V.I. Vernadskii Institute
of General and Inorganic Chemistry
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MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE

KYIV 2018

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ArtOK publisher

KYIV 2018

UDC 54.058+544.725.2

CHAPTER 7

LABORATORY AND INDUSTRIAL TESTING OF MEMBRANE ELECTROCHEMICAL DEVICES FOR PURIFICATION AND REGENERATION OF CHROMIUM-CONTAINING GALVANIC SOLUTIONS

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Abstract. *The regeneration process of galvanic solutions by transferring the contaminating Cd^{2+} and Zn^{2+} cations through a cation exchange membrane RALEX®CM-PES 11-66 in a two-chamber electrolyser has been researched. The cathode processes that are associated with the migration of ions through the membrane and the cathodic deposition have been investigated. Laboratory and industrial testing of devices was carried out. Cathode products were studied using scanning electron microscopy with X-ray phase microanalysis functions to determine the elemental composition of cathodic deposits. This process allows to regenerate galvanic solutions and maintain stable composition of passivation baths.*

Keywords: *electrolysis, cation-exchange membrane, chromium-containing solution, cadmium cations, zinc cations.*

Introduction. The use of Cr(VI) compounds for the applying protective conversion films on galvanic coatings to significant environmental hazard due to waste water pollution. These compounds possess toxic properties, they have mutagenic and carcinogenic effect on living organisms [1, 2]. Cr(VI)-containing solutions are applied to brightening and passivation baths, the main component of which is sodium dichromate, chromic anhydride and other aggressive reagents. The chrome plating process is accompanied by the reduction of Cr(VI), the solutions also accumulate heavy metal ions. The ratio of the essential components in these baths changes that entails the need for adjustment of the solution composition by adding new portions of reagents. This leads to instability of bath operation and declining quality of a coating. The problem could be solved by the development and implementation of membrane-type electrochemical devices, which provide simultaneous return of valuable components into a technological cycle (in the form of commercial products and secondary raw materials). Electrolysis with ion-exchange membranes is the most perspective method for the wastewater purification [3-5].

Experimental. In order to study the regeneration of chromium-containing solutions using a membrane system, laboratory and industrial membrane electrochemical electrolysers were produced [6, 7]. Electrochemical reactions were studied using a laboratory membrane system (LME), whereas an industrial membrane electrolyser (IME) was used to study the effectiveness of the process under real operation conditions (Table 7.1, Fig.7.1).

Table 7.1: Comparative characteristics of membrane electrolysers

Electrolyser characteristic	**LME**	**IME**
Material of the cathode	Titanium BT-1	Titanium BT-1
Cathode area S, дм^2	0,3	0,7
Membrane	RALEX®CM-PES 11-66	RALEX®CM-PES 11-66
Catholyte	1% sulphuric acid solution	1% sulphuric acid solution
Anode material	Lead C2	Lead C2
Anode area S, dm^2	0,72	2,1
Anolyte, g/l	Sodium dichromate $Na_2Cr_2O_7$ – 50 Sulfuric acid H_2SO_4 – 10 Ions Zn^{2+}, Cd^{2+} and Cr^{3+} 2,5 g/l each	1) brightening bath: Chromium trioxide CrO3 …80-110 H_2SO_4 …3-5 2) passivation bath: Sodium dichromate $Na_2Cr_2O_7$ …150-200 Sulfuric acid H_2SO_4 …8-12 Content of ions Zn^{2+}, Cd^{2+}, Cr^{3+} was not determined
Catholyte volume, dm^3	1	4,5
Anolyte volume, dm^3	10	150
Voltage, V	3-9	3-9
Current density, A/dm^2	0,3-3	1-5

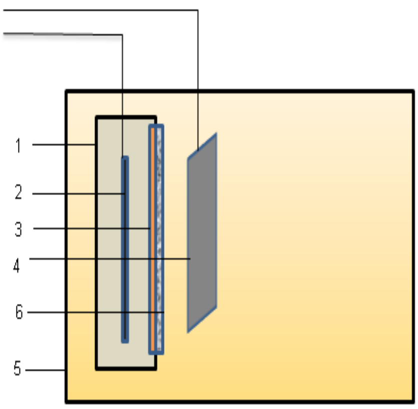

Fig. 7.1. *Scheme of membrane electrolyser. 1 –cathode chamber body; 2 – inner electrode - cathode; 3 – ion exchange membrane; 4 – external electrode - anode; 5 – chamber with chromium-containing solution; 6 – filtering cloth.*

Cathodic deposit was investigated by using the method of raster electron microscopy and X-ray diffraction analysis.

Results and discussion. While studying electrode reactions, we can assume the resulting products. Thus, the following reactions can occur:

$$Zn^{2+} + 2e = Zn; \quad (7.1)$$

$$Cd^{2+} + 2e = Cd; \quad (7.2)$$

$$2H_3O^{+} + 2e = H_2 + 2H_2O; \quad (7.3)$$

$$2H_2O + 2e = H_2 + 2OH^{-}. \quad (7.4)$$

Reactions 7.3 and 7.4 cause the change in catholyte pHm. Change in catholyte acidity (its shift towards the alkaline side), leads to the drop of electroconductivity of solution and formation of flaked insoluble metal hydroxides that results in module efficiency decrement.

X-ray diffraction analysis, conducted on an automated diffractometer DRON-4-07, and an electron microscopy were used to determine the elemental composition of products deposited on the cathode. X-ray microanalysis conducted using the scanning electron microscope "REM-106-i" allowed determination of mass fraction of elements in the samples of the studied cathodic deposits and average from field of view on the basis of energy values of the characteristic X-ray peaks of each chemical element. The results are shown in Figures 7.2, 7.3. As can be seen, among the compounds in the cathodic deposits there are metallic cadmium, cadmium carbonate $CdCO_3$, a small amount of mixed ferrous oxide Fe_3O_4, as well as insignificant (less than 3%) amount of amorphous impurities and sand.

Simultaneously with the removal of ions that contaminated technological solutions of passivation and brightening baths, regeneration of chromate and dichromate ions was observed.

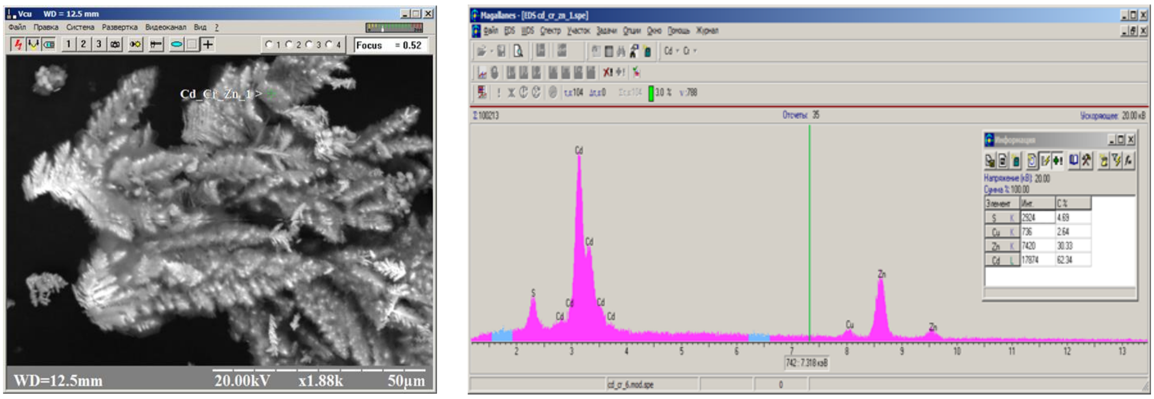

Fig. 7.2. *a) A REM photograph of cathodic deposit samples when the module is operated: the anolyte contains Zn^{2+} ions (2.5 g / l) and Cd^{2+} (2.5 g / l), x1880; b) Spectrograms of cathodic deposit samples and the results of microanalysis: the anolyte contains Zn^{2+} ions (2.5 g / l) and Cd^{2+} (2.5 g / l).*

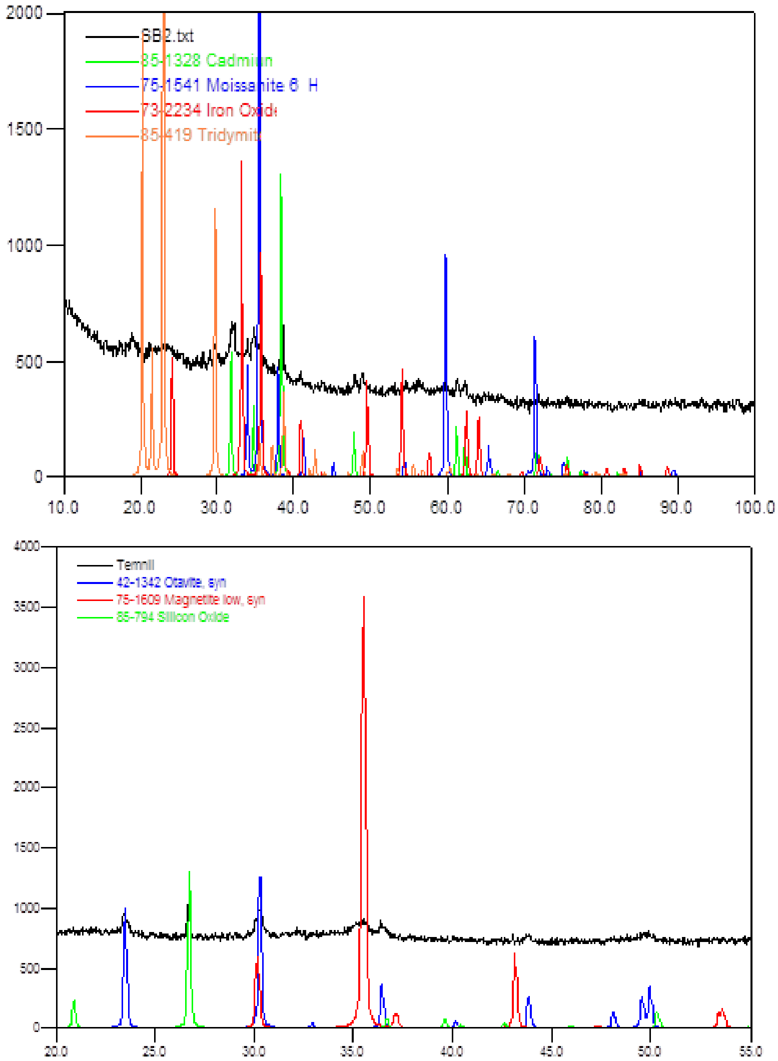

Fig. 7.3. *X-ray diffraction analysis of cathodic deposits samples conducted on IME.*

This process was provided by the ability of Cr^{3+} ions to be easily oxidized on a lead anode in accordance with the scheme of the process (7.5):

$$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \quad (7.5)$$

To evaluate the performance of the device, its efficiency was determined at different intervals of time in the passivation bath with 150 liters bath volume. The efficiency of the Cr^{3+} ion oxidation in Cr(IV) was evaluated by monitoring the change in the concentration of Cr(IV) ions in this bath, as shown in Fig. 4. The testing stages were related to the selection of operating and structural parameters of the membrane electrolyser and the production conditions. Characteristics of IME, shown in Table. 7.1, meet the requirements of the third stage of industrial testing. The regeneration efficiency of the content of hexavalent chromium ions in the solution is 52 grams per hour.

It is known that the recovery process in the cathode chamber is significantly influenced by the acidity of the catholyte medium [8, 9]. During laboratory studies, range of pH value (from 1.5 to 1.8) of a catholyte solution were determined, in which the most effective metal deposit on a cathode and regeneration of a chromium-containing solution are observed. At pH less than

1.5, hydrogen actively forms on the cathode, which interferes with the metal deposition process. And at a pH of more than 1,8-2, insoluble metal hydroxides are formed in areas close to the cathode. These conclusions were confirmed by industrial testing.

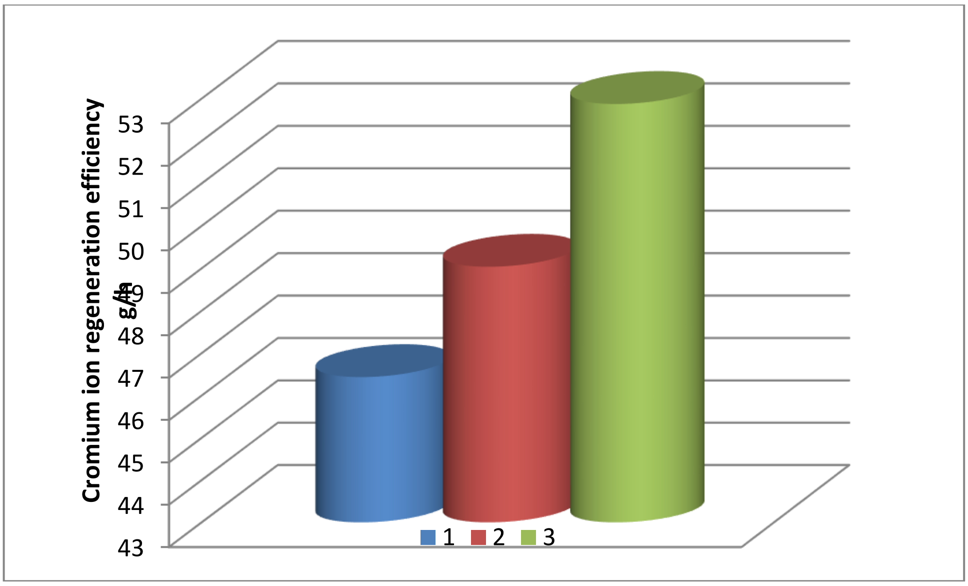

Fig. 7.4. *Effectiveness of IME at different stages: 1, 2, 3 - stages of testing in the factory passivation bath with 150 liters bath volume.*

Conclusions. This research has shown that the electrolysis of chromium-containing solutions using a laboratory model of electrolyser with a cation exchange membrane allows to regenerate the solution by removing the metal ions that contaminate it. Using an electron microscopy with X-ray phase microanalysis functions, it was found that cathode deposits contain cadmium and zinc atoms that were present in anolyte as impurities. Due to the use of the IME, optimal operating modes were selected in production conditions. As a result of implementation of IME, hexavalent chromium can be returned to the brightening and passivation baths (up to 50 grams per hour). Thus, the exploitation period of the brightening and passivation baths is significantly increased, and the costs of preparing new solutions are reduced

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УДК 54.058+544.725.2

ЛАБОРАТОРНІ ТА ПРОМИСЛОВІ ВИПРОБУВАННЯ МЕМБРАННИХ ЕЛЕКТРОХІМІЧНИХ ПРИСТРОЇВ ДЛЯ ОЧИЩЕННЯ ТА РЕГЕНЕРАЦІЇ ХРОМОВМІСНИХ ГАЛЬВАНІЧНИХ РОЗЧИНІВ

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Резюме. *Досліджено процес регенерації гальванічних розчинів, шляхом перенесення забруднюючих катіонів Cd^{2+} та Zn^{2+} через катіонообмінну мембрану RALEX®CM-PES 11-66 в двокамерному електролізері. Вивчені катодні процеси, що пов'язані із міграцією йонів крізь мембрану та виділенням металів на катоді. Проведені лабораторно-промислові випробування пристроїв та досліджено катодні продукти за допомогою методу скануючої електронної мікроскопії з функцією мікроаналізу та рентгенофазового аналізу для визначення елементарного складу катодних осадів. Даний процес дозволяє регенерувати гальванічні розчини та підтримувати стабільний склад ванн пасивування..*

Ключові слова: *електроліз, катіонообмінна мембрана, хромовмісний розчин, катіони кадмію, катіони цинку.*