Prevention of Hydrosphere Contamination with Electroplating Solutions through Electromembrane Processes of Regeneration

Vasyl Serdiuk[1], Vsevolod Sklabinskyi[1], Svetlana Bolshanina[1],
Alexey Ableyev[2], Tetiana Dychenko[1*]

[1] Sumy State University, 2, Rymskogo-Korsakova st., 40007 Sumy, Ukraine

[2] Kusum Pharm LLC, 54, Skryabina st., 40022 Sumy, Ukraine

[*] Corresponding author's e-mail: mikishasumy@gmail.com

ABSTRACT

The work studies the process of Cd^{2+} and Zn^{2+} cations transfer through a RALEX®CM-PES 11–66 cation-exchange membrane and the cations reduction as metals on the cathodes at the cathode chambers of the electrochemical units with a view to prevent the hydrosphere contamination with the electroplating solutions. Electrolysis of the solutions that imitated the possible composition of the passivating baths contained 50 g/l sodium dichromate, 10 g/l sulfuric acid and impurity ions of Cd^{2+} and Zn^{2+} in various concentrations. The designed passivation solutions with certain amount of impurity ions in the colour solution were *forcibly* mixed. The impact of the impurity ions concentration in the colour solution and of a forced mixing on the metal reduction was studied. Regularity in the increased metal reduction dependent on the metal concentration was found and the conditions favouring the ion migration through the cation-exchange membrane due to forced mixing were defined.

Keywords: electrolysis, electroplating solutions, cation-exchange membrane, cadmium cations, zinc cations, forced mixing.

INTRODUCTION

The technical advance and intensified anthropogenic activities made the contamination of hydrosphere with a number of organic and non-organic production contaminants a common practice, especially in the countries where low technological development restrains the advanced technology of production and treating wastewater. This eventually results in the global contamination of hydrosphere, intensifies the drinking water issue and becomes a threat to humanity. This ecological problem can be approached in two ways: through the application of advanced wastewater treatment and wastewater prevention technologies as a result of the production technology upgrade, and prevention of industrial effluents. As to the first approach, some techniques have been recently applied as common: standard biological treatment technologies for household sewage water (Malovanyy et al. 2016), biological treatment technolog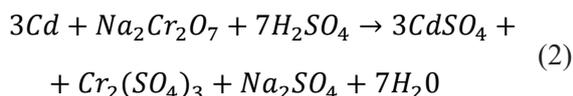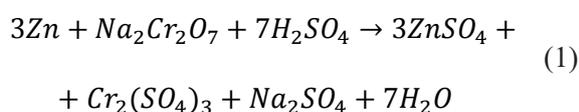ies for high concentrated organic sewages and landfill leachates (De Clippeleir et al. 2011, Malovanyy et al. 2018), chemical methods for combined slow-release fertilizer as a product (Tulaydan et al. 2017), application of membrane methods for wastewater treatment (Shmandiy et al. 2017). The most promising, however, is the industrial effluents prevention as a result of the production technology upgrade. The work is focused on studying the kinetic and hydrodynamic characteristics of the electromembrane process of regeneration in the electroplating solutions.

In heavy machine-building, electroplated coatings on the machinery parts must have improved anticorrosive properties. The electrochemical zinc and cadmium coatings are widely used as the protective electroplating coatings of the parts.

Zinc electroplating is performed for the parts to operate in temperate and Antarctic climate. The cadmium electroplating is used as a protection coating for the machinery parts to run under subtropical and tropical conditions.

Additional protection of these coatings is provided by the special protective membranes (Qian et al. 2018, Bolshanina 2016a). The membranes are the thin conversion nanofilms designed to protect the electroplated coatings from corrosion. These coatings are produced with chromate conversion coating to obtain the films represented by chromates and dichromates of zinc and cadmium.

Technologically, these protective membranes are obtained in the passivating (or chromating) baths with 50–200 g/l sodium dichromate and 5–12 g/l sulfuric acid. During the utilization of the solution, some changes occur: the acid and sodium dichromate are consumed, impurity metals are observed "Eq. (1)" "Eq. (2)":

$$3Zn + Na_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3ZnSO_4 + $$
$$+ Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O \quad (1)$$

$$3Cd + Na_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3CdSO_4 + $$
$$+ Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O \quad (2)$$

No decent chromating membrane is produced as acid and $Na_2Cr_2O_7$ are spent and impurity ions of various metals are accumulated;thus, the fresh portions of the reagents need to be added into the bath after a while. Specific functionality of the passivating solution is 0.5–1.0 m^2/l, removal of electrolyte with the parts is 0.48 l/m^2 (Vinogradov 2005). In 5–20 days of operation, these solutions become unusable and are disposed of in a deacidification station to be further neutralized (Vinogradov 2002). These releases are instantaneous and require considerable quantities of the reagents for neutralization. There are methods to maintain the passivating baths in function via regular addition of fresh portions of the reagents i.e. via bath composition correction. These procedures, as a rule, increase the concentration of sodium dichromate and accumulate the impurity Cd^{2+}, Zn^{2+} and Cr^{3+} ions in the bath (Vinogradov 2002). The excess of metal ions, sulfate anions and sodium dichromate are removed with the parts into the washing tanks and then infiltrate into the wastewater of the electroplating section. All these procedures for further neutralization and deposition require additional reagents. The disposal solutions of the electroplating industries, which are generally high concentrated and hazardous, require treatment. There are three main groups of the methods to treat the wastewater: a neutralization method, a utilization method and a regeneration method. The neutralization methods result in even greater accumulation of solid residue at the wastewater tanks and in an increase of their salt content. The utilization methods are rather specific and require separation of the wastewater by each component and considerable additional costs. The regeneration methods involve electrolyte regeneration via the removal of hazardous contaminants (Qian Yitong et al. 2017, Bolshanina et al. 2016b). These methods allow multiple use of the solution, hardly ever produce new wastes, require no reconstruction of the electroplating sections, and are the most promising as compared to the neutralization and utilization methods. On constant regeneration, the working solution flows in the system due to a regenerating device (Benvenuti et al.) applied to provide the long-term use of the solution and to reduce a number of reagents used in correction and fresh solution preparation as well as in the neutralization and utilization methods (Dimitris et al. 2013, Davoudi et al. 2014).

The reduction of energy costs and costs for neutralization of hexavalent chromium ions can be provided with the chromic solution regeneration method with electrochemical devices (units), which seems the most promising and relevant here. These devices recycle the valuable components as market products and as recyclable materials. Regeneration is performed at the electrolyzers of direct and alternate interaction with the membranes of well-known brands (MK-40, MA-40) (Kruglikov et al. 2013, Nekrasova et al. 2013). The working solutions of technological or washing tanks and solutions of sulfuric acid are used as catholytes and anolytes depending on type and purpose of the electrolyzer (Serdiuk et al. 2018, Kruglikov 2016). The principle of these devices is based on the accumulation of impurity metals in a cation-exchange electrolizer due to its chamber separated from the main tank with a cation-exchange membrane, under direct current at a cathode and in the cathode chamber (Kruglikov et al. 2018, Urtiaga et al. 2010) while there is a reduction of hexavalent chromium due to the Cr^{3+} oxidation at the anode in the main tank.

The subject of the work is to study the regularities in the transfer of impurity ions through the cation-exchange membrane as well as determine the effect of the Cd^{2+} and Zn^{2+}contaminant ions and forced mixing on the electromembrane process.

MATERIALS AND METHODS

For various parameters to be studied as to their effect on the chromic solutions regeneration, the electrogravimetric analytical method was applied at a developed experimental set-up – a two-chamber electrolizer (a cation electrochemical unit) comprising an anode and a cathode chamber split with a cation-exchange membrane. A diagram of the membrane electrochemical unit is depicted in Figure 1. The test solutions of anolytes to simulate the passivating baths were prepared in order to study the regularities of Cd^{2+} and Zn^{2+} mass transfer through the RALEX®CM-PES 11–66 cation-exchange membrane during the membrane electrolysis. The test solutions contained 50 g/l $Na_2Cr_2O_7$ and 10 g/l H_2SO_4 and different number of Cd^{2+} and Zn^2 ions.

The solutions concentrations were taken in such a way as to simulate the real technological environment and not to exceed its critical values. A catholyte was presented by a 1% aqueous sulfuric acid. A titanium plate (BT0) with working dimensions of 60x20x1 mm and working cathode area of 0.18 dm² was taken as a cathode, and lead (C2 grade) with working dimensions of 50x50x2mm and working anode area of 0.375 dm² was taken as an anode. The cathode/anode area ratio was 1:2.08. Direct electric current was maintained at 1.5 A and cathode current density was 8.32 A/dm²,

anode current density was 4 A/dm². The area of the membrane to participate in electrolysis was 50x50 mm and 0.25 dm² in area.

The efficiency of the process is mainly defined by a mass index for cadmium and zinc metals (Bolshanina 2016a) reduced on the cathode depending on their concentration in the test anolyte solutons with or without forced mixing. In order to prevent the formation of insoluble hydroxides of cadmium and zinc at a cathode region, the pH of the cathode was maintained within 1–2 (Serdiuk et al. 2018). A cathode deposit was identified with electron microscopy with X-ray phase analysis at an X-ray diffractometer DRON – 1 – UM and cadmium and zinc were confirmed in the deposits (Bolshanina et al. 2016b, Serdiuk et al. 2018).

The main structural parts of the electrochemical unit are depicted in Figure 1. The mechanical vertical two-bladed stirrer 7 was placed on the side of anode 4 and the cathode chamber 1. The stirrer directed the anolyte flow between the cation-exchange membrane 3 with the filter cloth 6 and the anode 4.

In order to study the effect of Cd^{2+} and Zn^{2+} concentration in the test anolyte solutions on membrane electrolysis efficiency and on metal reduction on the cathode, the concentration of the latter was changed (Table 1).
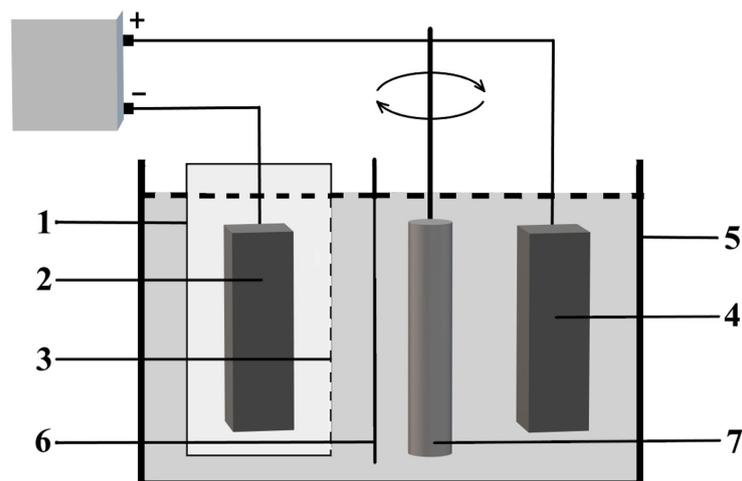

Fig. 1. Diagram of a membrane electrolizer with an external anode and a mechanical vertical two-bladed stirrer. 1 – anode chamber case; 2 – internal electrode – cathode; 3 – cation-exchanging membrane; 4 – external electrode – anode; 5 – chamber with a chromic solution; 6 – filter cloth; 7 – mechanical vertical two-bladed stirrer.

Table 1. Concentration of the basic components and impurities in the test passivation solutions of the electroplated coatings.

Solution No.	Concentration of Na2Cr$_2$O$_7$, g/l	Concentration of H$_2$SO$_4$, g/l	Concentration of Cd^{2+}, mmol-eq/l	Concentration of Cd^{2+}, g/l	Concentration of Zn^{2+}, mmol- eq/l	Concentration of Zn^{2+}, g/l
1	50	10	0.027	1.5	0	0
2	50	10	0.054	3.0	0	0
3	50	10	0.179	10.0	0	0
4	50	10	0	0	0.027	0.845
5	50	10	0	0	0.054	1.755
6	50	10	0	0	0.179	5.80

RESULTS AND DISCUSSION

Effect on impurity ions concentration on ion electroreduction at a cathode

The test solutions (Tab. 1) were used to define the effect of the impurity ion concentration on electrolysis rate. The obtained results are presented in Tab. 2.

As is seen from Tab. 2, the reduction of zinc and cadmium increases as their concentration grows in the anolyte. At the same initial concentrations of Cd^{2+} and Zn^{2+} in the anolyte, the metal volume reduced at the cathode is different (Fig. 2):

The laboratory experiments showed that the cadmium electroreduction rate increases te ion concentration grows in the anolyte. During the metal zinc reduction at the cathode, some balanced process is observed as metal ion concentration is over 0.05 mmol- eq/hour. Further increase of the Zn^{2+} concentration in the anolyte has no considerable effect on rate.

The above mentioned data confirm the dependence of the electroreduction rate of the metals on the cathode and their initial concentration in

Table 2. Reduction rate of metals on a cathode as function of the initial ion concentration in a solution

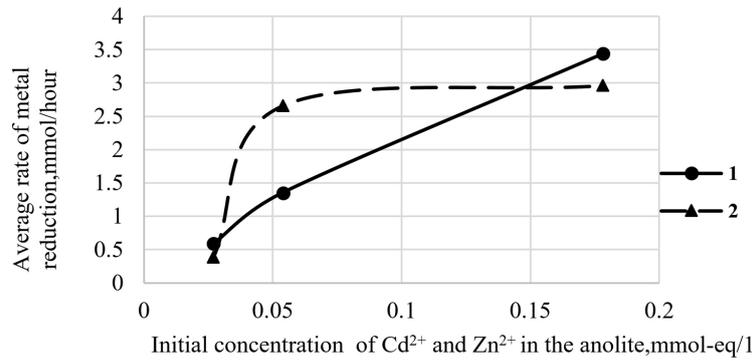| Solution No.	Ion and its concentration in anolyte, g/l	Hydrolysis duration, hour	Mass of obtained metal, g	Total mass of obtained metal, g	Average rate of metal reduction, g/hour	Average rate of metal reduction, mmol- eq/hour
1	Cd2+, 1.5	2	0.067	0.067	0,039	0,59
		4	0.063	0.13		
		6	0.13	0.26		
		8	0.05	0.31		
2	Cd2+, 3.0	2	0.148	0.148	0.090	1.36
		4	0.155	0.303		
		6	0.235	0.538		
		8	0.183	0.721		
3	Cd2+, 10	2	0.35	0.35	0.227	3.439
		4	0.293	0.803		
		6	0.314	1.323		
		8	0.493	1.816		
4	Zn2+, 0.845	2	0.005	0.02	0.0125	0.38
		4	0.012	0.03		
		6	0.08	0.07		
		8	0.03	0.1		
5	Zn2+, 1.755 g/l	2	0.145	0.145	0.087	2.66
		4	0.162	0.307		
		6	0.12	0.527		
		8	0.166	0.693		
6	Zn2+, 5.8 g/l	2	0.148	0.148	0.096	2.96
		4	0.231	0.379		
		6	0.277	0.656		
		8	0.114	0.77		

Fig. 2. Electroreduction of cadmium and zinc at a cathode as function of Cd^{2+} and Zn^{2+} concentration in the anolytes.

1 – cadmium reduction rate, mmol- eq/hour; 2 – zinc reduction rate, mmol- eq/hour.

the anolyte, and their different ability to transfer through the membrane. It is related to the nature of metals, hydration shell structure of their ions and the concentration polarization observed on the membrane surface and near the cathode (Nikonenko et al. 2010).

A considerable number of co-ions is accumulated on the external surface of the membrane as result of the concentration polarization, it increases the osmotic pressure and decreases the dynamics of ion transfer through the membrane. It also favours the salt gels deposition on the membrane. The concentration increase on the membrane surface occurs until a diffusion flow equals the convective flow of the substance up to the membrane and until a dynamic equilibrium is established (Urtiaga et al. 2010, Nikonenko et al. 2010).

Effect of forced mixing of electroreduction rate of the metals on the cathode

During electrolysis, an uncontrolled mixing of the anolyte solution is observed near the cathode chamber; this may be conditioned by two mechanisms:
1. oxygen reduction at the anode and an accompanying liquid-gas mixture, which causes the local pressure differences and a convection of the solution;
2. electroconvection caused by nonuniform current flow through the membrane and its partial reflection from a non-conducting case of the heterogeneous membrane. There is a repulsion of the liquid and a formation of whirls near the anode observed as some current is reflected (Zabolotsky et al. 2017, Nebavskaya et al. 2017). In order to define the sufficiency of the "passive" mixing, a number of experiments

with a forced mixing of the anolyte near the membrane were carried out. The solutions No. 2,3,5,6 (Table 2) were taken as anolytes, with their residual concentrations of Cd^{2+} and Zn^{2+} presented in Table 3.

For mixing the anolytes, a mechanical vertical two-bladed stirrer 20 mm wide, 60 mm high, 1 mm thick and rotation frequency of n=2.7 rot/sec was applied. The current rate ϑ_1 is 54 mm, based on the expression

$$\vartheta_1 = n \cdot d \qquad (3)$$

where hydrodynamic diameter of d=0.02 m (width of the stirrer) is schematically depicted in Fig. 3.

The flow caused by the stirrer is centrifugal and multidirectional with flow rate ϑ_1. However, when it reaches the hydrodynamic pass between the membrane and the anode (Figure 3), the whirls formed by direct current have effect on the forced flow of the liquid. As the flow enters the pass, it comes into resistance with a contra-directional whirl and the inlet rate is

$$\vartheta_{inlet} = \vartheta_1 - \vartheta_{whirl} \qquad (4)$$

At the outlet of the pass, the outlet rate increases by virtue of coincidence of a mechanical flow and the whirl flow:

$$\vartheta_{outlet} = \vartheta_1 + \vartheta_{whirl} \qquad (5)$$

The average flow rate in this hydrodynamic pass is $\vartheta_{1\ 1}$.

The experimental results are presented in Tab. 3, Tab. 4.

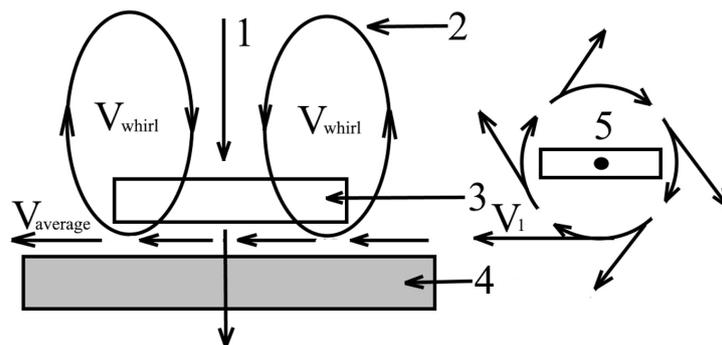The experimental results in Tables 2 and 4, and on the scheme (Fig. 4) allow drawing the

Fig. 3. Scheme of electrolyte flow near an anode with a mechanical mixing applied.
1 – direction of current, 2 – whirls formed in an electrolyte under electric current, 3 – anode, 4 – cation-exchange membrane, 5 –mechanical vertical two-bladed stirrer

Table 3. Basic components and impurities in the test solutions for studying the effect of forced mixing on a cathodic metal reduction

Solution No.	Concentration of Na2Cr$_2$O$_7$, g/l	Concentration of H$_2$SO$_4$, g/l	Concentration of Cd^{2+}, mmol-eq/l	Concentration of Cd^{2+}, g/l	Concentration of Zn^{2+}, mmol- eq/l	Concentration of Zn^{2+}, g/l
2a	50	10	0.054	3.0	0	0
3a	50	10	0.179	10.0	0	0
5a	50	10	0	0	0.054	1.755
6a	50	10	0	0	0.179	5.80

conclusion on the effect of forced mixing on rate of cathodic metal reduction and metal migration through the cation-exchange membrane.

The experiments on the effect of fixed mixing on electroreduction rate of metal ions have provided the grounds to drawing the following conclusions:

- forced mixing favours the electroreduction rate, as evidenced by mass increase of metals reduced at the cathode;
- mixing increases the ion migration rate through the cation-exchange membrane and decreases the concentration polarization. The maximum effect of mixing was observed in

Table 4. Rate of cathodic metal reduction with mechanical mixing and electrochemical unit applied

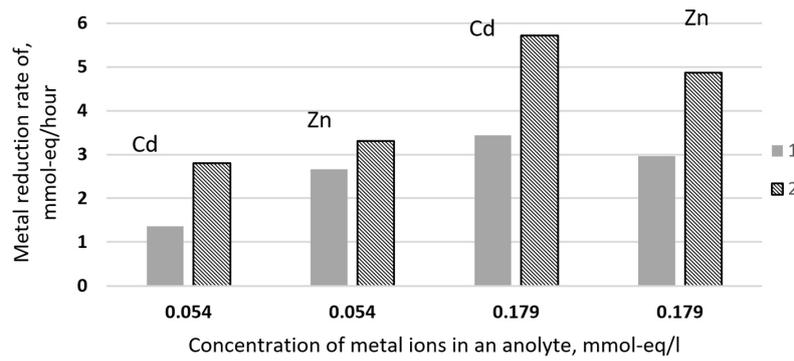| Solution No.	Hydrolysis duration, hour	Mass of obtained metal, g	Total mass of obtained metal, g	Rate of metal reduction, g/hour	Rate of metal reduction, mmol- eq/hour
2a	2	0.286	0.286	0.184	2.80
	4	0.294	0.58		
	6	0.241	0.821		
	8	0.66	1.477		
3a	2	0.309	0.622	0.377	5.714
	4	0.297	1.348		
	6	0.324	2.1		
	8	0.916	3.017		
5a	2	0.138	0.138	0.107	3.303
	4	0.153	0.291		
	6	0.16	0.451		
	8	0.408	0.859		
6a	2	0.244	0.244	0.158	4.863
	4	0.327	0.571		
	6	0.397	0.968		
	8	0.296	1.264		

Fig. 4. Effect of forced mixing on electroreduction rate of metal ions in anolyte solutions of various concentrations: 1 – without forced mixing, 2 – with forced mixing
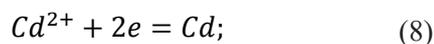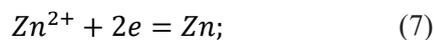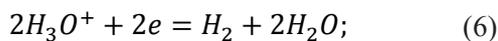
the anolytes with cadmium ions (current efficiency increased by 52%, as compared to the processes running without mixing);

- forced mixing has a considerable effect on the zinc reduction only at high concentrations of the zinc ions in the solutions.

Finding kinetic regularities and current efficiency during electromembrane regeneration of chromic solutions

Studying kinetic regularities of the electrochemical processes is associated with determination of the resultant current efficiency and is needed to select the best conditions for metal reduction during membrane electrolysis.

In the system under consideration, the cathode processes are related to some parallel reactions carried out. With no zinc or cadmium ions in the catholyte (the solution of sulfuric acid), the cathode process is ensured by the hydrogen ions. Intensive hydrogen emission is observed in this process ("Eq. (6)"). After passing through the membrane from the anolyte to the catholyte, the zinc and cadmium ions are discharged at the cathode and form some metal depositions on it (reactions 2, 3). Standard electrode potentials of these metals are negative (-0.763B; -0.404B); thus, the hydrogen ion discharge will also take place at the cathode.

$$2H_3O^+ + 2e = H_2 + 2H_2O; \qquad (6)$$

$$Zn^{2+} + 2e = Zn; \qquad (7)$$

$$Cd^{2+} + 2e = Cd; \qquad (8)$$

It may be concluded that cathode process rate depends on the hydrogen volume emitted and on metal mass reduced on the cathode as well. The current efficiency is calculated by the Faraday laws. The basic parameter to be calculated here is an electrochemical equivalent (g) that defines the mass of a substance (g) formed as a unit of electricity passes in an electrolyte per unit of time.

$$q = \frac{M}{n \cdot F} \qquad (9)$$

where: q is an electrochemical equivalent;
M is molar mass of a metal;
n is number of valency electrons;
F is Faraday constant (26.8 A-hour/mol).

Considering the average rate of metal reduction from the anolyte (table 2, 4), the metal current efficiency may be calculated.

$$\eta = \frac{\upsilon}{q} \cdot 100\% \qquad (10)$$

where η is current efficiency;
q is electrochemical equivalent, g/A hour;
υ is metal reduction rate, g/A hour

The data from Tab. 5 do not take into account some partial current spent on the hydrogen reduction.

The data from Table 5 and the resultants current efficiency obtained support the conclusion that forced mixing has a positive effect on the electrochemical reduction at the cathode. Low values for current efficiency (13–15%), even with forced mixing applied, are explained by a simultaneous cathodic reaction of hydrogen reduction. The hydrogen reduction proceeds rather intensively when the electrolizer starts at minimum Ph of the catholyte. Its decrease is observed at the cadmium ions presence in the solution.

Table 5.Data for calculating the current efficiency of electrochemical reduction at a cathode

Impurity ion	Hydrodynamical conditions	Metal initial concentration, mol-eq/l	Electrochemical equivalent, q	Average rate, g/hour	Effective current, %
Cd2+	Without mixing	0.027	2.46	0.039	1.585
Cd2+	Without mixing	0.054	2.46	0.090	3.659
Cd2+	Without mixing	0.179	2.46	0.227	9.228
Cd2+	Forced mixing	0.054	2.46	0.184	7.480
Cd2+	Forced mixing	0.179	2.46	0.377	15.325
Zn2+	Without mixing	0.027	1.21	0.0125	1.031
Zn2+	Without mixing	0.054	1.21	0.087	7.174
Zn2+	Without mixing	0.179	1.21	0.096	7.916
Zn2+	Forced mixing	0.054	1.21	0.107	8.823
Zn2+	Forced mixing	0.179	1.21	0.158	13.029

CONCLUSIONS

The study of chromic solution regeneration with the electrochemical units has demonstrated that the impurity metal ions can be reduced at the cathode in the cathode chamber during the regeneration. Maintenance of constant current density, temperature and pH ions of the catholyte showed that the regeneration depends on the initial concentrations of the impurity ions and on the mechanical mixing of the membrane area of the anolyte.

- The mass of the metals reduced on the chamber cathode increases as the metal ion concentration in the chromatic solution grows.
- The rate of zinc and cadmium reduction differs. At the same molar concentrations of the metal ions, cadmium electroreduction grows linearly in the initial solution as concentration increases. On the zinc metal reduction at the cathode, some balance in this process is observed at the metal ion concentration over 0.05 mol-eq./l. Further increase of the Zn^{2+} concentration in the anolyte has no considerable effect on the reduction rate.
- Forced mixing applied in the chromic anolyte solution accelerates the regeneration, the metal ion migration through the cation-exchange membrane and decreases the concentration polarization. The maximum effect of the forced mixing was observed in the anolytes with the cadmium ions (current efficiency increased by 52% as compared to that of the regeneration process without mixing applied).
- Forced mixing has a considerable effect on the zinc reduction only at high concentrations of the zinc ions in the solutions; therefore, this type of mixing is considered economically ineffective for the solutions regeneration when the zinc ion content is under 2 g/l.
- The calculated current efficiency of metal reduction proves the effect of concentrations and forced mixing on this process. Low current efficiency is conditioned by a simultaneous reaction related to the hydrogen emission.

The performed studies allow selecting the best performances and adjusting the chromatic solution components for a long-term use.

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