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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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ELECTROLYSIS OF COPPER FORM STRIPPING SOLUTIONS FOR ETCHING PRINTED CIRCUIT BOARDS

Abstract The article reviews the liquid extraction - electrolysis based etching solution regeneration process for printed circuit boards.

It describes process conditions providing the electrolysis of copper from sulphate solutions that are formed at the stage of stripping (re-extraction) of copper ions (II) from organic extractants.

Tests have been carried out in an industrial environment.

It shows that the electrolysis of copper proceeds generating high current efficiency where a stripping solution contains 1.0 mol/l of sulfuric acid and 0.8 - 1.0 mol/l of copper ions (II), the current density is 1.0 - 6.0 A/ dm^2 and electrolyte is mixing. An analysis has been made of the composition of cathode copper obtained as a result of electrolysis from the reference electrolyte and stripping solutions upon contact with organic extractants. It has been found that the purity of cathode copper reaches 95 - 98% of the base substance. It has also been found that stripping solutions progressively accumulates an insoluble precipitate comprising about 40% of lead, which may be attributed to the mechanical destruction of the active anode layer composed of lead oxides (PbO_2). The study shows that it is necessary to look for a anode material to replace lead dioxide anodes having poor stability in this process.

Keywords: printed circuit boards, etching, copper-ammonia solutions, copper-chloride solutions, regeneration, extraction, stripping solutions, electrolysis, anode, cathode copper, current density, current efficiency.

Introduction

The operation of etching the copper layer from the non-conductor surface is the requisite stage in the process of manufacturing printed circuit boards [1, 2]. At present, two types of etching solutions are primarily used, i.e. those of hydrochloric acid or alkaline ammonium. And in both cases, the formulation includes dichloride copper lending a distinct quality to the etching mechanism [3-5].

The dissolution process is driven by the interaction of metallic copper with ions of divalent copper acting as an oxidizing agent for the solution, resulting in a gradual increase in the total content of copper ions in the solution thus progressively slowing down the etching rate necessitating changing the solution. In up-to-date processes it is essential to maintain the etching rate at the same level. It is achievable by the fixed composition of the etching solution [6,7].

This can be done by using regeneration systems. The maximum desired effect has been produced by the regeneration process based on the recovery of copper ions by extraction from an aqueous etching solution [8-10]. Following the extraction stage, copper ions are re-extracting into the sulfate electrolyte depositing metallic copper onto the electrolyzer cathode [11–13]. The reactions describing the entire etching and regeneration process cycle are detailed in Table 1.

Table 1- The etching and regeneration reactions using the method of liquid extraction & electrolysis of copper-ammonia and copper-chloride based etching solutions

Item No.	Operations	Typical reactions for etching and regeneration	
		Copper ammonia solution	Copper chloride solution
1	Etching	a) $Cu^0_{met.} + Cu(NH_3)_4Cl_2 \rightarrow 2Cu(NH_3)_2Cl$; б) $2Cu\ (NH_3)_2Cl + 1/2O_2 + 2NH_4OH + 2NH_4Cl \rightarrow 2Cu(NH_3)_4Cl_2 + 3H_2O$.	a) $Cu^0_{met.} + CuCl_2 \rightarrow 2CuCl$; б) $2CuCl + 1/2O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$.
2	Extraction	$2HR^*_{(org.)} + Cu(NH_3)_4Cl_2 + 2H_2O \rightarrow CuR_2{}^*_{(org.)} + 2NH_4Cl + 2NH_4OH$	$2HR^{**}_{(org.)} + CuCl_2 \rightarrow CuR_2{}^{**}_{(org.)} + 2HCl$
3	Stripping	$CuR_2{}^*_{(org.)} + H_2SO_4 \rightarrow CuSO_4 + 2HR^*_{(org.)}$	$CuR_2{}^{**}_{(org.)} + H_2SO_4 \rightarrow CuSO_4 + 2HR^{**}_{(org.)}$
4	Electrolysis	a) cathode: $CuSO_4 + 2e \rightarrow Cu^0_{cat.} + SO_4^{2-}$; b) anode: $H_2O - 2e \rightarrow 1/2O_2\uparrow + 2H^+$	a) cathode: $CuSO_4 + 2e \rightarrow Cu^0_{cat.} + SO_4^{2-}$; b) anode: $H_2O - 2e \rightarrow 1/2O_2\uparrow + 2H^+$
5	The resultant reaction is as follows:	$Cu^0_{met.} \rightarrow Cu^0_{cat}$	$Cu^0_{met.} \rightarrow Cu^0_{cat}$
Legend: $HR^*_{(org.)}$ and $HR^{**}_{(org.)}$ - extractants, $CuR_2{}^*_{(org.)}$ and $CuR_2{}^{**}_{(org.)}$ - copper organic compounds, $Cu^0_{cath.}$ – non-conductor copper, $Cu^0_{cath.}$ – cathode copper			

It can be seen from the above-referenced reactions that the etching of copper and the regeneration of etching solutions using the liquid extraction & electrolysis method looks balanced making all solutions reusable and electrolytic copper the only by-product. In addition, it is evident that these etching solution regeneration systems have the common stage of electrically depositing copper from sulfate stripping solutions.

The process flow diagram of continuous regeneration of etching solutions for printed circuit boards is shown in Figure 1.

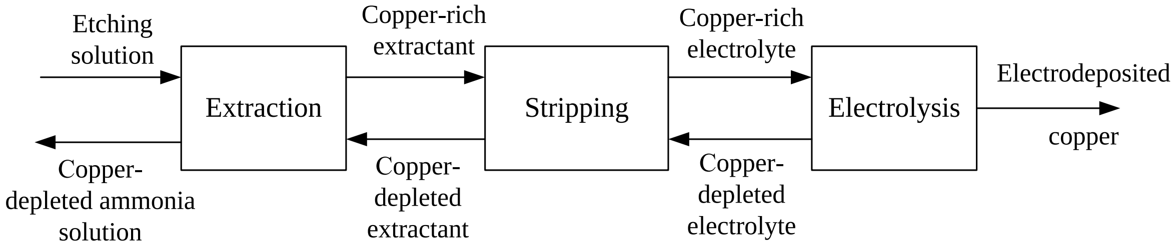


Figure 1 - Process flow diagram of continuous copper extraction and stripping followed by the electrochemical deposition of copper

The stages of extraction and re-extraction (stripping) have covered in sufficient detail earlier [14], while the features of copper electrolysis relating to this process have not been discussed.

Therefore, the purpose of this study was to examine the features of the cathode extraction of copper from stripping solutions.

Test Technique

To simulate the regeneration process and to obtain re-extraction copper-enriched solutions, the plant shown in Figure 2 was used.

The plant operates two ETs33F PTFE centrifugal extractors splitting the aqueous and organic phases under the impact of centrifugal forces at a rotor speed of 2,700 rpm [15]. The extractors enable a maximum of 15 l/h of the solution to be processed in a flow through mode.

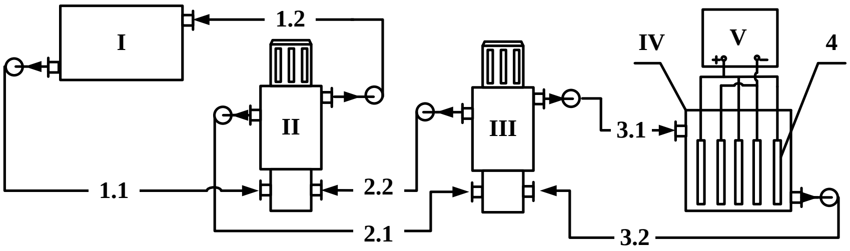
The plant includes a copper etching tank and a solution stripping copper electrolysis bath. During the test the plant was used in an industrial like environment. It was connected to a printed circuit board etching machine, as it is difficult to produce the requisite amount of etching solutions in laboratory conditions.

Polarization measurements were carried out in a three-electrode 50 cm^3 electrochemical cell using an IPC - Pro MF potentiostat/galvanostat. A copper plate with a 1 cm^2 surface was used as a working electrode; a platinum plate – an auxiliary electrode; a saturated silver chloride electrode –a reference electrode.

The obtained potential data were recalculated with respect to the reference hydrogen electrode (RHE). Polarization curves were recorded in a potential & dynamic mode with a potential sweep rate of 10 mV/s.

The assay test of the sediment was carried out using a JEOL JSM-5610 LV scanning electron microscope complete with an Oxford Instruments energy dispersive X-ray attachment. The dispersive parameters of the sediment were determined by laser diffraction using an Analysette NanoTec laser particle sizer.

To determine the concentration of copper (II) ions in the solution the complexometric titration method was applied. A 0.1 N solution of Trilon B (EDTA) was used as the titrant [16].



1.1 – Copper-rich etching solution; 1.2 – Copper-depleted etching solution; 2.1 – Copper-rich extractant;
2.2 – Copper-depleted extractant; 3.1 – Copper-rich electrolyte; 3.2 – Copper-depleted electrolyte; 4 – Electrodeposited copper;
I – Etching bath; II – Extractor 1; III – Extractor 2; IV – Electrolytic bath; V – DS source

Figure 2 - The test plant setup for solution etching and regeneration of solutions is given below

The current efficiency in% (CE) of cathode copper was obtained from polarization measurements using the formula:

$$CE = [(I_{copper}) / (I_{copper+hydrogen})] \cdot t \cdot 100\%, \qquad (1)$$

where:

I_{copper}– current strength (A) applied to extract copper is expressed as the difference between the current strength applied to extract both copper and hydrogen ($I_{copper+hydrogen}$) and extract hydrogen ($I_{hydrogen}$), t – electrolysis time (h).

The current applied to extract hydrogen was obtained from polarization measurements in the background electrolyte, i.e. a sulfuric acid solution. The current strength has been calculated by the formula $I = i \cdot S$, where: i is the current density (A/dm^2); S is the working electrode surface, dm^2.

In preparative electrolysis the specimen mass was determined before and after the electrolysis process while the current efficiency (CE) was measured gravimetrically:

$$CE = (m_{pr}/m_{\text{т}}) \cdot 100\% \qquad (2)$$

where:

$m_{pr.}$ – the weight of copper deposited on the specimen during electrolysis, r; $m_{\text{т}}$ – the calculated mass of copper that is presumed to be deposited during electrolysis r.

$m_{\text{т}} = g \cdot I \cdot t$, where: g is the electrochemical copper equivalent, 1.186 g/(A·h).

To extract copper from copper-ammonia solutions, a DH-510A [17] (Deltaplast LLC (Russia)) extractant was used.

To extract copper from copper chloride solutions a MX-90 (firm SIGMA –Engineering AB (Sweden)) extractant was used.

The anodes contain lead-base lead dioxide.

Test Results and Discussion Findings

Since the entire regeneration cycle for etching solutions is a chain in interrelated processes, it was essential to determine the parameters of copper extraction from stripping solutions and to set the process parameters that are to be maintained at this stage.

During the polarization measurements of solutions with different acid content the permissible values of current densities below the limit values at which dense copper deposits are formed were obtained (Figure 3).

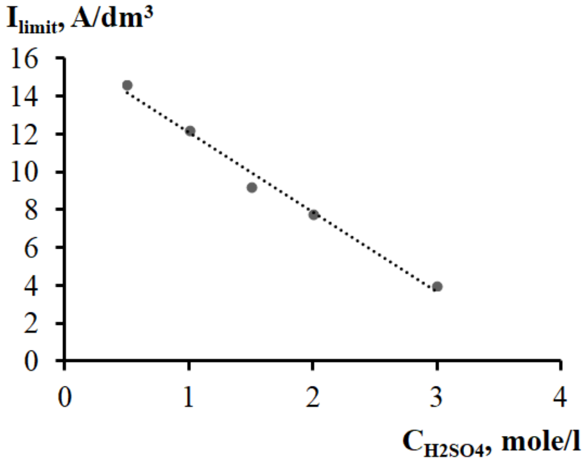


Figure 3 -The function of the limiting current density (i_{limit}) of copper extraction and a H_2SO_4 concentration in electrolyte The cathode potential is E = 220 mV (RHE)

It follows from the referenced data that solutions with a low content of sulfuric acid are more suitable for the electrolysis of copper, as they allow for a more expanded range of current densities at which compact copper deposits precipitate, which is well in accord with the literature data stating that dense copper coatings can be obtained with a sulfuric acid content of about 0.4– 0.7 mol/l [18].

But conversely, it is known that re-extraction runs rapidly with a sulfuric acid concentration of about 2.0 mol/l [19]. To finally settle on the process parameter in question, the value of copper current efficiency was determined as a function of sulfuric acid content in electrolyte. These data are reflected in figure 4.

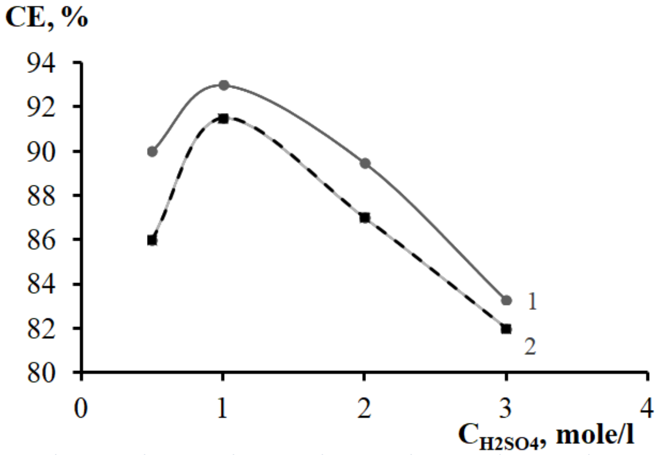


Figure 4 - The function of copper CE and the H_2SO_4 concentration in electrolyte during the electrolysis of the solution containing 0.50 mole/l of Cu^{2+} ions and i_c, A/dm^2 :1 – 1,5; 2 – 2

It was found that the maximum value of CE is observable with a sulfuric acid content of about 1.0 mol/l which is the most suitable for copper re-extraction and electrolysis.

On the other hand, the efficiency of copper electrolysis is much related to the content of copper (II) ions in a stripping solution. Figure 5 shows the relation between limiting current densities and the concentration of copper ions in a solution.

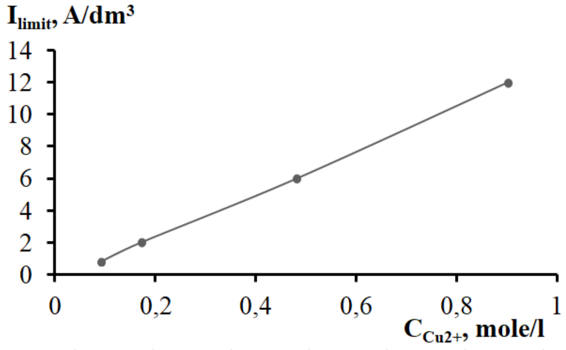


Figure 5 - The function of the limiting $i_{к}$ and the copper concentration
in a sulphate solution. C(H_2SO_4) 1.0 mol/l, E=0 mV (RHE)

A growing content of copper (II) ions in a stripping solution enables electrolysis in a wide range of current densities, and the linear function indicates that the diffusion of discharging copper ions to the cathode is critical. Stirring in electrolyte makes it possible to increase cathode current density by a factor of 1.5.

The obtained value of the current efficiency showed that copper is efficiently extracted from extraction solutions at the electrolyzer cathode reaching the limits of about 95-98% (Figure 6).

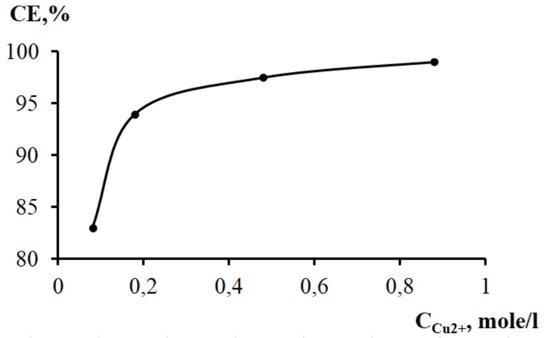


Figure 6 -The function of copper CE and a concentration of Cu^{2+} ions
in a sulfuric acid solution C(H_2SO_4) 1 mole/l, E=220 mV (RHE)

Figure 7 - Shows the relation of copper current efficiency and cathode current density at various concentrations of copper ions in a solution.

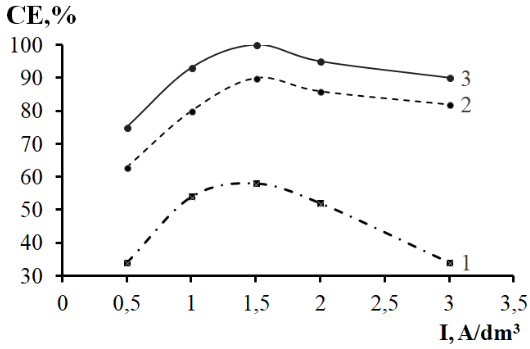


Figure 7 - The function of the copper CE and the cathode current density
at the concentration of copper ions in a solution, mol/l: 1- 0.08; 2- 0.39; 3-0.78

It was shown that while a high concentration of copper ions in a solution is maintained, the process performs well in a wide range of current densities. In the tests where a solution was mixed with air, current densities increased by a factor of a 1.5-2 can be used. The referenced results imply that the efficient electrolysis of copper requires a copper concentration in a stripping solution to be maintained at about 0.8-1.0 mol/l with the content of sulfuric acid being about 1.0 mol/L.

An analysis was mode of the composition of cathode copper obtained as a result of electrolysis from the reference electrolyte and stripping solutions upon contact with the organic extractants DX-510 A and MX-90 (table 2).

Electrically deposited copper comes out to be fairly pure. A small inclusion of oxygen can be attributed to partial deposit oxidation with ambient air oxygen. The inclusion of carbon can be accounted for by carbon dioxide present in electrolyte as well as the stripping solution being contaminated with an organic extractant.

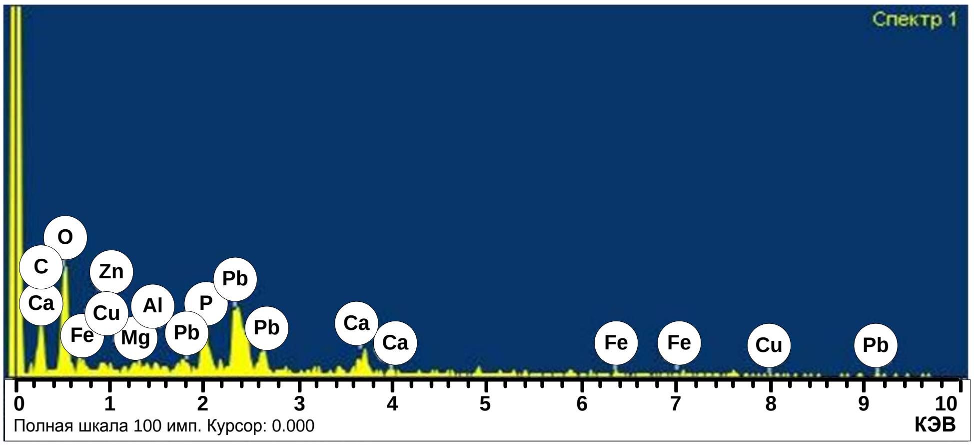
Table 2 - The element composition of copper obtained from solutions containing 0.80 mol/l of copper ions, 1.0 mol/l of sulfuric acid

Solution	Element	wt% in a deposit
Reference solution free of organic impurities	[C] / [O] / [Cu]	[0.11] / [2.67] / [97.22]
Stripping solution (using MX-90)	[C] / [O] / [Cu]	[0.73] / [3.98] / [95.29]
Stripping solution (using DX-510A)	[C] / [O] / [Cu]	[0.51] / [1.67] / [97.82]

When a reference plant is used to regenerate etching solutions, an insoluble precipitate is known to gradually accumulate in a stripping solution. The composition of this substance has been determined to find out what causes this phenomenon.

It was shown that the substance consists of amorphously structured inhomogeneous granules sized between 10 μm and 50 μm. Some impurities in the composition were found and quantified by a scanning electron microscope (Figure 8).

The deposit contains calcium, magnesium, aluminum, iron and zinc ions, which can be attributed to the fact that tap water was used to prepare the etching solution. It was found that the insoluble precipitate contains about 40% of lead. Lead can occur in a solution only as a result of mechanical destruction of the active anode layer comprising lead oxides (PbO_2). It is necessary to make allowance for the super high sensitivity of PbO_2 anodes to cathodic polarization that may take place when the electrolyzer is shut down. When powered off, the electrolyzer starts to function as a battery with the PbO_2 cathode, While PbO_2 gets partially reduced and the electrode gets covered by less stable phase lead oxides of lower valence [20-22].



Item No.	1	2	3	4	5	6	7	8	9	10
Element	C	O	Mg	Al	P	Ca	Fe	Cu	Zn	Pb
wt%	12.4	23.1	0.2	0.1	5.9	6.4	8.4	3.4	1.3	38.6

Figure 8 - The element distribution diagram for the insoluble precipitate in a stripping solution of sulfuric acid

Therefore, it can be stated that it is undesirable to use low-wearing anodes with an active layer containing lead oxides when copper is electrically deposited from stripping solutions in regeneration processes using etching solutions for printed circuit boards where such application requires electrolysis to be frequently stopped.

Conclusion

The tests have shown that the electric deposition of copper from stripping solutions in the regeneration process based on the liquid extraction-electrolysis system should be carried out under the following conditions:

a) the content of sulfuric acid etching solutions order is 1,0 mole/l; b) the content of copper (II) ions is 0.8-1.0 mol/l; c) the working current density is 1.0-6.0 A/dm^2; g) electrolyte mixing under these conditions an electrolytic deposit containing 95-97% of copper is produced.

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БАСПА ПЛАТАЛАРЫН ӨҢДЕУ РЕЭКСТРАГИРЛЕУ ЕРІТІНДІЛЕРІНЕН МЫС ЭЛЕКТРОЛИЗІ ЕРІТІНДІЛЕРДІҢ МЫСТЫҢ ЭЛЕКТРОЛИЗІ

Аннотация. Сулы экстракция –электролиз принципі бойынша жұмыс жасайтын баспа платаларын өңдеу ерітінділерін регенерациялау технологиясы қарастырылды.

Органикалық экстрагенттерден мыс (II) иондарын реэкстракциялау басқышында түзілетін күкіртқышқылды ерітінділерінен мыстың электрохомиялық жолмен бөлінуін қамтамасыз ететін технологиялық режимдер анықталды.

Тәжірибелер өндірістік шарттарда жүргізілді.

Мыстың электролизі реэкстрагирлеу ерітіндісінде 1,0 моль/л күкірт қышқылы, 0,8 - 1,0 моль/л мыс (II) иондары, ток тығыздығы 1,0 – 6,0 А/дм^2 болғанда және электролитті араластыру кезінде жоғары ток бойынша шығыммен жүретіндігі көрсетілді. Органикалық экстрагенттермен әсерлескен реэкстрагирлеу ерітінділерінің жзәне модельді электролит электролизінен кейін алынған катодты мыстың құрамы сарапталды. Негізгі зат бойынша катодты мыстың тазалығы 95-98 %-ды құрайды. Сонымен қатар, реэкстрагирлеу ерітіндісінде шамамен 40% қорғасыннан тұратын ерімейтін тұңбаның жиналатындығы анықталды. Бұл қорғасын оксидінен (PbO_2) тұратын анодтың белсенді қабатының механикалық бұзылуымен байланысты болуы мүмкін. Бұл технология үшін тұрақтылығы төмен болған қорғасын оксидінен жасалынған анодтарды алмастыра алатын материалды іздестіру керектігі көрсетілді.

Түйін сөздер: баспалы платалар, өңдеу, мыс-аммиак ерітінділері, мыс-хлоридті ерітінділер, регенерация, экстракция, реэкстрагирлеу ерітінділері, электролиз, анод, катодты мыс, ток тығыздығы, ток бойынша шығым.

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ЭЛЕКТРОЛИЗ МЕДИ ИЗ РЕЭКСТРАГИРУЮЩИХ РАСТВОРОВ ТРАВЛЕНИЯ ПЕЧАТНЫХ ПЛАТ

Аннотация. Рассмотрена технология регенерации растворов травления печатных плат, работающая по принципу жидкостная экстракция – электролиз.

Определены технологические режимы, обеспечивающие электровыделение меди из сернокислых растворов, образующихся на стадии реэкстракции ионов (II) меди из органических экстрагентов.

Эксперименты проводились в промышленных условиях.

Показано, что электролиз меди протекает с высоким выходом по току при содержании в реэкстрагирующем растворе 1,0 моль/л серной кислоты, 0,8 - 1,0 моль/л ионов (II) меди, плотности тока 1,0 – 6,0 А/дм^2 и перемешивании электролита. Проанализирован состав катодной меди, полученной при электролизе из модельного электролита и реэкстрагирующих растворов, после контакта с органическими экстрагентами. Установлено, что чистота катодной меди достигает 95 – 98 % по основному веществу. Вместе с тем было установлено, что в реэкстрагирующем растворе происходит постепенное накопление нерастворимого осадка, который примерно на 40% состоит из свинца. Это может быть связано с механическим разрушением активного слоя анода, состоящего из оксидов свинца (PbO_2). Показана необходимость поиска материала для анодов, заменяющих аноды из двуокиси свинца, малоустойчивых в данной технологии.

Ключевые слова: печатные платы, травление, медно-аммиачные растворы, медно-хлоридные растворы, регенерация, экстракция, реэкстрагирующие растворы, электролиз, анод, катодная медь, плотность тока, выход по току.

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