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Regeneration of Chromate Galvanic Solutions in Membrane Electrochemical Devices

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Abstract. The regeneration processes of industry technological passivating baths of electrochemical cadmium lines and electrochemical galvanizing lines as an applied result of two-chamber membrane cation-exchange electrochemical devices researched. Actual industrial passivation baths of cadmium and zinc galvanic coatings applied as anode chambers. The cathode chamber contained sulfuric acid 1 % solution and a titanium cathode (BT-0). A window was cut in one of the walls with a RALEX®CM-PES 11-66 cation exchange membrane placed in it. The lead (C-0) was used as the anode. A comparative analysis of the performance of these technological baths before and after the using cation exchange membrane electrochemical devices was carried out. As a result of long-term experimental studies, the ecological and economic feasibility of their use was proven.

Keywords: electrolysis, environmental hazard, reagent, energy efficiency, pollutant tax.

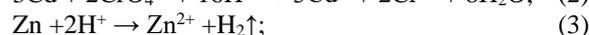
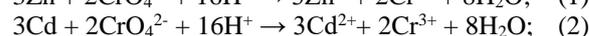
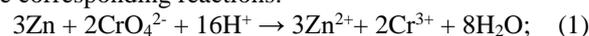
1 Introduction

Passivation baths are used in the electrochemical cadmium coating processes and electrochemical galvanization at the galvanic production of JSC Sumy Plant Nasosenergomash. These baths are technologically necessary thanks to their protective aid conversion films created on the corresponding galvanic coatings [1, 2]. The conversion film is formed from cadmium and zinc chromates, respectively, and serves as additional protection for this type of coating against corrosion. The thickness of the conversion film is several tens of nanometers. The protective properties of the created conversion films are controlled by a lead (II) acetate solution following the requirements of the product control rules for nuclear power plants.

The passivating solutions, accordingly, to the galvanic works technological process of JSC “Nasosenergomash” (Sumy, Ukraine), are an aqueous solution containing: Na₂Cr₂O₇ – 150–200 g/l, H₂SO₄ – 10–12 g/l.

As a result of these baths operation, the sodium dichromate and sulfuric acid concentrations gradually decrease, and polluting ions Cr³⁺, Cd²⁺, and Zn²⁺

accumulate as a result of the corresponding reactions: of the corresponding reactions:



As a result of the passivation of parts with a considerable surface area in these technological baths, the concentration of the reagents decreases, and the impurity ions concentration increases to a critical level because the bath function is lost: the creation of a high-quality protective conversion film on the surface of the coating. To restore their properties, it is necessary to increase the Na₂Cr₂O₇ and H₂SO₄ concentration by adding a certain amount of them to the bath solution or dilute the bath solution if possible to reduce the contaminating metal ions critical concentrations or combine these methods of adjusting the contents of the bath.

When correcting the passivation baths by adding new portions of sodium dichromate and sulfuric acid, the baths restore their efficiency only for a short time. Adjustments occur with a certain periodicity. As a result of such adjustments to the bath content, the concentration of both reagents and reactions 1–4 products gradually increases.

Such actions are a consequence to an increase in the amount of reagent removal and reaction products in the washing water. It is common knowledge that the average removal of chromate solutions is 0.2-0.4l/m² of the total parts area [3]. Consequently, the amount of reagents and products increases significantly in the wastewater of galvanic production, as a consequence, the costs of reagents for neutralization as dichromate anions increase, as well as for the precipitation of heavy metal ions.

As a result of such work, chromating baths are an irrational use of resources: reactive substances and water. Due to the electrolysis laws, the ion-exchange membranes properties, and their application in world practice for electro dialysis, membrane filtration, and membrane electrolysis, a scheme of membrane electrolysis is introduced for cleaning and regeneration of passivation baths.

2 Research Methodology

To regenerate and rationally use resources and reduce the burden on wastewater treatment, an industrial electrochemical membrane device similar to a laboratory device, which is used to study the patterns of metals electrodeposition, was created [4, 5].

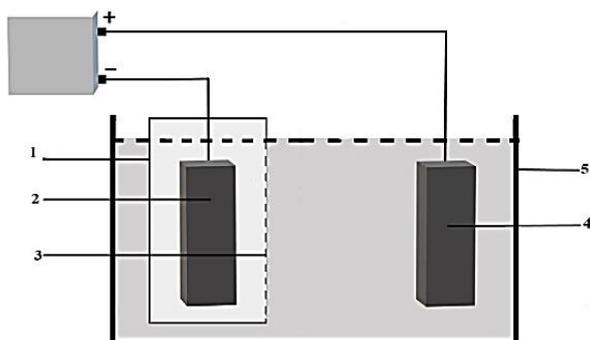
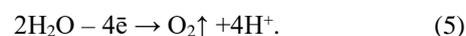


Figure 1 – The design scheme of an industrial membrane cation exchange electrochemical device: 1 – cathode chamber, 2 – cathode; 3 – cation exchange membrane with a filter cloth; 4 – anode; 5 – anode chamber – industrial passivation bath.

Unlike the laboratory membrane electrochemical device, the industrial sample differs in size. Since industrial passivation baths have a volume of approximately 150 l, the industrial electrochemical device must have significantly larger dimensions of the membrane, cathode, anode, and cathode chamber, but at the same time be compact - not take up a large volume in the working process bath. For the manufacture of an industrial electrochemical cell, considering account compactness, the dimensions of the membrane, anode, and cathode chamber were increased several times compared to the laboratory model. The cathode chamber case 1 (Fig. 1) was made of chemically resistant polypropylene of the PPH brand with a catholyte volume of 3.7l, a height of 400mm, a width of 190mm, and a thickness of 55mm. A window was cut in one of the chamber walls for fixing the RALEX®CM-PES 11-66 membrane with a height of 300mm and a width of 60mm, while the area of membrane

3 (Fig. 1) was 1.8 dm². A BT0 titanium plate with working dimensions of 350x20x1 mm was used as cathode 2 (Fig. 1) the cathode working area was 1.05 dm². As anode 4 (Fig. 1) lead C0 was used with working dimensions of 320x60x3mm, the working area of the anode was 2.88 dm². The ratio of the cathode area to the anode area was 1:2.74. The anode was located in the working chamber of the passivation bath 5 (Fig. 1) at a distance of 8-10mm from the membrane. The cathode chamber of the industrial membrane device contained a 1% solution of sulfuric acid as a catholyte. The electrolysis was conducted with the help of a direct current source VU12/6 at a voltage of 9 V and a current of 5 A. Thus, the cathodic current density was 4.76 A/dm². At the same time, the anode current density was 1.736 A/dm², and the membrane current density was 2.77 A/dm².

The passivation solutions are anodic chambers 5 (Fig. 1) and contain anodes made of lead (C0) on which the head electrochemical reaction is the water oxidation reaction with the oxygen release and acidification of the solution:



A feature of lead anodes is the ability to oxidize Cr³⁺ ions into CrO₄²⁻ ions [6-8]. Cr³⁺ ions are formed in passivation baths due to the interaction of cadmium or zinc coating in the formation processes of protective conversion films on them. Thus, these ions are always present in working technological baths and constantly accumulate and consequently of constant work pollute them (reactions 1, 2). But the Cr³⁺ oxidation reaction ions with accompanying acidification of the solution take place at the lead anode:



The rate of Cr³⁺ ions oxidation to CrO₄²⁻ ions at the anode depends on the concentration of Cr³⁺ ions in the solution, temperature, and current density at the anode [9]. Thus, to maintain the concentration at approximately 1 % in electrochemical chromium plating electrolytes, it is necessary to have a ratio between the cathode areas and anodes in the bath of 1:2 [8]. The lack of proportionality between the reaction rate and the anode current density indicates that the Cr³⁺ ion's oxidation to CrO₄²⁻ ions at the anode is not a purely electrochemical reaction [9, 10].

Therefore, consequently of the electro-membrane device operation, the hexavalent chromium compounds regeneration [11, 12] of the passivation solutions and the harmful impurities removal of heavy metal ions in the cathode chamber, which accumulate as a result of these technological baths operations, happens. Thus, with the constant electric current help, a cation exchange membrane that separates the cathode chamber from the main composition of the bath, regeneration of the head components of the capacity, and removal of polluting impurities takes place.

Research on the restoration of chromate concentrations in passivation solutions of cadmium and zinc galvanic coatings happened in the applying membrane electrolysis procedure with the industrial membrane electrochemical devices help. These studies were carried out in working

technological baths. To find out the content of Cr⁺⁶ ions and Cr⁺³ ions in the passivation baths, titrimetric and photocolometric methods of analysis were used. Detection of the content of Cr⁺⁶ ions and Cr⁺³ ions determined after certain intervals of operation in technological baths of electrochemical membrane devices, are shown in Table 1.

From the obtained results of analyzes of the chromium ions concentrations, it was established that the Cr⁺⁶ ions concentration in the passivation baths of galvanic coatings

increases, and the Cr⁺³ ions concentration decreases due to the operation of membrane electrochemical devices. This change in the Cr⁺⁶ ions concentrations and Cr⁺³ ions is caused by reaction 6 occurring at the lead anode. During the operation of the baths, the total chromium concentration in them gradually decreases due to the deposition of the formed metal chromates on the parts in the form of conversion films and the electrolyte removal to the portions into the washing water.

Table 1 – Dynamics of changes in the Cr⁺⁶ ions and Cr⁺³ ions concentrations in the passivation baths of cadmium and zinc coatings during the operation of membrane electrochemical devices

| Pollutant ion | Concentrations of ions, g/l | | | Temperature, °C | Time, h | Growth of Cr ⁺⁶ ions, g/l | The total increase of Cr ⁺⁶ ions, g | The rate of Cr ⁺⁶ ions regeneration | |
|------------------|-----------------------------|------------------|---------|-----------------|---------|--------------------------------------|--|--|--------|
| | Cr ⁺⁶ | Cr ⁺³ | Gen. Cr | | | | | g/hour | mole/h |
| Cd ²⁺ | 44.01 | 39.25 | 83.26 | 18 | 0 | – | – | – | – |
| | 45.10 | 37.80 | 82.90 | 18 | 24 | 1.09 | 163.5 | 6.8125 | 0.1310 |
| | 46.53 | 35.19 | 81.72 | 18 | 24 | 1.43 | 214.5 | 8.9375 | 0.1718 |
| | 46.99 | 33.92 | 80.91 | 17 | 24 | 0.46 | 69.0 | 2.8750 | 0.0553 |
| | 47.59 | 32.64 | 80.23 | 18 | 24 | 0.60 | 90.0 | 3.7500 | 0.0721 |
| | 48.66 | 31.08 | 79.74 | 18 | 24 | 1.07 | 160.5 | 6.6875 | 0.1286 |
| Zn ²⁺ | 59.14 | 28.27 | 87.41 | 18 | 0 | – | – | – | – |
| | 60.17 | 26.94 | 87.11 | 18 | 24 | 1.03 | 154.5 | 0.6042 | 0.0116 |
| | 61.07 | 25.18 | 86.25 | 17 | 24 | 0.90 | 135.0 | 5.6250 | 0.1082 |
| | 61.68 | 24.22 | 85.9 | 18 | 24 | 0.61 | 91.5 | 3.8125 | 0.0733 |
| | 62.83 | 22.34 | 85.17 | 18 | 24 | 1.15 | 172.5 | 7.1875 | 0.1382 |
| | 64.42 | 20.45 | 84.87 | 18 | 24 | 1.59 | 238.5 | 13.6875 | 0.2632 |

As shown in Table 1, the magnification of the Cr⁺⁶ ions concentration in the baths occurs unevenly. Such results are explained by uneven loading of the baths, resulting which reactions 1 and 2 happening at different speeds. The dynamics of changes in the Cr⁺⁶ ions concentrations and Cr⁺³ ions are the differences between the rates of reactions 1 and 2 and anodic reaction 6. Therefore, thanks to the constant formation of Cr⁺⁶ ions at the anode, the technological solution is constantly enriched with the main component - CrO₄²⁻ ions, which does not require the addition of sodium dichromate additional portions due to its regeneration. Thus, from the data in Table 1, it can be concluded that, on average, at an anodic current density of 1.736A/dm² on a lead anode with an area of 2.88 dm², thanks to a side reaction, about 6 g/h of hexavalent chromium ions are recovered in the chromating bath.

Therefore, during the operation of industrial electrochemical devices in the cadmium or zinc coating passivation bath, the bath solution is cleaned of polluting ions Cd²⁺ and Zn²⁺ and enriched with chromates.

3 Results and Discussion

As a result of the conducted experimental studies, the amounts of cathode-formed metals per unit of time were also found experimentally. The obtained results are shown in Table 2.

Thus, with the help of the operation of these membrane electrochemical devices, at a maximum current density of 2.77 A/dm², 0.74 g/h of cadmium and 0.27 g/h of zinc are formed on the cathodes.

Table 2 – Dynamics of the cathodic release of metal Cd and Zn in the membrane electrolysis process in passivation baths

| No. | Electrolysis time, h | Cadmium release, g | | Zinc release, g | |
|-----|----------------------|-----------------------------|--------------------------|-----------------------------|--------------------------|
| | | <i>m</i> _{general} | <i>m</i> _{hour} | <i>m</i> _{general} | <i>m</i> _{hour} |
| 1 | 7.5 | 5.5461 | 0.7395 | 2.0754 | 0.2767 |
| 2 | 16.5 | 12.3523 | 0.7486 | 4.4927 | 0.2723 |
| 3 | 8.0 | 5.9621 | 0.7453 | 2.2079 | 0.2760 |
| 4 | 16.0 | 11.6894 | 0.7306 | 4.4123 | 0.2758 |
| 5 | 8.0 | 5.8936 | 0.7367 | 2.1823 | 0.2728 |
| 6 | 16.0 | 11.2578 | 0.7036 | 4.3568 | 0.2723 |
| 7 | 7.0 | 5.4676 | 0.7811 | 1.9482 | 0.2783 |
| 8 | 17.0 | 12.2339 | 0.7196 | 4.4937 | 0.2643 |
| 9 | 8.5 | 6.2825 | 0.7391 | 2.3354 | 0.2748 |
| 10 | 15.5 | 11.4176 | 0.7366 | 4.2568 | 0.2746 |
| 11 | 8.0 | 5.9482 | 0.7435 | 2.2243 | 0.2780 |
| 12 | 16.0 | 11.5893 | 0.7243 | 4.3612 | 0.2726 |
| 13 | 7.5 | 5.5424 | 0.7390 | 2.0747 | 0.2766 |
| 14 | 16.5 | 11.9651 | 0.7252 | 4.3674 | 0.2647 |
| 15 | 8.0 | 5.8264 | 0.7284 | 2.1758 | 0.2720 |
| 16 | 15.5 | 11.3739 | 0.7338 | 4.2165 | 0.2720 |
| 17 | 7.0 | 5.2376 | 0.7482 | 1.9548 | 0.2793 |
| 18 | 16.5 | 12.0742 | 0.7318 | 4.5337 | 0.2748 |
| 19 | 8.5 | 6.2488 | 0.7351 | 2.3285 | 0.2739 |
| 20 | 15.5 | 11.5686 | 0.7464 | 4.2374 | 0.2734 |
| Σ | – | 175.4774 | – | 65.2358 | – |
| μ | – | – | 0.7373 | – | 0.2741 |

Therefore, during the operation day of these membrane electrochemical devices, Cd²⁺ and Zn²⁺ ions are extracted from the passivation baths into the cathode chamber and deposited on the cathode in the form of simple metal

substances masses that are about 17.70 g and 6.58 g, respectively.

Analyzing the data in Table 1, it is obviously that the chromate anions concentration increases during the operation day of the membrane device due to the anodic reaction 6 by 0.60–1.59 g/l. At the same time, the total mass of chromate anions recovered at the anodes ranges from 90.0 g to 238.5 g per day. And the content of total chromium gradually decreases by 0.30–1.18 g/l, which is 0.6 g/l on average. The changing dynamics of the increase in the chromates concentration and the unstable decrease in the concentration of total chromium were reasoned by the uneven removal of the electrolyte from the surface of the parts immersed for processing.

Before the industrial membrane electrochemical devices introduction in the passivation baths of cadmium and zinc galvanic coatings in the electroplating section of workshop No. 3 of JSC “Nasosenergomash” (Sumy, Ukraine), the baths lost their functions 1–2 times a month.

It was necessary to periodically restore the functionality of passivating baths by adjusting their composition - by adding reagents to 1/3. Thanks to such actions, 5 kg of sodium dichromate and 0.3 kg of sulfuric acid were added to the baths. If the addition of new portions of reagents did not restore the functions of the bath, then the contents of the baths were partially or fully poured into the neutralization station, and new solutions had prepared accordingly. The solutions replacement by ½ part or the total replacement took place 1–2 times a year.

After the industrial membrane electrochemical devices' commissioning, the passivation baths of galvanic coatings began to work stably and efficiently, and there was no deterioration of their functions. As a result of the constant anodic renewal of chromate anions (reaction 6), the need to frequently add new sodium dichromate and sulfuric acid portions disappeared. Thus, the need to add new reagents portions arose only after six months of these electrochemical devices operations due to a decrease in the hexavalent chromium ions concentration to 20–25 g/l as a result of removal from the surface of the parts to the washing baths and the neutralization station. Thus, owing to the operation of industrial membrane electrochemical devices, the chromates load to the neutralization station was reduced by six times. Before these membrane electrochemical devices use, the need for sodium dichromate was at least 5 kg/month for each passivation bath, and as a result of their working, it was 0.833 kg/month.

The technological solution ecological hazard (EH) is the ratio of the pollutant concentration in the solution (C0) to the maximum permissible concentration (MPC) [10]. Thus, before working industrial membrane electrochemical devices in cadmium and zinc passivation baths, the Cr⁺⁶ ions concentration fluctuated between 100–200 g/l, which averaged about 150 g/l. As a result of the

operation of these electrochemical devices, the Cr⁺⁶ ions working concentration decreased to 30–50 g/l, which is also an average of about 40 g/l.

According to the order of the Ministry of Regional Development, Construction and Housing and Communal Services of Ukraine dated 01.12.2017 No. 316, Appendix 5 to the rules for accepting wastewater into centralized drainage systems MPC (Cr⁺⁶ ions) = 0.1 g/m³, in accordance:

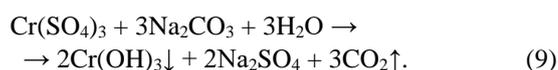
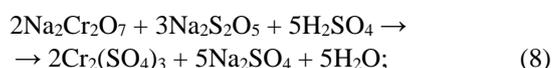
$$\begin{aligned} EH &= C^0/MPC; & (7) \\ EH_{\text{before}} &= (150\text{g/l})/(0,1\text{g/l}) = 1500; \\ EH_{\text{after}} &= (40\text{g/l})/(0,1\text{g/l}) = 400. \end{aligned}$$

In this way, the environmental hazard of technological passivation solutions of cadmium and zinc galvanic coatings decreased by an average of 3.75 times.

The difference in the use of sodium dichromate before the electrochemical membrane devices operation and when they are exploited in one bath is:

$$\Delta m(\text{Na}_2\text{Cr}_2\text{O}_7) = 5\text{kg/month} - 0,833\text{kg/month} = 4,167\text{kg/month};$$

This difference shows the effectiveness of the use of reagents for technological purposes and the costs for the neutralization of wastewater. Thus, in the electroplating section of workshop No. 3 of JSC “Nasosenergomash” (Sumy, Ukraine), a reagent wastewater treatment method of electroplating production is used. Neutralization takes place in two stages. In the first stage, sodium metabisulfite is the application, and in the second stage - sodium carbonate:



After carrying out calculations according to reaction equation 8, it had defined that for the transformation of sodium dichromate weighing 4.167 kg into Cr³⁺ ions, it is necessary to spend theoretically sodium pyrosulfite Na₂S₂O₅ weighing 4.533 kg and sulfuric acid weighing 3.897 kg. To transform the received Cr₂(SO₄)₃ weighing 6.235 kg into insoluble chromium(III) hydroxide (reaction 9), it is necessary to spend theoretically 5.058 kg of soda ash.

According to data for January 2021, the prices (P), excluding VAT, for the listed substances were, in UAH/kg: P(Na₂Cr₂O₇) = 120.00, P(Na₂S₂O₅) = 24.75, P(H₂SO₄) = 35.18, and P(Na₂CO₃) = 11.67.

The total cost of reagents C_{reag.}, participating in the reactions, is found by the ratio:

$$\begin{aligned} C_{\text{reag.}} &= (P(\text{Na}_2\text{Cr}_2\text{O}_7) \cdot m(\text{Na}_2\text{Cr}_2\text{O}_7) + \\ &P(\text{Na}_2\text{S}_2\text{O}_5) \cdot m(\text{Na}_2\text{S}_2\text{O}_5) + \\ &+ P(\text{H}_2\text{SO}_4) \cdot m(\text{H}_2\text{SO}_4) + \\ &+ P(\text{Na}_2\text{CO}_3) \cdot m(\text{Na}_2\text{CO}_3)) \cdot 1.2, \end{aligned} \quad (10)$$

where 1.2 is the coefficient for taking into account 20 % VAT, then $C_{\text{reag}} = 970$ UAH.

As calculated above, as a result of using an industrial membrane electrochemical device in one technological passivation bath per month, the savings on unspent reagents working in this bath and their neutralization is theoretically 970 UAH.

During the operation of the membrane electrochemical device, electricity had consumed. The direct current source used for membrane electrolysis had powered by alternating current from a 220V power grid. The AC power used to power this DC source was measured with a DT-399B clamp-on multimeter. The alternating current power was 1.3 A, so the power consumption according to ratio 11 is equal to:

$$\begin{aligned} P_{\text{cons.}} &= I \cdot U; \\ P_{\text{cons.}} &= 1.3 \text{ A} \cdot 220 \text{ V} = 286 \text{ W/h.} \end{aligned} \quad (11)$$

For a day of work and for 30 days, which is conventionally one month, this electrochemical device consumes, respectively, $P_{\text{cons.day}} = 6.864$ kW and $P_{\text{cons.month}} = 205.92$ kW/month.

As of January 2021, the total price of electricity 1 kW for JSC "Nasosenergomash" (Sumy, Ukraine) amounted to Sel. = 2.54 UAH/kW. Thus, the electricity consumption S for the electro-membrane device operation per month was:

$$S = P_{\text{cons.month}} \cdot \text{Sel.} = 523.04 \text{ UAH/month.} \quad (12)$$

The operation efficiency E of an industrial membrane electrochemical device is the difference between the reagents cost C_{reag} , it was saved per month and the electricity cost S for the device operation:

$$E = C_{\text{reag}} - S = 446.95 \text{ UAH/month.} \quad (13)$$

But the efficiency of this device is not fully calculated. For its calculation, the polluting substances tax for the discharge had not been considered. According to Article 249.5 of the Ukraine Tax Code: the tax amount paid for discharges of polluting substances into water bodies (Ps) is calculated by the payers independently every quarter based on the actual discharges volumes, tax rates, and adjustment factors according to the formula:

$$\Pi_{\text{c}} = \sum (M_i \cdot H_i \cdot K), \quad (14)$$

where M_i is the volume of discharge of that pollutant per year, in tons (t); H_i – tax rates in the current year for a ton of the i -th type of polluting substance, in UAH; K – a multiplier equals to 1.5 and is used in the incident of pollutants discharge into ponds and lakes (in other cases, the coefficient is equal to 1).

Based on equation (14), we calculate the difference in the amount of the monthly tax by which the payments decrease as a result of the operation of a definite membrane electrochemical device $\Delta \Pi_{\text{c}}$:

$$\begin{aligned} \Delta \Pi_{\text{c}}(\text{Cd}) &= \Delta M(\text{Cr}^{+6}) \cdot H(\text{Cr}^{+6}) \cdot K + \\ &+ \Delta M(\text{Cd}^{2+}) \cdot H(\text{Cd}^{2+}) \cdot K; \end{aligned} \quad (15)$$

$$\begin{aligned} \Delta \Pi(\text{Zn}) &= \Delta M(\text{Cr}^{+6}) \cdot H(\text{Cr}^{+6}) \cdot K + \\ &\Delta M(\text{Zn}^{2+}) \cdot H(\text{Zn}^{2+}) \cdot K. \end{aligned} \quad (16)$$

The $\Delta M(\text{Cr}^{+6})$ is the difference in the amount of sodium dichromate used per month before the use of membrane electrochemical devices and, because of their application, as mentioned above, is 4.167 kg or 0.004 tons. The tax rate of $H(\text{Cr}^{+6})$, which includes highly toxic Cr^{+6} ions, for the discharge of 1 ton of substances with a concentration of 0.001–0.100 mg/l is 122,347.23 UAH. Cd^{2+} ions are also highly toxic, so $H(\text{Cd}^{2+}) = 122347.23$ UAH. The $H(\text{Zn}^{2+})$ tax rate is 21,092.69 UAH/t for dumping 1 t of substances with a concentration of 0.1–1.0 mg/l.

The differences in the discharges volumes $\Delta M(\text{Cd}^{2+})$ and $\Delta M(\text{Zn}^{2+})$ are the masses of cadmium and zinc released on the cathodes of the cathode chambers during one month of its operation.

In January 2021, the masses of cadmium and zinc released on the cathodes in the cathode chambers of these electrochemical devices were 457.8 g and 178.1 g, respectively. The K_{oc} coefficient is equal to 1 since harmful substances are not discharged into ponds and lakes. Therefore, $\Delta \Pi(\text{Cd}) = 565.83$ UAH, and $\Delta \Pi(\text{Zn}) = 513.58$ UAH.

Thus, the average monthly tax on polluting substances due to the saving of sodium dichromate and cathodic deposition of metals is decreasing by the amounts calculated above. Therefore, the work total performance E_{sum} of industrial membrane electrochemical devices in passivation baths of cadmium and zinc galvanic coatings, respectively, are:

$$E_{\text{sum}} = E + \Delta \Pi_{\text{c}}. \quad (17)$$

Therefore, $E_{\text{sum}}(\text{Cd}) = 1012.78$ UAH, and $E_{\text{sum}}(\text{Zn}) = 960.53$ UAH.

As well known, passivation reactions of cadmium or zinc galvanic coatings occur directly on the coating surface. Therefore, it is advisable to calculate the membrane electrochemical devices' performance per unit surface area of the corresponding galvanic coating, i.e., 1m². Thus, according to the work data of 2019 and 2020, the total area of S_{gen} parts covered with cadmium and zinc in the electroplating section of workshop No. 3 of JSC "Nasosenergomash" (Sumy, Ukraine) is 1287.74 m² and 604.35 m², respectively. We use these data to find the average monthly areas of parts covered with cadmium and zinc S_{month} :

$$S_{\text{month.Me}} = S_{\text{gen.Me}}/24; \quad (18)$$

So, $S_{\text{month.Cd}} = 53.66$ m², and $S_{\text{month.Zn}} = 25.18$ m².

Knowing the total effectiveness of industrial membrane electrochemical devices E_{sum} , and the general area of cadmium- and zinc-coated parts during one month S_{month} , we find the benefit E_s of these devices per 1 m² of the corresponding galvanic coating:

$$E_s = E_{\text{sum}}/S_{\text{month}} \quad (19)$$

So, $E_s, \text{Cd} = 18.74 \text{ UAH/m}^2$; $E_s, \text{Zn} = 38.15 \text{ UAH/m}^2$.

Therefore, the above practical calculations show that the working membrane electrochemical devices in galvanic coatings passivation baths is economically beneficial. So, it is understandable that the efficiency of these industrial electrochemical devices is within 1000 UAH/month. And it should be noted that owing to the use of industrial membrane electrochemical devices, the price of cadmium and zinc galvanic coatings is decreasing by 18.74 UAH/m^2 and 38.15 UAH/m^2 , respectively.

4 Conclusions

As a result of the conducted experimental studies, it had established. Firstly, the effectiveness of the anodic regeneration process of hexavalent chromium ions in passivation baths under realistic production conditions is established. Secondly, a decrease in the working concentrations of chromate anions in the passivation baths was ascertained owing to the constant cleaning of the solution from polluting metal cations and the permanent anodic synthesis of hexavalent chromium ions.

Also, calculations of the ecological and economic efficiency of industrial electrochemical modules had done because of their operation for six months.

A significant reduction in the environmental hazard of passivation solutions had established as a result of a reduction in the working concentrations of chromates into them from 100–200 g/l to 30–50 g/l.

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