1987) 'Solvent Extraction of Copper from a Silver Electrolyte', Separation Science and Technology, 22: 2, 325 — 334
To link to this Article: DOI: 10.1080/01496398708068955
URL: http://dx.doi.org/10.1080/01496398708068955

SEPARATION SCIENCE AND TECHNOLOGY, 22(2&3), pp. 325-334, 1987

Solvent Extraction of Copper from a Silver Electrolyte

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ABSTRACT

This paper presents a process for treatment of an $AgNO_3$ electrolyte. Ag/Cu separation is done with conventional solvent extraction (SX). Cathode copper is electrowon in a diaphragm electrolysis cell while silver scrap is simultaneously dissolved anodically. The process proves to be a very effective recycling technique and is now being investigated on a pilot scale.

INTRODUCTION

Silver is one of the oldest metals in use. Traditionally it is found in coins and jewellery. However, there is a considerable demand for it in today's industry. Since primary production of Ag cannot cover today's requirements there is a need for an effective recycling technique. Technical alloys have a silver content in the range of 40 to 92.5 %. The remaining percent is mainly copper. For this reason there is a need for a purification procedure to remove copper. Without this it would be impossible to produce fine silver in an electrolysis cell.

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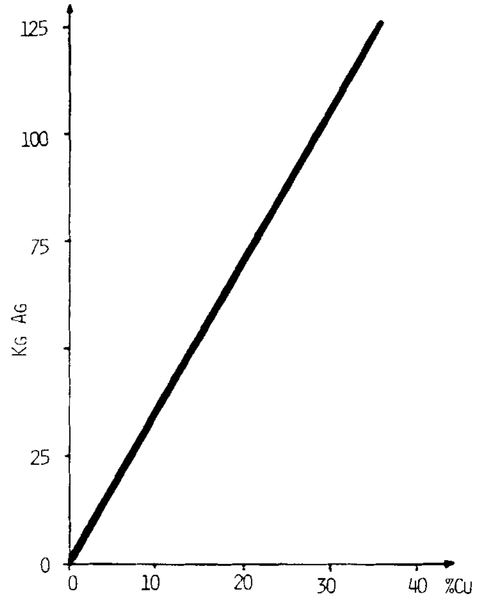

Fig. 1. Addition of silver to the electrolyt as function of Cu in scrap

Conventional Procedure

Electrolytical silver recovery can be done in a conventional Möbius- or Balbach/Thum cell. For direct production of fine silver the scrap should be at least 95 % silver. At silver percentages lower than this an addition of $AgNO_3$ to the electrolyte is needed as indicated in figure 1.

During silver electrowinning copper remains in solution and may be tolerated up to 60 g/l. Beyond this point the whole electrolyte has to be removed. This is done in several steps. The first step is Ag cementation with copper wires followed by Cu cementation with iron scrap. The remaining nitric acid electrolyte is neutralized and disposed of.

The disadvantage of this procedure is the high costs of the copper removal procedure which also produces undesirable effluents. The expensive addition of $AgNO_3$ makes the use of low grade feed material not attractive.

Alternative Procedure

An alternative process (1) has been developed, which removes copper continuously via SX technique (2,3). The result is in a longer endurance of the Cu/Ag electrolyte. Furthermore, addition of $AgNO_3$ may be drastically reduced. Even copper rich srap is an acceptable feedstock. With this process cementation is subtituted and the resulting effluents are considerably reduced.

EXPERIMENTAL

The scope of the work is to extract copper selective from a silver matrix. It is generally known that chelating agents of different origin, like LIX64N (Henkel Corp.), SME 529 (Shell Int.) or Acorga PT5050, P5300 (ICI Chem.) are useful tools to extract copper. In all cases organic phases with 20 % at ion exchanger in a kerosene diluent, MSB210 (Shell Int.), was used. Equilibrium isotherms are measured in shaking funnels. Analyses were performed on an atomic spectrometer, IL Video 22. Calculation of the mixer settler computer program were done on a VAX11/750.

RESULTS AND DISCUSSION

Extraction

Typical extraction isotherms are in figure 2. Here SME and Acorga P5300 are used, respectively. SME has twice as much copper loading ability as P5300.

The problem in the extraction process is in a co-extraction of silver. A silver extraction isotherm is in figure 3.

In comparison with copper, silver extraction is considerably low.

Coextraction of silver demands a scrubbing procedure which becomes costly when the silver content in the organic phase is increased. For this, selectivity factors are given in table 1.

O/A=1, 20°C, pH=1, Möbius g/l : 66 Ag, 37,7 Cu				
	SME 529	LIX64N	P5300	PT5050
g/l Cu org.	9,6	6,9	5,9	10,4
g/l Ag org.	0,25	3,9	0,02	0,005
Cu:Ag	38	1,76	300	2100

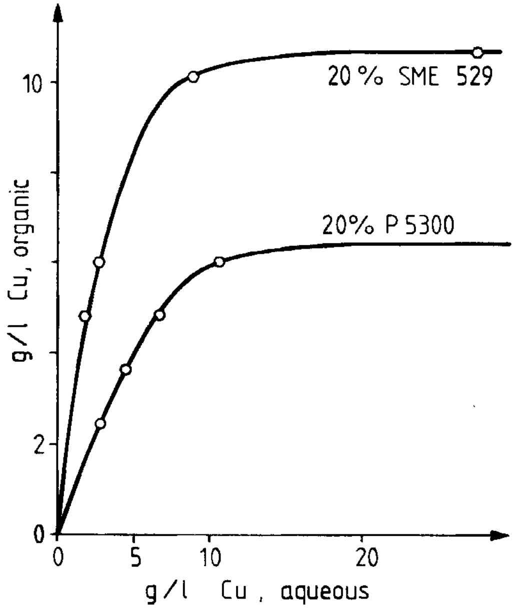

Fig. 2. Extraction isotherms of copper. Organic phase with 20 % ion exchanger in kerosene. Aqueous phase: 150 g/l Cu $(NO_3)_2$, 40 g/l Ag, pH = 2.

In therms of maximal copper loading, PT5050 and SME 529 are equivalent. The same is true with LIX64N and P5300. In regard to selectivity, PT5050 is the dominating compound.

Reextraction

Regeneration of the organic phase is best done with nitric acid. Figure 4 shows the effect of concentrations between 1,0 and 2,5 mol/l HNO_3.

Stripping efficiency is improved with increasing acid concentration. Similarly to this, degradation of the organic phase is enhanced with rising acid concentration. Degradation of the organic phase is given in figure 5 with 2,0 mol/l HNO_3 (4).

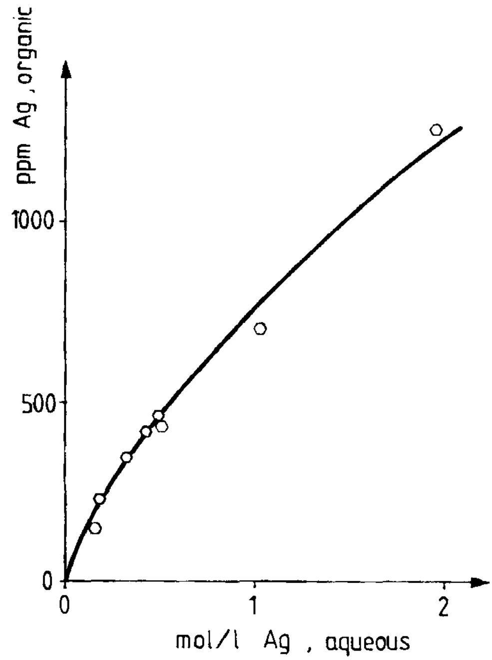

Fig. 3. Extraction isotherms of silver
Organic phase: 20 % SME 529 in kerosene
Aqueous phase: $AgNO_3$ at pH = 4

The effect is the continuous reduction of copper loading capacity. In this same way the stripping efficiency is improved. The net result is a constant copper transfer of the organic phase which can be guaranteed for months. The economical aspect of this point is considered to be significant. After about one year's use the transfer capacity of the organic phase is at zero. For these terms the stripping operation has to be optimized in reference to feed acid concentration, phase ratio and stripping stages. Optimization is done with a mass balance calculation program, MIXSET (5). The results are in figure 6.

MIXSET solves mass balances in regard to the proton balances. The dependence of the equilibrium line on pH is demonstrated in the diagram. AB is the operating line on a phase ratio O/A=2. ABC is a calculation with one,

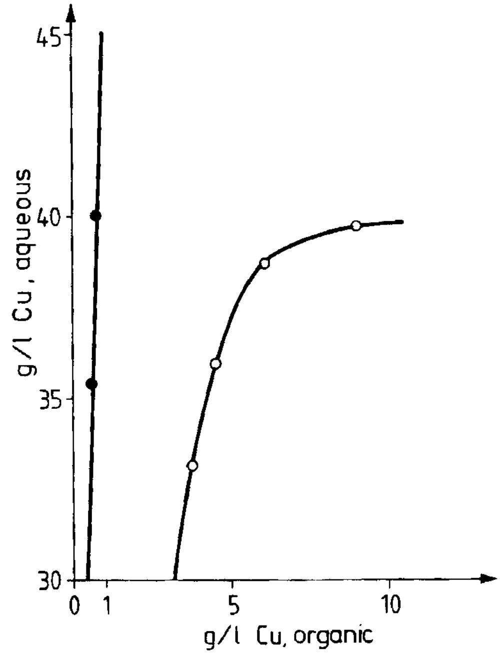

Fig. 4. Reextraction isotherms of copper
Organic phase: 20 % SME in kerosene.
Aqueous phase: 30 g/l Cu,● 2,5 mol/l,
○ 1,0 mol/l HNO_3.

and ABDEF with two stripping steps. The calculated proton balances are in table 2.

In that Mc Cabe Thiele like construction raffinat point C meets equilibrium line at 1,4 mol/l H^+.In the case of a two step reextraction, raffinat point D is exactly at 1,0 mol/l H^+.

As can be seen from table 2 a two-step reextraction can achieve the same stripping effect with weaker acid concentrations than a one-step reextraction with higher acid concentrations.

Pilot Plant Investigations

For the pilot project we used a plant whose flowsheet is shown in figure 7.

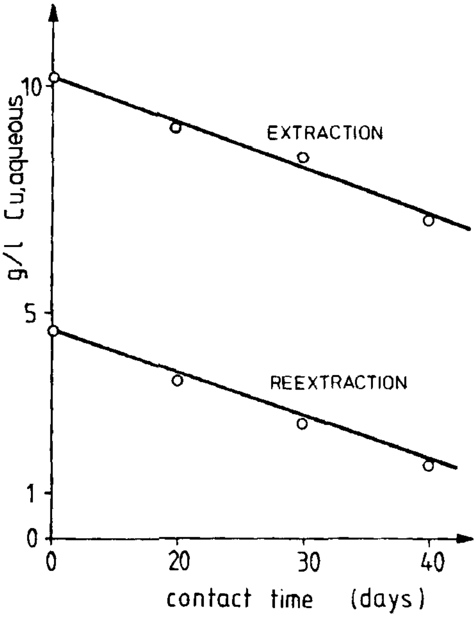

Fig. 5. Degradiation of the organic phase
Organic phase: 20 % PT5050 in kerosene
Aqueous phase: 2,0 mol/l HNO_3

TABLE 2
Mass balance calculation, MIXSET

g/l	ONE STEP in	ONE STEP out	TWO STEPS in	TWO STEPS out
Cu^{++} organic	10,2	5,2	10,2	5,2
Cu^{++} aqueous	30	40	30	40
H^{+} aqueous	1,8	1,4	1,3	1,0

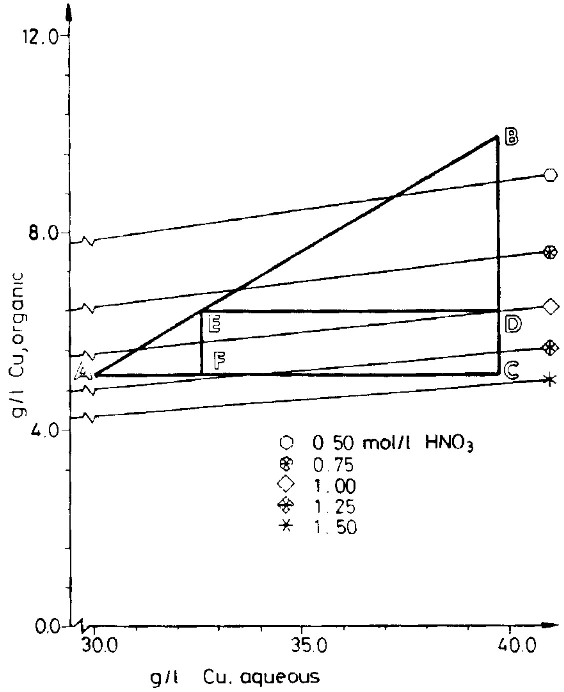

Fig. 6. Reextraction isotherms of copper
Organic phase: 20 % PT5050 in kerosene
Aqueous phase: 30 g/l Cu, nitric acid
AB: operating line, organic/aqueous phase = 2
ABC: One step reextraction
ABDEF: Two steps reextraction

Copper extraction is performed in a two stage mixer settler unit (4,5). The copper barren electrolyte is sent to the Möbius cell (1), where silver is electrolytically won. The copper loaden organic phase is scrubbed (6) and then regenerated (7) with nitric acid and is ready for further use. The aqueous scrub solution, E3, is combined with the Möbius electrolyte, E1, in a storage tank (3). The copper strip solution, E2, is regenerated in the cathode half of the diaphragm electrolysis cell (8). In the anode half of the cell (2) 3,37 kg silver is dissolved when 1 kg copper is won cathodically. The chelating agent used in the organic phase is Acorga PT5050. Depending on the selectivity values obtained in the pilot plant circuit,

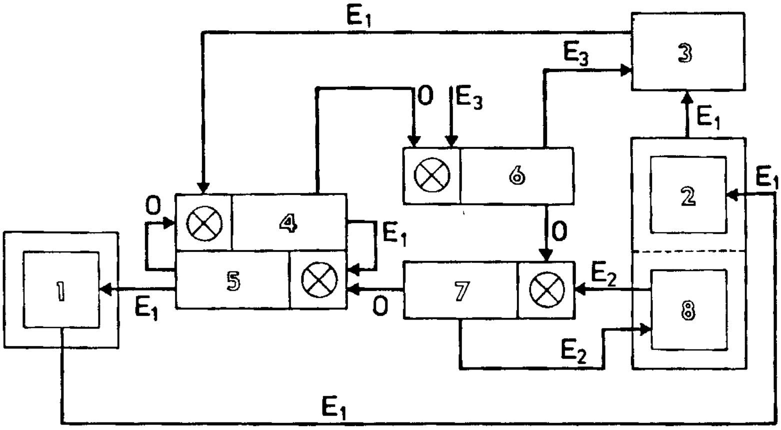

Fig. 7. Cu/Ag separation plant
(1) silver electrolysis, (2) anodic side of the diaphragm electrolysis cell, (3) tank, (4,5) extraction, (6) scrubbing, (7) reextraction, (8) cathodic side of the diaphragm cell (O organic phase, E1 Möbius electrolyte, E2 strip solution, E3 scrub solution)

the scrubbing stage may be omitted. The new optimized plant may then consist of two extraction and two stripping stages. As a result, lower acid concentrations can be used for stripping as is discussed with table 2.

CONCLUSIONS

A complex inline process was developed to separate copper via SX from a silver electrolyte. Depending on the copper extractant used a broad selectivity range is resulting. With the very selective Acorga PT5050, a very simple extraction circuit without any scrub operation may arise. As is demonstrated with a mass balance calculation optimal reextraction is done in a two step operation. With this weaker nitric acid may be used during stripping which consequently gives lower degradation of the organic phase. A diaphragm electrolysis cell simultaneously operated with the refining electrolysis cell permits cathodic recovery of copper. The electrolyte is replenished with $AgNO_3$ with anodically dissolving silver scrap. Direct electrolytic refining of copper-rich silver bullion is thus economically possible. Besides its economic feasibility, the method has little negative effect on the environment.

ACKNOWLEDGMENT

The authors wish to thank ÖGUSSA, Vienna, for financial support of this work.

SYMBOLS

E1	Möbius electrolyte
E2	stripping electrolyte
E3	scrubbing electrolyte
O	organic phase
A	aqueous phase

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