

PURIFICATION OF ELECTROPLATING WASTE WATER WITH TITANIUM ANODES COATED WITH MAGNETITE AND LEAD DIOXIDE

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Received 14 May 1997

Abstract. Hydrocyclone and parallel-plate electrolytic cells with lead dioxide and magnetite coated titanium anodes were applied for the purification of electroplating waste water. The kinetics of both the oxidation of cyanides and the deposition of copper was investigated. The turbulent swirling flow in the hydrocyclone cell enhances the mass transfer. The titanium anode coated with lead dioxide, which was prepared using a tin interlayer, had a sufficient durability and lower anode potential than that coated with magnetite.

Key words: electroplating waste water, cyanide oxidation, copper recovery, hydrocyclone electrolytic cell, lead dioxide anode.

INTRODUCTION

The waste waters coming from electroplating processes contain toxic complex cyanides of copper, zinc, iron, and other metals, as well as sodium cyanide. To develop a technology for the purification of this kind of wastes one has to solve two problems: the oxidation of cyanides to less toxic compounds and the recycling of metals. Several technologies can be applied for the purification of electroplating waste water, among these chemical and electrochemical methods are the most widely used. The main disadvantages of a chemical method with sodium hypochlorite as reagent are the expensiveness of reagents, the precipitation of sludges containing heavy metals, and the formation of AOX [1, 2]. The advantages of the electrochemical process over a chemical method are a closer

control of each reaction step, lower process temperature and cost, less waste and byproducts, safer operating conditions [3], and the possibility of recovering and reusing metals simultaneously with solving an environmental problem. The choice of a suitable purification method is a complicated problem, which depends on many factors, such as composition of waste water, concentration and utilization possibility of the component being removed. However, mostly economic aspects are decisive. Often the purification of a galvanic waste water does not pay regardless of the recycling of heavy metals. In most cases the main aim is to fulfil the environmental protection requirements. Nevertheless, it has been demonstrated that in case of high concentrations (above 30 g dm^{-3}) of copper and sufficient productivity (above 1500 kg Cu per year), the recycling of copper from electroplating waste water is profitable [4]. For environmental protection purposes the electrochemical method has been found to be reasonable when the initial concentration of cyanide is 200 mg dm^{-3} [5] or less [2]. Graphite, lead dioxide, and magnetite have been proposed [5] as anode material. In recent years, titanium anodes coated with lead dioxide and magnetite have been used as these are light and have good mechanical properties [6, 7], although the deposition procedure, is complicated.

In case of a fast electrochemical reaction of the deposition of copper and the oxidation of cyanide the overall process rate is limited by the rate of the diffusional mass transfer, thus the turbulent flow of the electrolyte should be favourable. Therefore, in our previous work [8] a hydrocyclone electrolytic cell with a turbulent swirling flow developed by Dharmo [9] was used. Unfortunately, the graphite anode used has proved to be insufficiently durable.

In this paper application possibilities of lead dioxide and magnetite coated titanium anodes for the purification of a waste water coming from electroplating copper are discussed. To enhance the mass transfer by the turbulent flow of electrolyte a new design of the hydrocyclone cell with an undivided electrolyte compartment and tubular electrodes was developed. To avoid the formation of chlorine on the anode and allow recycling of water no supporting electrolyte (NaCl) was used.

EXPERIMENTAL

Our investigations were carried out in both parallel-plate and hydrocyclone electrolytic cells. The undivided parallel-plate cell has two copper cathodes, the anode was placed between them. Lead dioxide coated and magnetite coated titanium anodes were used. The gap between electrodes was 7 mm. The experiments in the parallel-plate cell were performed in the periodic mode of operation, the process time varying from 5 to 100 min. During the experiment the current was kept constant. The current density varied in experiments from 0.2 to 2 A dm^{-2} . The anode potential was measured against a calomel reference electrode.

Another part of our investigations was carried out in a hydrocyclone cell with an undivided electrolyte compartment. A scheme of the cell is given in Fig. 1. The copper cathode with 49 mm inlet diameter was placed on the inner side of the hydrocyclone wall. The tubular anode with 41 mm outlet diameter and 50 mm active height was situated in the centre of the hydrocyclone, acting simultaneously as a vortex finder. The electrolyte entered the hydrocyclone tangentially, flew helically downward between the electrodes, and issued entirely from the central tube (vortex finder) as long as the apex valve of the cyclone was kept closed.

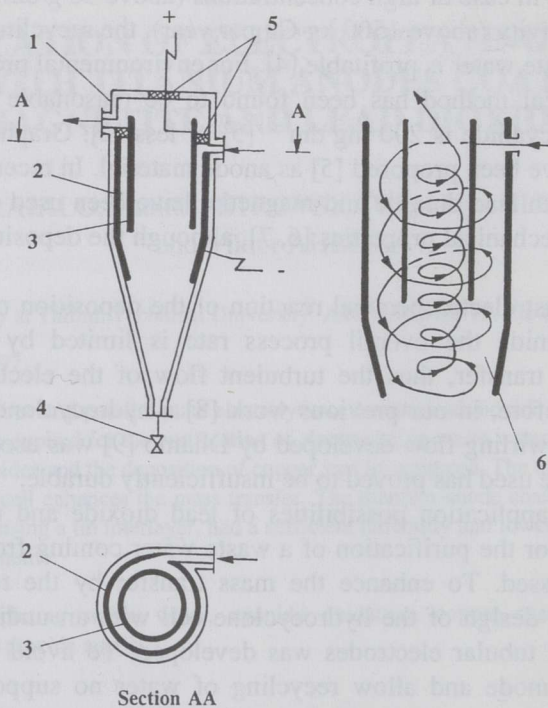


Fig. 1. Scheme of the hydrocyclone electrolytic cell. 1, hydrocyclone wall; 2, cathode; 3, anode; 4, apex valve; 5, Teflon gaskets; 6, scheme of the electrolyte flow.

The experiments were carried out at batch recycle mode of operation in a circulatory system consisting of a hydrocyclone cell, an electrolyte tank ($V = 2.9 \text{ dm}^3$), and a rotary pump for electrolyte circulation. The general scheme of the experimental equipment was presented in our previous report [10]. The process time of batch experiments was varied from 1 to 8 h. During the experiment the current was kept constant at 1.0 A dm^{-2} , the electrolyte temperature at $19 \pm 2^\circ\text{C}$, and the flow rate of the circulating electrolyte at $106 \text{ cm}^3 \text{ s}^{-1}$.

As electrolytes we used a residual solution from the electroplating of copper containing as main components 11.5 g dm^{-3} copper, 0.34 g dm^{-3} iron, 16.4 g dm^{-3} cyanide, 11.8 g dm^{-3} sodium carbonate, and 1.2 g dm^{-3} sodium hydroxide, and also rinsewater diluted 80 times and containing 0.14 g dm^{-3} copper and 0.19 g dm^{-3} cyanide. The samples for analysis were taken from the electrolyte at the beginning and at the end of the process. The total cyanide concentration after distillation was determined by argentometric titration [11, p. 235] and the content of cyanides amenable to chlorination ('toxic' cyanides) by Bucksteeg's method binding the hexacyanoferrate ions with zinc acetate before distillation [11, p. 243]. Copper was determined by complexometric titration with murexide as indicator [12, p. 68] and iron photometrically by means of sulphosalicylic acid [12, p. 75], both after decomposing the cyanides. The electrodeposited copper on the cathode was measured by weight. Ammonium and cyanate ions after alkaline or acidic leaching, respectively, and distillation were determined colorimetrically using Nessler's reactive [11, pp. 166–171 and 246–247]. The oxalate ion after separation as calcium oxalate was determined by titration with permanganate. The concentrations of NaCN, NaOH, and Na_2CO_3 were determined by standard volumetric methods [12, pp. 69–72].

For the electrolysis of a strongly alkaline cyanide solution an insoluble anode of high durability is required. In addition to the graphite anode, which we used previously [8], the possibility of using magnetite and lead dioxide coated titanium anodes was studied. For electrodeposition of lead dioxide on the titanium substrate some conducting interlayer is needed. For this purpose a $\text{RuO}_2\text{-TiO}_2$ interlayer has been applied [6], but we got higher durability of the anode with a tin interlayer electrodeposited similarly to [7]. The titanium plate was degreased with acetone and then etched in 6 N HCl solution at 70°C for 45 min. After that the plate was coated with a solution consisting of *n*-butanol, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, and HCl (100%) at a ratio 20:20:1, dried, and baked at $450\text{--}500^\circ\text{C}$. This cycle was repeated 10 times. PbO_2 was deposited on the tin interlayer electrolytically in a solution of 1 M $\text{Pb}(\text{NO}_3)_2$ and 0.1 M $\text{Cu}(\text{NO}_3)_2$. The current density, i , was 1.4 A dm^{-2} and temperature $50\text{--}55^\circ\text{C}$. This procedure yielded quite a durable PbO_2 layer with a thickness of $80 \mu\text{m}$. The magnetite coated titanium anode was produced by Sintez Co (Moscow).

RESULTS AND DISCUSSION

The concentration of copper in the electrolyte and the amount of the deposited copper per volume unit of the electrolyte, both depending on time, are shown in Fig. 2. In Fig. 3 the analogical dependences for the total cyanide concentration and for the content of 'toxic' cyanides are presented. These dependences were obtained in a parallel-plate cell using a lead dioxide coated titanium anode. Similar concentration curves were obtained with a magnetite coated anode.

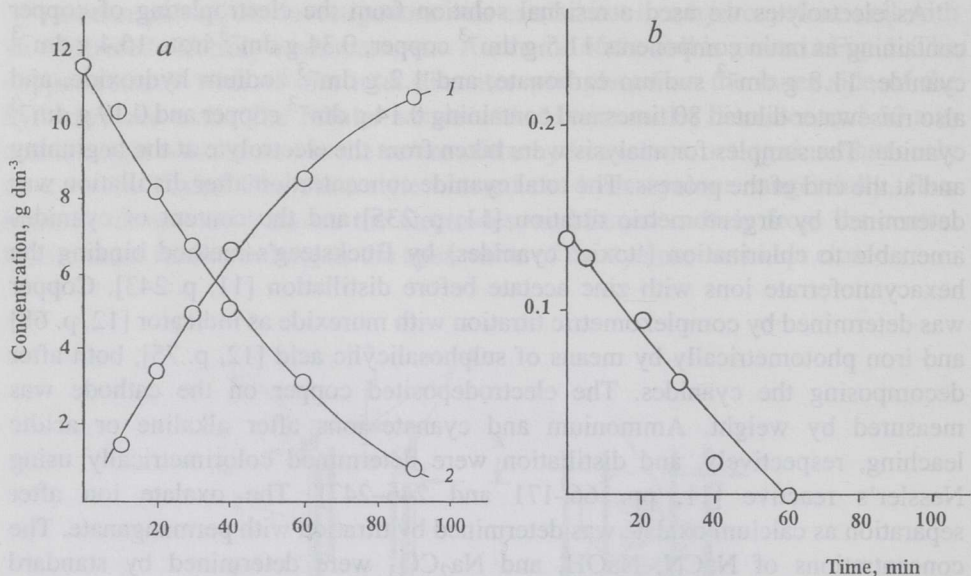


Fig. 2. Amount of deposited copper per volume unit of the electrolyte (1) and concentration of copper in the electrolyte (2) vs time. Parallel-plate cell, lead dioxide anode, current density 1.4 A dm^{-2} . High-concentrated waste water (a) and low-concentrated waste-water (b).

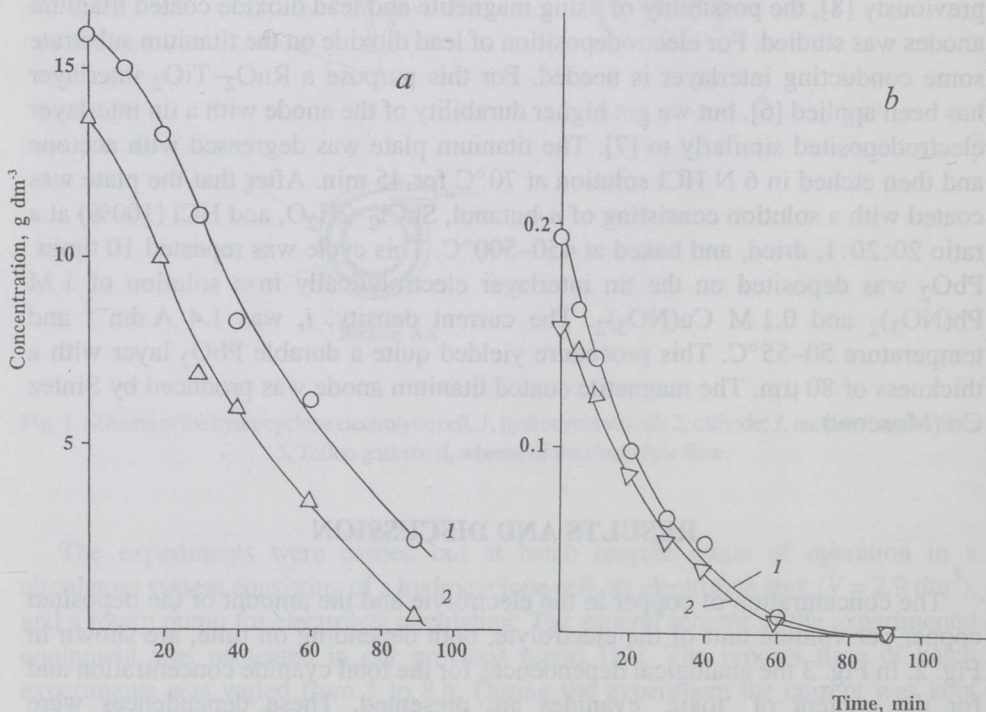


Fig. 3. Dependence of the concentration of total cyanide (1) and 'toxic' cyanide (2) on time. Parallel-plate cell, lead dioxide anode, current density 1.4 A dm^{-2} . High-concentrated waste water (a) and low-concentrated waste water (b).

As it can be seen, the concentrations of both copper and cyanides decrease continuously in time until they are practically removed. The concentrations of both total and 'toxic' cyanides are continuously decreasing but the difference between them, i.e. also the content of 'untoxic' cyanides (mainly cyanoferrates II and III), remains at first constant and falls just at the end of the process. Therefore, we can conclude that first the 'toxic' cyanides – sodium cyanide and cyanocuprates – are oxidizing, and after that the cyanoferrates.

The dependence of the sodium cyanide concentration on time is presented in Fig. 4. The minimum in the concentration curve is probably connected with the consumption of free cyanide and the following decomposition of cyanocuprate complexes. The latter is accompanied with the generation of more than one cyanide ion for one copper ion deposited.

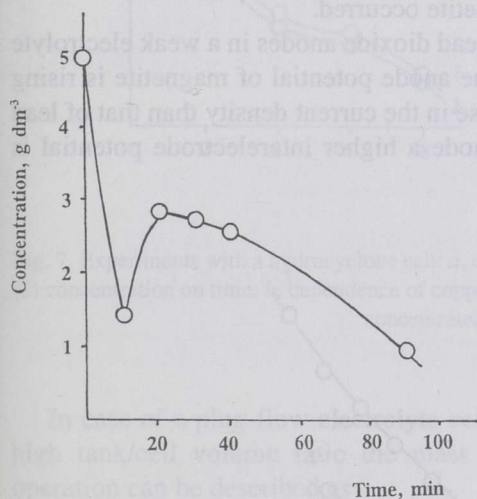


Fig. 4. Dependence of sodium cyanide concentration on time. Parallel-plate cell, lead dioxide anode, current density 1.4 A dm^{-2} .

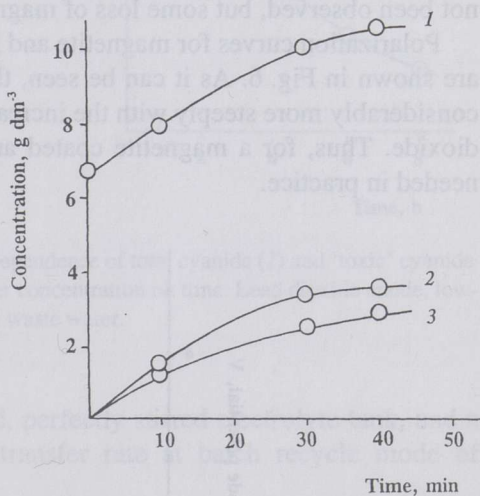
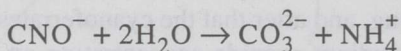
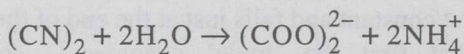
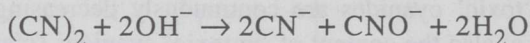
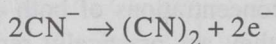


Fig. 5. Concentration of carbonate (1), ammonium (2), and oxalate (3) ion depending on time. Parallel-plate cell, lead dioxide anode, current density 1.4 A dm^{-2} .

In Fig. 5 the concentrations of carbonate, ammonium, and oxalate ions depending on time are presented. The formation of carbonate and part of the ammonium ions is connected with the decomposition of cyanate. The formation of oxalate and the other part of the ammonium can be explained with the hydrolysis of cyanogen. Thus, we can describe the reactions of the main components on the anode as follows:



Similar results and concentration curves were obtained also at the magnetite coated anode. At both anodes a high level of the removal of cyanide as well as of copper can be achieved. At the end of some long experiments with a highly concentrated electrolyte the potential of magnetite anode jumped up and at the same time the anode was covered with a brownish precipitation, containing probably copper oxyhydroxide. In case of a weak electrolyte this phenomenon has not been observed, but some loss of magnetite occurred.

Polarization curves for magnetite and lead dioxide anodes in a weak electrolyte are shown in Fig. 6. As it can be seen, the anode potential of magnetite is rising considerably more steeply with the increase in the current density than that of lead dioxide. Thus, for a magnetite coated anode a higher interelectrode potential is needed in practice.

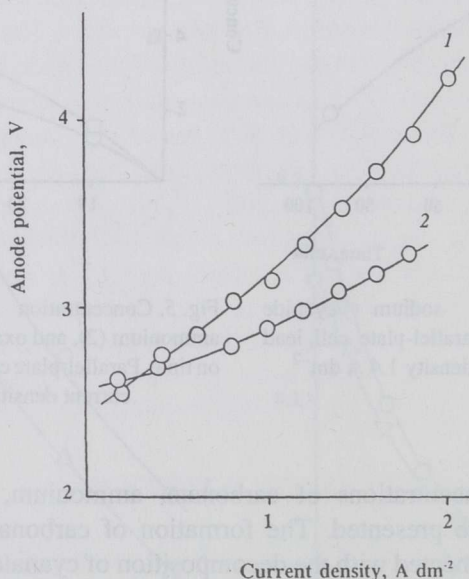


Fig. 6. Polarization curves for magnetite (1) and lead dioxide (2) anodes.

Results of the experiments with a hydrocyclone cell are presented in Fig. 7. The concentrations of total and 'toxic' cyanides and of copper depending on time

are given respectively in Fig. 7a and 7b. The experiments were carried out with waste water of a low concentration of pollutants. As it can be seen, similarly to the parallel-plate cell, the concentrations of both copper and cyanides are continuously decreasing in time.

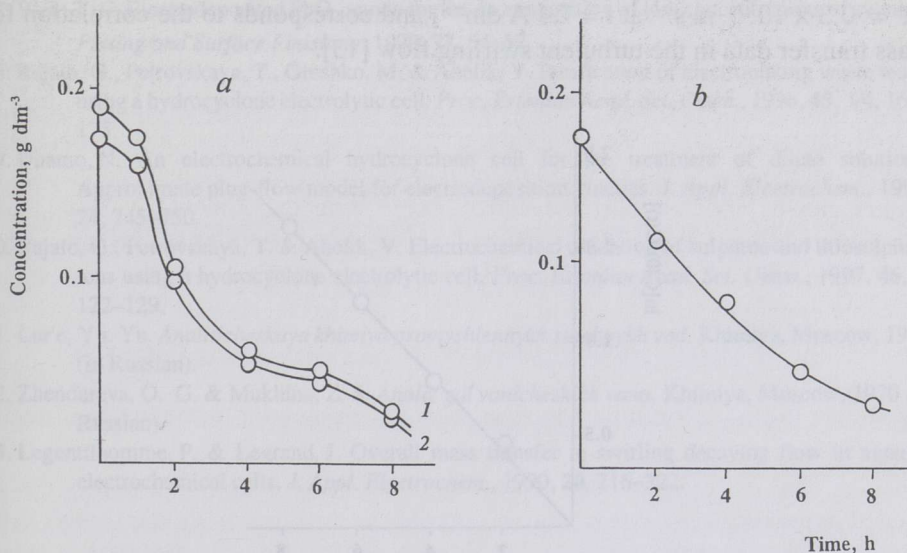


Fig. 7. Experiments with a hydrocyclone cell: *a*, dependence of total cyanide (1) and 'toxic' cyanide (2) concentration on time; *b*, dependence of copper concentration on time. Lead dioxide anode, low-concentrated waste water.

In case of a plug-flow electrolyte cell, perfectly stirred electrolyte tank, and a high tank/cell volume ratio the mass transfer rate at batch recycle mode of operation can be described as

$$-dC/dt = \tau^{-1}[1 - \exp(K_L/Q)]C, \quad (1)$$

where $K_L = \pi DKL$; K is the mass transfer coefficient, $m s^{-1}$; D and L are the diameter and active length of the anode, m ; Q is the volumetric flow rate, $m^3 s^{-1}$; τ designates the mean residence time of the electrolyte in the tank, s ; C is the concentration of the reacting component, and t the process time, s .

The integration of Eq. (1) gives a linear plot of $\ln[C(0)/C(t)]$ vs t , where $C(0)$ and $C(t)$ are respectively the initial and end concentrations of the reacting component. From the slope of this plot we can calculate the mass transfer coefficient as

$$K = -Q(\pi DL)^{-1} \ln[1 + \tau t^{-1} \ln(C(0)/C(t))]. \quad (2)$$

In Fig. 8 the copper concentration vs time is given. As it can be seen, the experimental data points are close on a linear plot, demonstrating the adequacy of the above presumptions and Eq. (1). The value of the mass transfer coefficient calculated from experimental data for copper removal ($K = 2.6 \times 10^{-5} \text{ m s}^{-1}$ at $i = 1.0 \text{ A dm}^{-2}$) is considerably higher than that obtained in the parallel-plate cell ($K = 0.3 \times 10^{-5} \text{ m s}^{-1}$ at $i = 1.4 \text{ A dm}^{-2}$) and corresponds to the correlation for mass transfer data in the turbulent swirling flow [13].

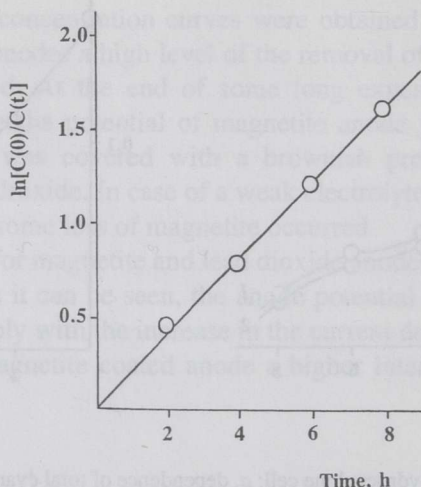


Fig. 8. Copper concentration ratio vs time. Hydrocyclone cell, lead dioxide anode, low-concentrated waste water.

In both apparatus used the lead dioxide that electrodeposited on the titanium substrate when a tin interlayer was used proved to be a rather durable anode material. The obtained results demonstrate the suitability of both lead dioxide and magnetite coated titanium anodes for the purification of electroplating waste water. However, the energy consumption is lower in case of a lead dioxide anode thanks to its lower anode potential.

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GALVAANIKAHEITVEE PUHASTAMINE MAGNETIIT- JA PLIIDIOKSIIDKATTEGA TITAANANOODIDEGA

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Pliidioksiid- ja magnetiitkattede titaananoodidega varustatud hüdrotsüklon- ja plaatelektrolüüsereid on kasutatud galvaanikaheitvee puhastamiseks. On uuritud nii tsüaniidide oksüdatsiooni kui ka vase eraldumise kineetikat. Elektrolüüdi turbulentsed pöörivool elektrolüüseris kiirendab massiülekannet. Tinavahekihi abil titaanalusele kantud pliidioksiidanood osutus küllaldaselt püsivaks ning sellel on võrreldes magnetiitanoodiga madalam anoodpotentsiaal.