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3

Methods for the Enhancement of Mass Transport at the Recovery of Metal Ions from Hydroelectrometallurgical Processes

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1. Introduction

The electrochemical deposition of metals from aqueous solutions represents the basis of the hydroelectrometallurgical processes: the extraction of metals from ores (electroextraction or electrowinning) and their purification by electrolysis (electrorefining). Some of the metals that are obtained and refined from hydroelectrometallurgical processes are copper, nickel, zinc, cadmium, tin, lead, silver, gold and manganese. The hydroelectrometallurgical processes lead to the obtaining of technical pure metals and to an economic recovery of metals from poor ores. Electrodeposition may be also used as preconcentration technique for trace analyses.

Another important application of this process is represented by the treatment of the waste waters that contain metal ions. The classical depollution methods are no longer sufficient to the new, harsher legal provisions and they are also characterized by high costs. As a consequence, modern methods as the removal by electrodeposition of the pollutant metallic ions from effluents and from the processes flows have been developed. In these procedures, ions are deposited on the structure of a support electrode in order to be recycled or removed. It is thus prevented the dissipation of toxic metals in soil from the waste storage dumps from industrial processes.

It was necessary to establish the effects of pollutants that contain metal ions, which can act on short or long term, due to accumulation of toxic substances and their derivatives in the human body (Walsh and Reade, 1994). Regulations in this area have considered the nature of polluting materials, applicable limits of long- and short-term exposure, procedures/rules for handling and storage of toxic substances.

A credible recycling must be supported both in environmental and in economic terms (Emery et al., 2002; Zhang & Forssberg, 1998). According to the principles and to the strategic elements for a sustainable development, current trends are converging more and more towards the treatment of the waste waters at source. This approach of the problem is advantageous for substances that can be recycled in the process or that can be recovered in order to exploit them in other processes or as by-products (Iorga et al., 2007).

2. Sources of pollution with metal ions vs. the need for their recovery

Pollutants are present in certain concentrations in the environment as a result of human activity, having a significant negative impact on it. Due to the complexity and the high cost of the methods for their treatment, a detailed analysis in order to determine the best methods for their elimination is required.

The main sources of pollution with metal ions are the residues from industrial processes in the following areas:

- metallurgy (etching, polishing);
- mining (primary output of ores, mine waters);
- hydroelectrometallurgy (depleted electrolytes);
- electrochemistry (depleted electrochemical sources – batteries and accumulators, electroplating, electrodeposition, contaminated baths);
- chemistry (catalysts, chemical reagents, dyes);
- leather (tanning);
- photographic technique (fixing solution), etc.

It must be mentioned that in each industrial unit wastewater containing metal ions are obtained. It must be not forgotten the fact that all installations and objects made of metal are subjected both to erosion and especially to chemical corrosion and atmospheric agents (Kuhn, 1971; Walsh & Reade, 1994).

Metal recovery from recyclable waste is a less energy consuming process than getting the metal from raw mineral resources (also taking into account the increasing limitation of resources). According to some authors (Damgaard et al., 2009), in terms of environmental management, metal recycling processes involves reduced emissions of greenhouse gases – thus significantly contribute to the environmental protection.

Electrochemistry studies how electricity causes chemical changes, while chemical changes are reflected in electricity production. This interaction creates a huge variety of processes, from heavy industry to the batteries industry and to biological phenomena (Bockris, 1972; Walsh & Reade, 1994).

One of the main directions of electrochemistry is in the environmental protection area and addresses to: monitoring various substances that pollute or affect the environment, removal of pollutants of any kind, production and transport of energy, etc. (Iorga et al., 2009).

The main purpose of treating wastewater containing metal ions is the removal of these ions in order to reach the concentration required by law for those waters to be discharged. Process cost can be reduced if the metal can be recovered (especially for valuable metals) (Mirica et al., 2006; Rajeshwar & Ibanez, 1997).

3. Overview of methods for recovery of metal ions

Removal of metal ions from aqueous solutions may be made by conventional or electrochemical methods. In the treatment of effluents containing metal ions there are more classical approaches that can be used individually or combined (Rojanschi et al., 1997; Walsh & Reade, 1994). These are:

- diluting of the solutions to the allowed legal limit;
- mixing solution until a neutral pH;
- precipitation with a cheap precipitating agent;
- ion exchange;
- membrane separation: reverse osmosis, ultrafiltration, electrodialysis;
- storage and transport to specialized companies;
- selective solvent extraction (especially with macrocyclic compounds like crown ethers and functionalized calixarenes).

Electrochemical methods used to treat solutions with metal ions can be recuperative or destructive. Destructive electrochemical methods can be applied both to the inorganic and organic pollutants, which can be subject to reduction or oxidation. Processes are generally conducted on inert electrodes and involve complex studies because, apart from the dominant process from the electrode, parallel reactions occur due to the by-products.

Electrochemical methods for the recovery of metal ions from dilute solutions are receiving an especially attention in recent years due to difficulties encountered in treatment of contaminated waters, which often can't be destroyed or removed efficiently by conventional methods. They refer to the treatment or pre-treatment of water containing ions of heavy metals. Electrochemical methods for their recovery are based on the discharge of the metal ions at the cathode, when the reaction conditions are ensured by an appropriate design of the electrochemical reactor (Iorga et al., 2006).

Electrodeposition is a process of separation and deposition of an element or compound on an electrode, by passing an electric current between two electrodes that are immersed in an electrolyte (electrolysis). The deposition of ions can be selectively made, depending on the current or voltage applied between the electrodes. Separation and identification of metal ions from a solution can be achieved as a function of normal potentials.

Electrochemical recovery of copper from the industrial effluents is necessary for two reasons, namely:

- the improvement of the environmental conditions, in order to accomplish the environmental requirements and integration into European technology standards regarding the content of metal ions allowed in the industrial effluents;
- increasing the use of raw materials by the revaluation of the recovered metals, according to the decline of the global reserves.

4. Methods for the enhancement of mass transfer processes at the recovery of metallic ions by electrodeposition

The process of electrodeposition of metals is extremely complex, because in addition to the electrochemical steps, adsorption and mass transport, also formation and dissociation equilibria of complex, incorporation of impurities and/or additives intentionally introduced into the bath are involved.

Experimental investigation of the kinetics of cathodic deposition of the metals is a complicated operation due to characteristic features of this process. During electrolysis the cathode surface does not remain intact, it is constantly changing while the metal deposit

occurs. Growth essentially depends both on the nature of the metal deposit and the conditions of electrolysis (Antropov, 2001).

Four main stages are encountered at the discharge of a metal ion (Facsko, 1969):

- cation transport by diffusion, migration or convection from the solution on the surface of the electrode – mass transport;
- desolvation of the solvated cation or dissolution of the complex ion into a simple ion – the chemical reaction;
- neutralization of the cation on the cathode surface – charge transfer;
- transition of the atom in the steady form of deposited matter (the bonding of hydrogen atoms in molecules or the input of the metal atoms into the crystalline lattice) – crystallization.

The above mentioned stages are presented in Figure 1:

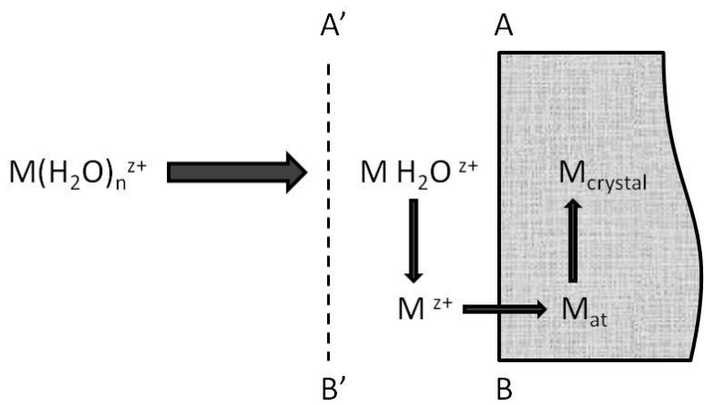


Fig. 1. Scheme of the deposition of the metal ions on the surface of the cathode: AB – surface of the electrode; A'B' – reaction zone border.

where:
AB represents the surface of the electrode;
A'B' – layer in the near vicinity of the electrode (also named reaction zone);
$M(H_2O)_n^{z+}$ – the solvated ion;
M^{z+} – simple ion.

The vast majority of the electrodeposition processes is carried out using a current source to obtain a constant current to the cathode. Optimum current density range for which satisfactory deposits are obtained is much lower than the limiting current density (Pletcher & Walsh, 2001).

Diffusion layer thickness, δ, is defined by the Nernst diffusion layer model, as shown in Figure 2. This model assumes that the concentration of the M^{z+} ions in the solution is c_a until the distance δ to the electrode surface and then decreases linearly to c_s, at the electrode surface. In this model it is assumed that the liquid layer thickness δ is practically stationary. At a distance from the surface greater than δ, reactant concentration is assumed to be equal to the one from the mass of the solution. To reach the electrode surface, M^{z+} ions must pass through the diffusion layer. At these distances, agitation of the solution becomes effective.

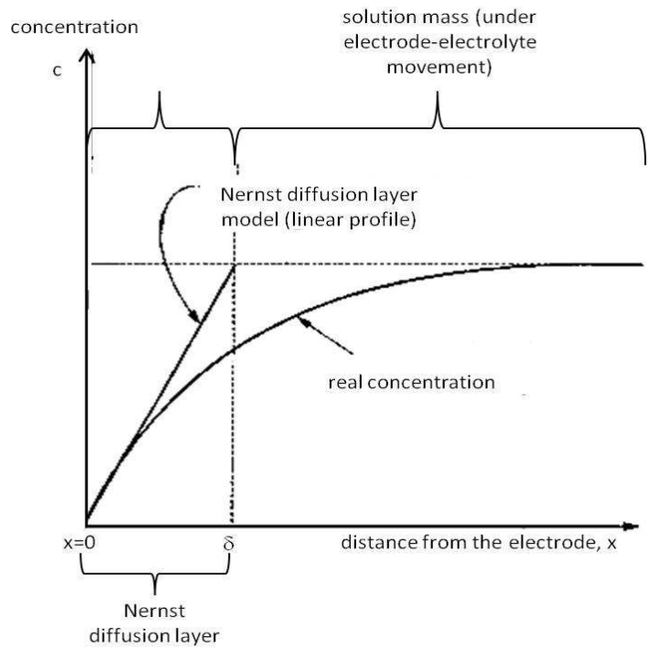


Fig. 2. Concentration profile near cathode describing the mechanism of electrodeposition process under electrode-electrolyte movement (Schlesinger & Paunovic, 2000).

When the limiting current density values reach the maximum, M^{z+} species are reduced as they reach the electrode surface. Under these conditions, the concentration of the reactant M^{z+} at the electrode is zero, and the deposition rate is controlled by the transport rate of the M^{z+} reactant to the electrode.

For this reason, the rate determining step of the process is the transport of M^{z+} ions from solution to the cathode surface. The development rate of the transport process depends on the Nernst diffusion layer (δ), which is included in the mass transport coefficient (k_m), the two quantities depend at their turn on the speed of stirring of the solution near the electrode. Thus, the stirring speed controls the diffusion limiting current density (i_L), i.e. the current density concentration where the concentration of metal ions on the cathode surface tends to zero ($c_{1s} \rightarrow 0$). The above mentioned quantities are related by equations (1) and (2):

$$i = -zFD\frac{c_{1a} - c_{1s}}{\delta} \tag{1}$$

$$i_L = -zFD\frac{c_{1a}}{\delta} = zFk_m c_{1a} \tag{2}$$

where:
i represents current density;
i_L – limiting current density;
D – diffusion coefficient of metallic ions;
k_m – mass transport coefficient;
δ – Nernst diffusion layer thickness;

c_a – solution concentration;
c_s – concentration at the surface of the electrode.

Transport overvoltage usually occurs only at low concentrations and/or high current densities, as given by equation (3):

$$\eta_t = \frac{RT}{zF} \ln\left(1 - \frac{i}{i_L}\right) \tag{3}$$

At the current crossing and the deposition of the cations, the space in the immediate vicinity of the cathode becomes poorer in ions and a concentration gradient occurs. Consequently, the cations diffusion within the solution to the cathode surface begins (Antropov, 2001).

For a given current density and concentration, transport overvoltage is lower even the higher value of the $K = \frac{zFD}{\delta}$ constant.

Value of the K constant can be increased either by raising the diffusion coefficient D, or by decreasing the diffusion layer thickness, δ. Increasing the diffusion coefficient (D) can be done by heating the solution. Decrease in diffusion layer thickness (δ) is achieved by solution agitation, as shown in Figure 2. So, for a current density and a given concentration, both heating and stirring of the solution lead to a lower value of the transport overvoltage.

Thus, for a given electrolyte, the deposit increasing is favoured by increasing the current density by:

- high concentrations of the dissolved metal;
- high temperature;
- relative movement between the electrode and electrolyte.

The first two options are limited in practice by the following reasons:

- metal concentration is restricted by the solubility, the cost of metal (for precious metals) and considerations of storage (and/or disposal) and effluent treatment;
- too high temperatures can aggravate corrosion problems of the equipment used in the process, losses by evaporation, chemical decomposition (e.g. when using chemical additives), prolonged duration of cooling, not to mention high energy costs for heating.

In electrochemistry, one of the main ways to increase the mass transfer of various processes is the relative movement of the electrode-electrolyte. Besides allowing the use of higher current densities and thereby increasing the production rate and improving the flow regime, it can also help for the removal of the air or of the generated hydrogen gas, or to provide a steady pH and temperature in the cathode area.

According to Gomaa et al., using the ultrasounds and vibrations to improve the mass transfer in electrochemical processes has attracted the interest mainly due to the ability of reducing the diffusion controlled processes which limit the maximum allowable current density and the energetic efficiency of the cell. This case is specific to dilute solutions where the low concentration of the active species would require supplementary actions, like the use of electrodes with higher surface or the recirculation of the electrolyte solution. For

electrodeposition, metal recovery from depleted solutions and wastewater treatment, the controlled vibration technique has been applied (Gomaa et al., 2004).

The main processes applied for the improvement of electrode-electrolyte relative movement are: the use of turbulence promoters, particle fluidized bed, electrolyte recirculation, mechanical stirring of the electrolyte, electrode spinning, vibration of electrode/electrolyte, ultrasonication of electrode/electrolyte.

4.1 The use of turbulence promoters

A method for the increasing of the mass transfer at electrolytic processes that occur with release of bubbles is the induction of turbulence near the surface electrode (Vilar et al., 2011).

This alternative for the improvement of the mass transfer was applied to a system in which the electrochemical reaction on the surface of the electrode is controlled by diffusion and by the release of gas bubbles (Vilar et al., 2011). It was concluded that the mechanism leading to an increased mass transfer varies depending on the type and orientation of the metal electrode and on the electrolyte flow direction. Thus, the mass transfer is improved when the geometry of the electrode does not inhibit the release of bubbles that are generated by the electrochemical process. It was also investigated the effect of the use of triangular/semi-circular/cylindrical promoters that are placed on the bottom of a rectangular electrolytic cell. The results show that the mass transfer coefficient increases with the increasing height/radius ratio of the promoter (Venkateswarlu et al., 2010).

4.2 Use of fluidized bed particles

By using particles in fluidized bed the increasing of the surface and the intensifying of the solution movement towards the electrode are achieved. It may be achieved through a large number of metal electrodes or electrode in filling form (from small pieces) in fixed or fluidized bed. Another option is to deposit the metal on a cathode-shaped grille, which during electrolysis is surrounded by a fluidized bed consisting of small glass beads, their movement continuously destroying the polarization film from the electrodes surface.

4.3 Electrolyte recirculation

Recirculation processes of the electrolyte by pumping determine the increase of flow rate or the degree of mixing of the electrolyte. Electrolysis cells do not contain electrodes or other moving parts, which determine reduced power consumption and mechanical wear. Dynamic flow regime allows the use of relatively high current densities even for small concentrations and also the achievement of an advanced degree of exhaustion of the solution subjected to electrolysis (Pletcher & Walsh, 2000). Cathodes on which the recovered metal is deposited are periodically removed from the electrolytic bath and replaced with new plates.

4.4 Mechanical stirring of the electrolyte

Mechanical mixing processes of the electrolyte are characterized by a strong movement of the solution that is subjected to electrolysis, which is achieved by using mechanical stirrers. The cell has an optimum design for a turbulent flow of the solution. The stirrer consumes less energy than a circulator pump, which would achieve the same degree of agitation.

There are used flat cathodes, with simple forms. To avoid the complete coverage of cathodes, they are provided with plastic masks, placed on the edges.

4.5 Spin of electrodes

Rotating process of the electrodes is a way to achieve the relative movement of the electrolyte to the electrodes by rotating one of them, usually the anode. There are mentioned experiments (Eisenberg et al., 1954) that studied the effect of the rotational speed on the rate of mass transfer in the case of rotating electrode. It is also mentioned (Eisenberg et al., 1954) the use of rotating electrodes in order to study the speed of dissolution of Mg and its alloys in HCl solutions. Thus, they determined that dissolution rates increase with rotation speed (when using a diluted solution of HCl). If more concentrated solutions of acids are used, reaction rates are completely independent of the speed of rotation, as the shaking effect produced by the release of H_2 bubbles to surface prevails. In some cases, a rotating disc-shaped electrode is combined with high-speed radial flow of electrolyte.

Recendiz et al. had used rotating cylinder electrodes for the study of mass transport in a turbulent flow regime. Mass transport control is imposed by the speed of rotation of the inner cylinder and by the applied limiting current density. Studies regarding the mass transport at RCE (for the case of copper electrodeposition) were performed in turbulent regime (Re > 100). Experimental determination of mass transport coefficients was made by using electrolysis experiments at a given potential (Recendiz et al., 2011).

4.6 Vibrating of the electrode/electrolyte

One of the most effective methods for the enhancing of the mass transport in electrolytic cells is represented by the vibration. The vibration technique is a method of increasing the electrode-electrolyte relative movement and is defined as initiating and sustaining of a regular movement with well defined mechanical parameters (amplitude A, frequency ω) between the active surface electrode and electrolyte. The strong effect of stirring the solution layer in the immediate vicinity of the electrode determines the reducing of the diffusion layer and the limiting current density may be increased for 10-15 times. As such, current yields are significantly improved, the electrolysis voltage decreases, the specific consumption of electricity is accordingly reduced, and the electrolysis cells productivity significantly increase.

Generation of the pulsing field at the electrode-electrolyte interface can be achieved either by vibrating the electrode surface, either the volume of the electrolyte. As regards the relative motion, both methods work in the same way, but the specific energy consumption clearly favours the first procedure. This is due to the fact that, the afferent energy of the vibration manifests in the boundary layer adjacent to the electrode surface and not in the volume of solution, such as the second alternative does (Gomaa et al., 2004).

Vibrating electrode provides particularly advantageous conditions for conducting electrochemical processes controlled by mass transfer, especially due to the fact that it provides a substantial increase of the ionic species transport to and from the electrode surface (mass transfer coefficient k increases when d decreases, which happens when forced convection conditions by lowering h_c and i_{lim}).

Vibration technique can be successfully applied for dilute solutions. Vibrating electrodes can be done by using two main modes of vibration:

- longitudinal (parallel movement to the active surface);
- transverse (movement occurs perpendicular to the active surface).

Vibration of the electrode substantially modifies the boundary layer that appears at the electrode-electrolyte interface in the case of free convection, the layer that also contains the reaction product. Previous studies regarding the effect of vibrations on the mass transfer rate proved that the vibrations are an efficient method for the improvement of the mass transfer (Fakeeha et al., 1995).

Literature data present a number of researches regarding the improvement of the mass transfer by vibrations. There are many relations regarding the mass transfer and a number of applications on electrodes of various shapes. For the case of spherical vibrated electrodes, the obtained relation is equation (4) (Venkata Rao et al., 2010):

$$Sh_v = 2 + 0.24\left(\frac{f\rho dH}{\mu}\right)^{\frac{1}{2}} \tag{4}$$

In the case of mass transfer at the copper spherical vibrated electrodes, the equation (5) was proposed (Venkata Rao et al., 2010):

$$\frac{Sh_v}{Sc^{\frac{1}{3}}} = 0.97\,Re_v^{0.4} \tag{5}$$

For the case of copper and stainless steel cylindrical electrodes, the mass transfer is characterized by the relation (6) (Venkata Rao et al., 2010):

$$J_{dv} = 0.41\,Re_v^{-0.38} \tag{6}$$

The influence of the sinusoidal vibrations on the mass transfer by forced convection between a solid sphere and a liquid is given by the empirical relation (7) (Venkata Rao et al., 2010):

$$\frac{Sh_v}{Sc^{\frac{1}{3}}} = 0.477\,Re_v^{0.538}\left[1 + 1.05\left(V - 0.06\right)^{1.26}\right], \tag{7}$$

where: Sh, Sc, Re are the dimensionless numbers of Sherwood, Schmidt and Reynolds criteria.

Venkata Rao et al. (2010) investigated the efficiency of the mass transfer in the case that a disc electrode was vibrated. Vibrating the electrode leads to instability into the electrolyte (around the electrode surface) due to the wave's formation and results in a reduced thickness of deposited film on the electrode surface. Thus, the vibration rate of the electrode also influences the thickness of the deposited film and the transfer coefficient. The highest the vibration rate, the highest the mass transfer coefficient is.

Takahashi and collaborators (Takahashi et al., 1992) have studied the effect of the vibrations on local and global mass transfer for the cylindrical tube vibration in a stationary electrolyte.

The vibration effects were mainly observed on the local transfer coefficients, in the side positions of the electrode. Noordsiji and Rotte (Noordsiji & Rotte, 1961) studied the vibration effect on the mass transfer for a spherical nickel electrode and have presented the relationships that describe the mass transfer criteria.

Takahashi and co-workers (Takahashi & Endoh, 1989) have studied the effect of the vibrations on spherical-, disc- or cylinder-shaped electrodes. Noordsiji and Rotte (Noordsiji & Rotte, 1961) have studied the mass transfer at vertical cylindrical vibrated electrodes at large amplitudes. The same study, but for horizontally electrodes can be found in the study of Venkateswarlu and co-workers (Venkateswarlu et al., 2002).

Other authors (Rama Raju et al., 1969) have studied the ionic mass transfer in mixed convection conditions, for the specific case of pulsating flow. In terms of energy consumption compared to vibration mechanical parameters (A, ω), it was found (Takahashi et al., 1993) that an increase in amplitude and frequency has similar effects on the mass transfer enhancement.

Gomaa et al. investigated the longitudinal vibration effect on the improvement of the mass transfer. It may be said that, the mass transfer rate at vertical surfaces can be significantly improved by vibrating in a longitudinal direction parallel to their surfaces. The degree of the improvement of mass transfer coefficient depends on the amplitude and frequency of the vibrations and of the length of the electrode. An improvement up to 23 times of the mass transfer was recorded. Average coefficient of mass transfer at vibrating electrodes can be predicted by using a conventional mass transfer equation for plane surfaces in that a pseudo-equilibrium rate is used (Gomaa et al., 2004).

The improvement of the mass transfer by vibrations that are applied to electrochemical process leads to a significant increase of the performance of the process. This reduces the polarization of the concentration, together with the acceleration of the deposited metal, the degree of dissolution and also with increased current yields. It facilitates the formation of fine metal deposits (as powders) and release of gas bubbles. It is also noted a significant reduction in the volume of processing units necessary for the electro-processing, which determines lower processing costs.

Fakeeha et al. have studied the effect of oscillatory movement on the mass transfer at vibrating electrodes, causing the current limit values for each applied frequency of the frequency range (0÷26 Hz). Around the value of 13 Hz, a sudden drop in the limit current values occurs, and then its growth is resumed.

The effect of frequency on the mass transfer rate can be explained by Stoke solution for the case of the flow near a vibrating electrode (Fakeeha et al., 1995):

$$U(\eta, t) = A e^{-\eta} \cos(Ft - \eta) \tag{8}$$

$$\eta = \frac{yF}{2\nu} \tag{9}$$

where:

U is the electrolyte flow velocity induced by vibration;
y – distance to the electrode surface;
t – time;
F – frequency of the vibration;
A – amplitude of the vibration;
v – cinematic viscosity.

The increase of the mass transfer seems to be due to the decreased thickness of the adjacent layer to the electrode surface which is induced by vibration. The vibration-induced flow seems to be stronger than the continuous flow of electrolyte, thereby improving the mass transfer coefficient. Although the influence of hydrodynamics on the transport mechanisms from the electrochemical cells has been previously investigated, the situation is different for cells in which vibrations are used to improve mass transfer; there are still some deficiencies in understanding the various mechanisms that are contributing to the overall improvement of the mass transfer coefficient.

4.7 Ultrasonication of the electrode/electrolyte

Influence of an ultrasonic field on electrochemical processes is manifested as follows: in a fluid, the propagation of an ultrasonic pressure wave produces the cavitation effect, consisting of the formation of bubbles containing gas and liquid vapours. These bubbles, at low intensities of the ultrasonic field, oscillate in the electrolyte volume and they essentially contribute to the mass transfer and to the changes of the diffusion layer around the electrodes.

The use of ultrasonic techniques in electrochemistry has several advantages, such as a limited accumulation of gas bubbles at electrode and a high efficiency of the ions transport through the double layer. In addition, there is a continuous cleaning and activation of the electrode surface (http://www.coventry.ac.uk/researchnet/Sonochemistry/Pages/Sono-chemistry.aspx).

All these improvements have beneficial effects on the diffusion processes, of the yields and the rate of electrodeposition processes and they are due to the cavitation effect applied to the electrolyte (Mallik & Ray, 2009). The electrode surface causes the bubbles collapse leading to the formation of a liquid jet that is directed toward the surface with high speed. Thus, the double layer destruction and, consequently, the improvement of the mass transfer occur.

There are two methods for the use of ultrasound in electrochemistry: ultrasonication of working electrode by using the ultrasonic transducer or ultrasonication of the electrolyte.

The literature mentioned the ultrasonic-assisted electrodeposition of various metals and alloys. This process provides a considerable improvement of the mass transfer compared to the conventional electrodeposition methods (Grunwald, 1995). It was found that ultrasonic agitation during electrodeposition produces smoother and more compact deposits, with increased corrosion resistance.

In the case of electrodepositions, the influence of intensity and frequency of ultrasound on the deposits hardness, particle size and morphology of surfaces is studied. Application of ultrasound to electrochemical processes increases the transport of the electroactive species to/from the electrode both in the diffusion layer and inside the double layer by electrolyte stirring due to cavitation and pressure waves.

At the overcoming of the field intensity above a certain threshold value, the phenomenon of collapse of these bubbles (implosion) appears, leading to local conditions of extremes temperature and pressure. The phenomenon is associated with the microflow or with the microcurrents and with the emergence of elevated electric fields. This leads to mechanical phenomena of corrosion, the fragmentation of solid particles and emulsifying of immiscible liquids. In terms of electrochemistry, the above mentioned effects are studied in terms of their influence on electroplating, electrodeposition and electrosyntheses, increased reaction rates and change of the electrodeposition quality (Doche et al., 2001; Hardcastle et al., 2000; Mason and Lorimer, 2002; Walton and Phull, 1996).

For the electrodeposition of copper and zinc, the fewer gaps in the structure of the metal is due to crushed crystals or pushed into holes by air pressure or by shock wave pressure. Copper electrodeposition has been performed in the narrow channels of the electronics and electrical parts. The phenomenon is attributed to cavitation and to the improvement of mass and heat transfer and copper electrodeposition, while hydrogen is discharged.

Coverage of aluminium includes the application of ultrasound in the electrolysis baths that contain molten salt, in order to remove oxygen. In the case of nickel electrodeposition, ultrasonication influences the crystallization process through the effect of cavitation in the electrolyte, the quality of the deposit being also greatly influenced from the current density.

Using the ultrasonic stirring together with plating, much durable black platinum deposits than platinum wires without stirring are obtained. This provides considerably larger surfaces of the precious metal wire, by increasing the flow of $PtCl_6^-$ ions, due to ultrasonic agitation. In the case of silver electrodeposition, due to the effect of ultrasonic cavitation, the adherence is improved and deposits cracks are removed. It results a mate aspect of the silver surface. In the case of chrome plating, the ultrasonic bath and the appearance of cavitation lead to the obtaining of deposits with higher hardness, but with several cracks. In contrast, the obtained deposits are more shiny and spotless.

For the electrodeposition of iron, the deposits obtained by ultrasonication have higher hardness, reduced porosity and surface staining. The ultrasound-assisted electrodeposition of Ni-Zn alloys favours the accumulation of more shiny zinc deposits.

Application of ultrasound for the electrodeposition of Ni-Fe alloys leads to an increased iron content, lack of roughness and increased hardness of the deposit. Electroplating with noble metals like Au, Rh, Ru and corresponding alloys from electrolyte solution containing organic compounds in order to prevent the corrosion of the substrate is mentioned.

By using ultrasound in electrochemical processes electrodynamics of the electrolysis cell is improved. The effects are similar to those produced by known hydrodynamic techniques, such as agitation, recirculation or vibrating. There can't be neglected the thermal effect of ultrasonication that leads to the warming of the solution. Unlike other methods for the increasing of the electrode processes, in this case the cavitation effect is involved.

5. Comparative analysis of procedures to enhance the relative electrode-electrolyte movement to the electrochemical deposition of metal

Laboratory studies regarding copper electrodeposition processes are presented below. Based on previous works (Iorga et al., 2011), various possibilities have been investigated to improve the mass transfer in the electrodeposition of Cu from $CuSO_4/H_2SO_4$ solutions.

In order to observe the influence of the electrode-electrolyte relative movement, the electrodeposition processes were investigated in several operating modes, namely: mechanical stirring of the electrolyte, vibration of the electrode and electrolyte ultrasonication regime. Thus, comparisons among the obtained results of the electrodeposition under stirring, vibrating and ultrasonic conditions were made.

Experiments were performed in a standard cell with three electrodes. A number of solutions of different concentrations of $CuSO_4$ (0.05M ÷ 0.65M concentration range) in 0.25, 0.5 and 0.75 M H_2SO_4 have been used. The polarization curves were drawn with a potentiostat PGZ Voltalab 402.

A volume of 50 ml $CuSO_4/H_2SO_4$ solution, a copper working electrode with an active area of 0.05 cm^2, an Ag/AgCl (sat. KCl) reference electrode and an auxiliary electrode (Pt wire) with an area of 0.25 cm^2 were used for the experimental determinations. Scanning speed was set at 20 mV/s in a potential range from 100 mV ÷ -1100 mV. To ensure the reproducible results and to ensure constant conditions, the working temperature was chosen the ambient temperature, 22÷24 °C.

During the experiments, several parameters (ultrasonic bath functional parameters, frequency of vibration of the electrode) have been varied and the optimal values for each operating mode were determined.

For the deposition of copper under mechanical stirring a magnetic stirrer was used.

To achieve the vibrating regime, a vibration system for static elements / electrodes patented in INCEMC Timisoara (Buzatu et al., 2011) was used. The system covers a wide range of frequencies (with a very good resolution, at least 1 Hz) and has the possibility of using a wide range of waveforms (sine wave, rectangular, triangular or saw wave, etc.).

Ultrasonication regime used an ultrasonic bath from FALC Instruments, Italy, at 25 °C and 59 kHz.

5.1 Results of the mass transfer improvement methods that were applied to the electrolyte solution

5.1.1 Ultrasonication of the electrolyte

In order to determine the optimum conditions for copper ultrasound electrodeposition, variations of the functional parameters of the ultrasonication bath have been performed.

Polarization curves of copper electrodeposition process from a 0.05 M $CuSO_4$ solution have been recorded for the both working frequencies of the bath, namely 40 and 59 kHz, and are presented in figure 3.

As one can observe from figure 3 the difference between the results obtained at two different values of the working frequencies is insignificant. For further determination was chosen a working frequency of 59 kHz (due to the slight pronounced deposition plateau).

Another parameter that can be varied is the power at which the ultrasonication bath works. The results are presented in figure 4:

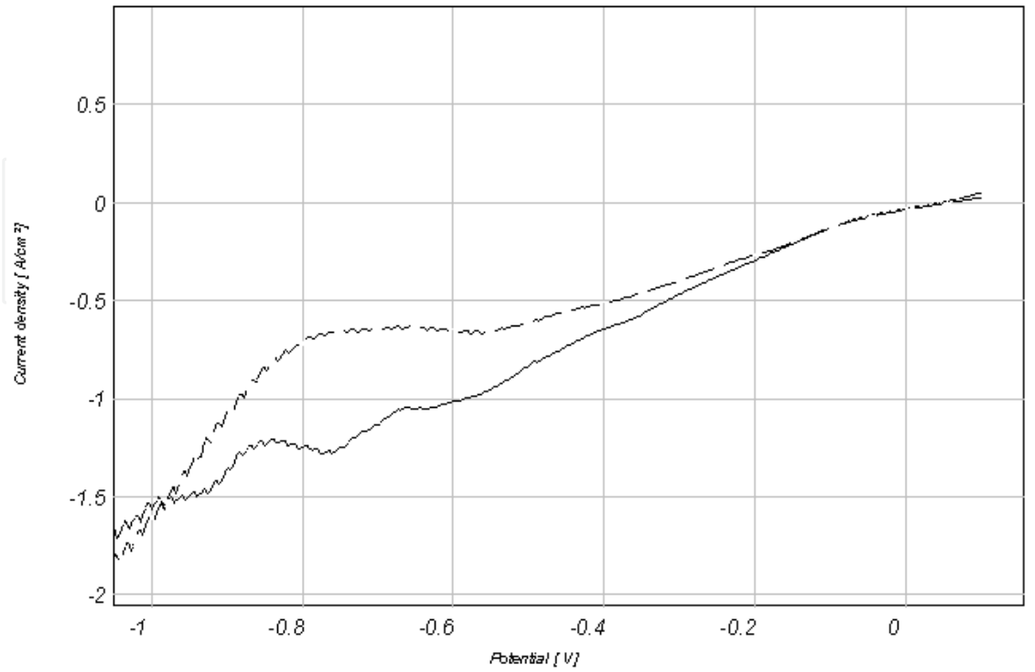


Fig. 3. Polarization curves at copper electrodeposition from a 0.05 M $CuSO_4$ solution, for different working frequencies: _____ 40 kHz; _ _ _ 59 kHz.

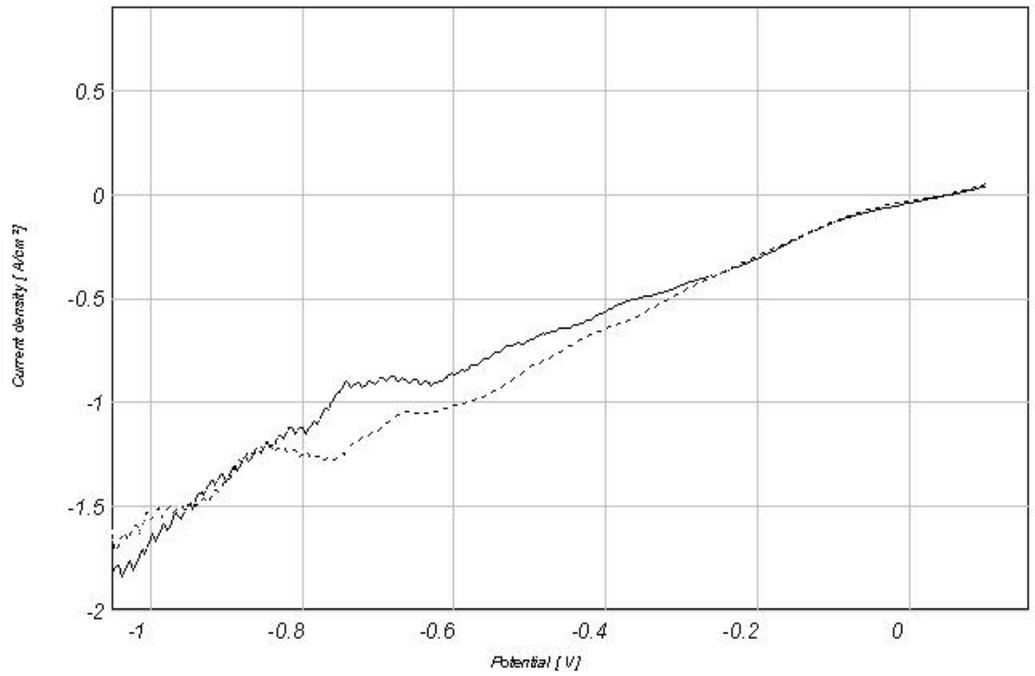


Fig. 4. Polarization curves at copper electrodeposition from a 0.05 M $CuSO_4$ solution, for different percents of bath power: _____ 50 %; ……. 75 % (from 285 W, total bath power).

The results presented in Figure 4 shows that is no significant difference between the two values of the power. As a consequence, for further determination was chosen the option that uses 50 % of the total power (due to the slight pronounced deposition plateau).

5.1.2 Comparison between the ultrasonication and the mechanical stirring of the electrolyte

There were two methods for the mass transfer improvement that were applied to the electrolyte solution, namely the mechanical stirring and the ultrasonication. Both assays were applied to a 0.05 M $CuSO_4$ solution and the results are presented in figure 5.

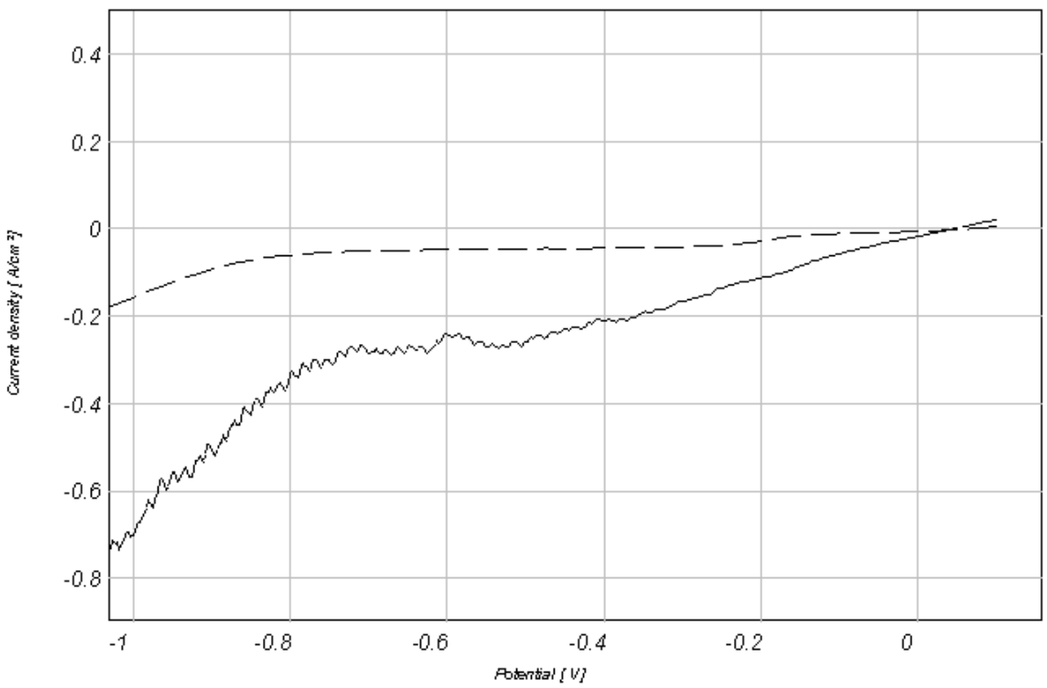


Fig. 5. Polarization curves at copper electrodeposition from a 0.05 M $CuSO_4$ solution: _____ ultrasonication of the electrolyte; _ _ _ mechanical stirring of the electrolyte.

From figure 5 it may be seen that the ultrasound-assisted electrodeposition of copper is favoured (if the current intensity is taken into account), but also one of the major drawback of the method appears, namely a less pronounced deposition plateau. This is due the fact that the ultrasounds also affect the electrode that is immersed in the electrolyte solution, and, consequently, it alters the metal deposition.

5.2 Results of the mass transfer improvement methods that were applied to the electrode

The experiments were conducted by using a vibrating electrode system that allows variation of both frequency and waveforms. The variable parameter was chosen to be the vibration frequency, while the waveform was set to the sine one. For the first set of frequencies (below 100 Hz), the results are presented both in graphic (figure 6) and table (table 1) form.

5.2.1 Frequencies < 100 Hz

The data from Figure 6 and Table 1 show that, better results are obtained for the two of lowest employed frequencies, namely 30 Hz and 20 Hz.

Frequency (Hz)	i (mA/cm^2)	ε (V)
20	-72.172	-0.42689
30	-79.750	-0.44258
40	-62.471	-0.43159
60	-55.825	-0.46141
80	-39.875	-0.47397

Table 1. Limit current densities and potential values (frequencies < 100 Hz).

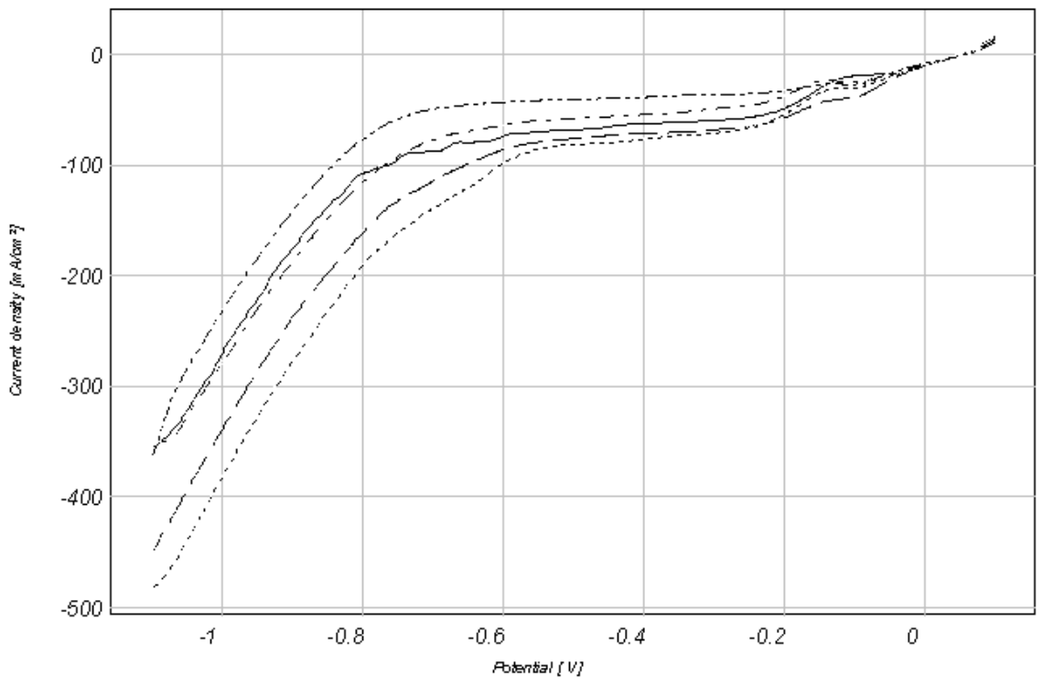


Fig. 6. Polarization curves at copper electrodeposition from a 0.05 M $CuSO_4$ solution, at different frequencies (<100 Hz): _ _ _20 Hz; .....30 Hz; ___40 Hz; ---- 60 Hz; —·—·— 80 Hz.

5.2.2 Frequencies > 100 Hz

Results from Figure 7 and Table 2 show a significant difference between the obtained results at a frequency of 100 Hz and all other three higher frequencies. It may be concluded, together from the data presented in Figures 6 and 7, that the frequency of 100 Hz is the most favourable for the copper electrodeposition.

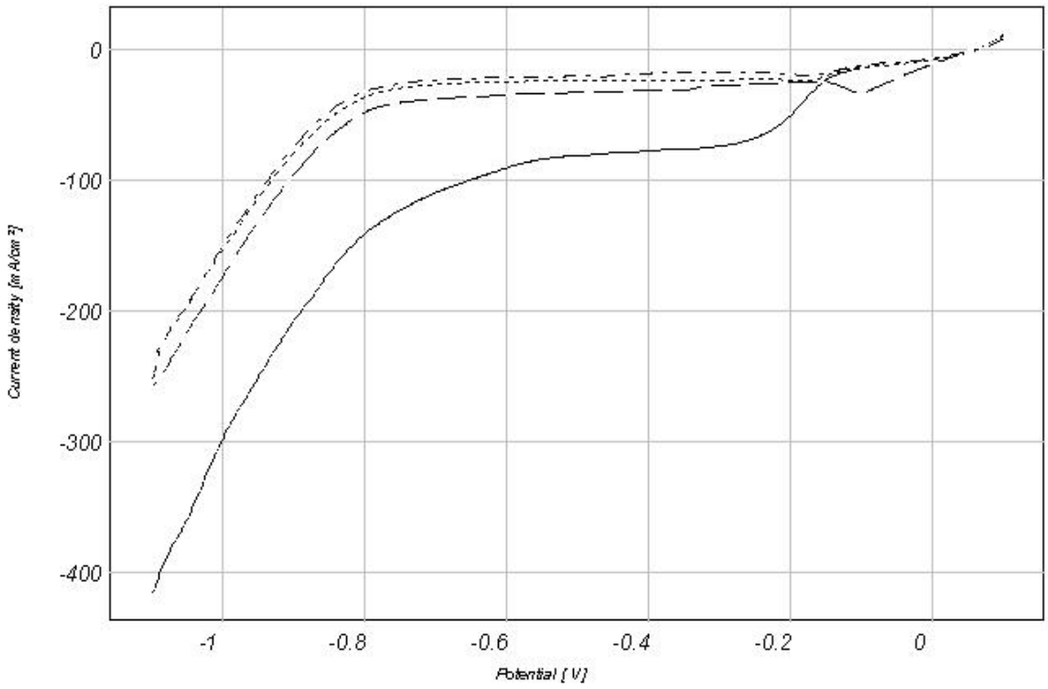


Fig. 7. Polarization curves at copper electrodeposition from a 0.05 M $CuSO_4$ solution, at different frequencies (>100 Hz): ____100 Hz; _ _ _150 Hz; …..200 Hz; - - - - - - 300 Hz.

Frequency (Hz)	i (mA/cm²)	ε (V)
100	-78.772	-0.44415
150	-32.385	-0.49908
200	-24.462	-0.48339
300	-16.679	-0.41433

Table 2. Limit current densities and potential values (frequencies > 100 Hz).

5.3 Comparison between the mass transfer enhancement methods applied to the electrode and to the electrolyte, respectively

The polarisation curves obtained at the electrodeposition of copper when the three above presented working regimes are presented all together in the Figure 8 and Table 3:

The allure of the polarization curves presented in Figure 8 clearly shows an increased efficiency of the ultrasound-assisted working regime. Also, it may be observed that in the case of a more concentrated $CuSO_4$ solution, the plateau that corresponds to the electrodeposition of metals is better defined than in the case where electrolytes with a lower concentration in $CuSO_4$ were used (see Figure 5). The almost double performance of the ultrasound-assisted working regime towards the vibrating electrode assay (in terms of i values) recommends this method for further investigations as regards its use at larger scales.

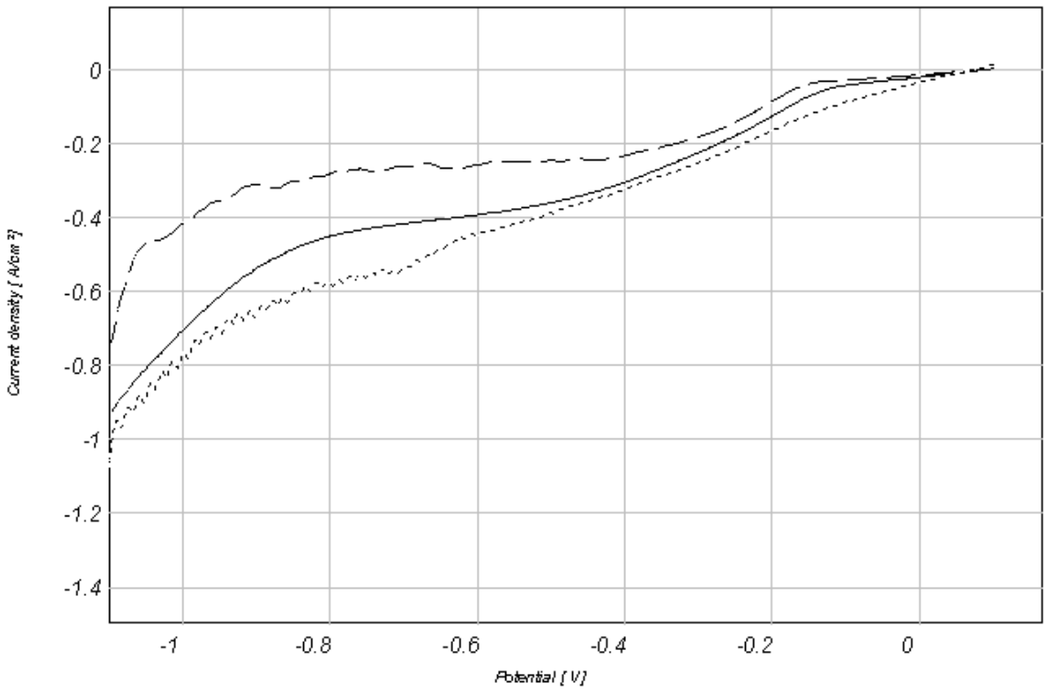


Fig. 8. Polarization curves at copper electrodeposition from a 0.35 M $CuSO_4$ solution: _ _ _ mechanical stirring of the electrolyte; ___ vibrating electrode; ..... ultrasound-assisted electrodeposition of copper.

Working regime	i (A/cm^2)	ε (V)
Mechanical stirring	-0.2609	-0.645
Vibrating	-0.4033	-0.693
Ultrasonication	-0.5456	-0.751

Table 3. Limit current densities and potential values.

6. Conclusions

The paper presents the main methods for the increasing of mass transport during the electrochemical deposition of the metals. The enhancement of the electrode processes represents the key problem of the hydroelectrometallurgical processes and, as in the case of diluted solutions, the processes are controlled by the transport of the reactant species to the electrode. The literature study presented underlines the main methods (and especially the ones with industrial applications) that are applied for the enhanced mass transfer: the use of turbulence promoters, particle fluidized bed, mechanical stirring of the electrolyte, electrode spinning, electrode/electrolyte vibration and electrode/electrolyte ultrasonication.

The experimental part deals with three of the most widely applied techniques for the increasing of the mass transfer. A diluted solution of $CuSO_4$ was chosen as electrolyte and three different regimes, namely mechanical stirring, ultrasonication and vibrating were developed. The results show a better performance of the ultrasound-assisted electrodeposition of copper, followed by the vibrating electrode method and by the mechanical stirring of the electrolyte, respectively.

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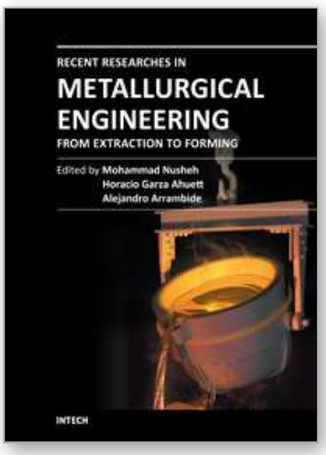
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Recent Researches in Metallurgical Engineering - From Extraction to Forming

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Metallurgical Engineering is the science and technology of producing, processing and giving proper shape to metals and alloys and other Engineering Materials having desired properties through economically viable process. Metallurgical Engineering has played a crucial role in the development of human civilization beginning with bronze-age some 3000 years ago when tools and weapons were mostly produced from the metals and alloys. This science has matured over millennia and still plays crucial role by supplying materials having suitable properties. As the title, "Recent Researches in Metallurgical Engineering, From Extraction to Forming" implies, this text blends new theories with practices covering a broad field that deals with all sorts of metal-related areas including mineral processing, extractive metallurgy, heat treatment and casting.

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