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METHOD OF OBTAINING OF METAL OXIDE ANODES THAT DO NOT CONTAIN NOBLE METALS

Volodymyr H. Mykhailenko
port342017@gmail.com
ORCID: 0000-0003-3082-6148

Oleksii V. Antonov
ORCID: 0000-0001-6319-535X

Olha I. Lukianova
ORCID: 0000-0001-7235-7293

Yevhen F. Lukianov
ORCID: 0000-0001-8839-091X

Oleksandr Ye. Khinievich
ORCID: 0000-0003-1902-534X

Tamara S. Vitkovska
ORCID: 0000-0001-6890-0441

A. Pidhornyi Institute
of Mechanical Engineering
Problems of NASU,
2/10, Pozharskyi str., Kharkiv,
61046, Ukraine

In the mining and industrial regions of Ukraine, a large amount of mine and quarry waters is formed. Due to high mineralization, they cannot be discharged into natural hydrographic objects without deep processing, including demineralization. Most of such waters are significantly contaminated with concentrates of sulfides and dissolved iron compounds, which hinder their further purification. At the same time, thermal power plants located in these regions consume a significant amount of scarce drinking water for their needs. Deep processing of mine and quarry waters allows to clean them and obtain feed water for heating systems, boilers of TPPs and CHPs. A method of obtaining stable inert titanium-based anodes with an active coating of PbO_2*, which do not contain noble metals and their compounds, has been developed. The method consists in protecting titanium from passivation with an oxide film by thermally applying a* MnO_2 *coating, and later applying to the base with this coating a thin layer of* PbO_2 *from an alkaline complex electrolyte containing 2.5* mol/dm^3 *NaOH, 0.6* mol/dm^3 *EDTA, ethylene glycol additive and is a saturated PbO. The main 3–5 mm thick layer of coating is applied from the nitrate electrolyte, which includes* $Pb(NO_3)_2$ *1* mol/dm^3*,* $Cu(NO_3)_2$ *0.4* mol/dm^3*,* $Al(NO_3)_3$ *0.2* mol/dm^3 *and the gelatin additive. A method of extending the service life of an alkaline electrolyte by reduction of Pb (IV) compounds during the contact with the active surface of metallic plumbum is described. The conducted resource tests of this anode for 1400 hours proved its stability when processing solutions containing a mixture of sodium sulfate and sodium chloride. On the basis of this anode, the technology of electrochemical deironing of mine waters and removal of sulfides from them before demineralization was developed and experimentally tested. This technology is the only possible method of reagent-free iron removal and removal of sulfides from waters with high mineralization. Such anodes significantly expand the scope of application of electrochemical processes. They can be used not only for water treatment in thermal power generation, but also for the treatment of wastewater of various mineral and organic composition, chemical and technological processes for obtaining oxidants, etc.*

Keywords*: inert anodes,* PbO_2*,* MnO_2*, removal of iron and sulfides, water treatment, purification of mine and quarry waters.*

Introduction

In the mining regions of Ukraine, there is a large amount of highly mineralized mine and quarry waters, which cannot be discharged into surface waters without deep purification. At the same time, almost all such regions in Ukraine are water-deficient, that is, a significant amount of scarce drinking water is used for the needs of the thermal power industry. As a result of deep purification of such waters, high-quality water for thermal power generation can be obtained, and mineral salts are separated in the form of accompanying commercial products.

Unfortunately, a significant part of these highly mineralized waters, in addition to mineral salts, is also contaminated with soluble compounds of iron and sulfides, which are formed as a result of sulfate reduction and redox processes during a long stay of water in anaerobic conditions in contact with soils containing insoluble compounds of iron and organic substances [1]. For example, in the brines of the Dombrovsky quarry (Kalush mining area), the concentration of iron and sulfides exceeds 15 mg/dm^2 for each component, and in the water of the "Rodina" mine (Kryvorizkyi Iron Ore Basin) iron concentration exceeds 30 mg/dm^3. The presence of soluble compounds of iron and sulfides significantly complicates the deep processing of mine and quarry

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waters because it contributes to the formation of stony scale, which can be removed from the devices only mechanically, on the equipment surfaces.

The most attractive method of removing such harmful impurities is electrolysis with an insoluble anode. In this process, active oxidants (chlorine and peroxide compounds), which oxidize sulfides to sulfates, and iron - from a divalent to a trivalent state, are formed at the anode. In turn, trivalent iron hydroxide does not dissolve at neutral pH of water, it precipitates and can be separated from the liquid mechanically (by filtration, sedimentation or pressure flotation). Unfortunately, anode materials commonly used in electrochemistry are either too expensive (platinum, iridium, platinum-plated or iridized titanium) or unstable (graphite, titanium covered with a thin layer of oxide ruthenium) in solutions containing a mixture of chlorides and sulfates in significant concentrations (more than 5 g/dm^3 of each component). Thus, there is a need for research and development of a method of obtaining a relatively cheap low-wear anode that would not contain noble metals and their compounds.

Known anodes are made of manganese dioxide (MnO_2) applied on a titanium base by thermal decomposition of manganese nitrate or carbonate [2–6]. To improve the adhesion of the oxide coating to the titanium base, the latter is preliminarily embossed with mechanical processing [6]. However, during the electrolysis of a sulfate-chloride solution (these are the main impurities in mineralized mine and quarry waters), MnO_2 is gradually destroyed [5], and over time, overactive atomic oxygen diffuses through the loose film of MnO_2 to the surface of the titanium base. As a result, a semiconducting film of titanium oxide is formed, the transition resistance and, accordingly, the voltage on the anode increases, and, ultimately, the anode is passivated. To prevent this phenomenon, before applying the MnO_2 coating, the base is covered with a thin layer of platinum or iridium or their oxides [5], or ruthenium oxide [4].

Another oxide material that is used for the production of low-wear anodes is plumbum (lead) (IV) dioxide (PbO_2). It is also applied to a base made of valve metal (titanium), but when applied directly to titanium, the latter quickly oxidizes from the surface to TiO_2, while rapid passivation of the anode also occurs. To slow down this phenomenon, the titanium surface is pre-coated with a thin layer of platinum, iridium or their oxides [7–9].

Titanium-based plumbum dioxide anodes are sufficiently stable in the conversion of Cr (III) compounds to Cr (VI) ones [8], oxidation of harmful organic substances in wastewater [9], membrane separation of antibiotics [10], ozone production [11–13] and other processes that require inert anodes. The physico-chemical properties of such coatings confirm their high electrochemical stability [14]. However, the use of noble metals or their compounds in the production of these electrodes makes them too expensive for wide implementation, in particular, in the processes of purification of large volumes of wastewater.

The purpose of this research is to develop an anode based on titanium coated with PbO_2, while avoiding the use of noble metals or their compounds.

The idea behind the research was the use of a thin sublayer of MnO_2 previously applied to titanium, the purpose of which is to create a transition layer of titanium and manganese mixed oxides on titanium, to protect titanium from direct contact with the active oxidant PbO_2 and, due to this, to avoid the anode passivation. The purpose of a thick layer of the main coating with PbO_2 is to prevent the growth of the potential of the titanium surface before the formation of the passivating layer TiO_2.

Materials and methods

The main method of obtaining the PbO_2 main coating layer was electrodeposition from various electrolytes. The sublayer of manganese oxide was obtained by thermal decomposition of manganese nitrate on the surface of a previously prepared titanium sheet at a temperature of 400 ºC. The manganese nitrate solution was prepared by dissolving manganese carbonate in concentrated nitric acid.

The study of the anode service life was carried out in laboratory conditions on a 24-hour test plant with online control (Fig. 1).

To determine the composition of electrolytes and its changes, standard methods of chemical analysis were used. The concentration of tetravalent plumbum (Pb (IV)) in the alkaline complex electrolyte was measured using the author's methodology described in [15].

Fig. 1. Plant for resource tests of anodes

Experimental part

In order to achieve the goal of the research – obtaining a plumbum dioxide anode that would not contain noble metals and their compounds – it was necessary to determine the conditions under which PbO_2 is electrochemically deposited on thermal MnO_2.

To obtain the PbO_2 coating, a following nitrate electrolyte composition was used: $Pb(NO_3)_2$ – 1 mol/dm^3; $Cu(NO_3)_2$ – 0.4 mol/dm^3; $Al(NO_3)_3$ – 0.2 mol/dm^3; gelatin – 1 g/dm^3, as a solution from which electrodeposition of PbO_2 occurs most easily. The pH of such solution is 1–2, and the temperature of the process is 60 ºC. When trying to deposit PbO_2 on a titanium plate that was previously thermally covered with MnO_2, instead of electrodeposition, gaseous oxygen is released intensively even at a current density of 600 A/m^2. The desired process in the electrodeposition of PbO_2 from a nitrate electrolyte is the reaction (1)

$$Pb^{2+}+H_2O–2e^-=PbO_2+H^+. \tag{1}$$

A competing process is the release of oxygen according to the reaction (2)

$$2H_2O–4e^-=O_2+4H^+. \tag{2}$$

The equilibrium potential of reaction (1), calculated by the Nernst formula, will be

$$E_0=1.465–0.118pH–0.03lg[Pb^{2+}];$$

$$E_0=1.465–0.118\cdot 1.5–0.031\cdot lg(1)=1.288.$$

The equilibrium potential of reaction (2) will be equal to

$$E_0=1.23–0.118pH;$$

$$E_0=1.23–0.118\cdot 1.5=1.053.$$

Thus, there is a significant difference of 0.235 V between the potentials of reactions (1) and (2), and accordingly, PbO_2 during the anodic process can be released together with oxygen only under the condition of high overvoltage of the latter process.

Therefore, it is impossible to deposit a PbO_2 coating from a nitrate electrolyte directly on a MnO_2 base, even at the indicated current densities, since manganese dioxide has a very small overvoltage in the process of anodic oxygen release.

In addition to nitrate, alkaline electrolytes for electrodeposition of PbO_2 (plumbitic and complex with sodium EDTA-sodium salt) are also widely known [16].

To carry out the process of precipitation of PbO_2, the following electrolyte composition was chosen: NaOH – 2.4 mol/dm^3; PbO – 0.6 mol/dm^3; EDTA-disodium salt – 0.6 mol/dm^3; ethylene glycol – 6 g/dm^3. The current density was 100 A/m^2, and the process temperature was 60 ° C.

PbO_2 is released from this solution by reaction

$$HPbO_2^-=PbO_2+H^++2e. \tag{3}$$

The equilibrium potential of this reaction is determined by the equation

$$E_0=0.621–0.0293\ pH.$$

At the pH of the selected electrolyte, which consisted

$$pH=14–lg(f\cdot C_{OH^-})=14–lg(0.735\cdot 2.4)=13.75,$$

the equilibrium potential of equation 3 is 0.22 V.

A competing anodic process during the precipitation of PbO_2 can be the release of oxygen according to the equation

$$2H_2O=O_2+4H^++4e; \tag{4}$$

$$E_0=1.228–0.0591\ pH.$$

At an electrolyte pH of 13.75, the equilibrium potential of oxygen release will be 0.41 V.

Thus, PbO_2 is released from the alkaline electrolyte at a potential that is 0.19 V lower than the potential of oxygen release. Therefore, at low current densities recommended in [16], it is possible to obtain a coating of plumbum dioxide on the MnO_2 sublayer.

A titanium laboratory sample with an active area of 1 cm^2 was coated with MnO_2 by thermal decomposition of manganese nitrate. After that, this sample was coated with a layer of PbO_2 by electrodeposition from the alkaline complex electrolyte described above at a current density of 100 A/dm^2 for 12 hours. The solution was supplemented with technical PbO. The thickness of the PbO_2 coating was 0.5 mm. During the electrodeposition, oxygen was not released at the anode.

At the same time, it was established that the electrolyte is kinetically unstable during electrodeposition. When a relatively small quantity of electricity (4–6 A·h/dm^3) flows through it, the solution acquires a pinkish-orange color, and brick-red sediments begin to deposit from it on the electrodes and the bath surface. Deposition of these sediments on the anode and their subsequent inclusion in the coating plumbums to its destruction and exfoliation. Filtration of the electrolyte gives only a partial effect, since the formation of bottom sediments in the filtered solution begins after the flow of 0.5–1 A·h/dm^3, that is, actually right after the start of electrolysis. Therefore, it was necessary to study this phenomenon and find ways to fight it.

It is assumed that bottom sediments are formed as a result of the gradual accumulation of compounds of Pb (IV) $HPbO_3^-$ in the electrolyte during electrolysis. After reaching a saturated concentration of plumbate anions, the formation of bottom sediments begins according to the reactions

$$2HPbO_2^- + HPbO_3^- = Pb_3O_4\downarrow + 3OH^-; \quad HPbO_2^- + HPbO_3^- = Pb_2O_3\downarrow + 2OH^-.$$

To establish the saturated concentration of plumbates in the alkaline electrolyte, the following studies were conducted. A solution with a saturated concentration of Pb (IV) compounds was obtained. To do this, the complex electrolyte was kept in thermostatic conditions for one hour with continuous stirring in contact with Pro Analysi (p.a.) brand of Pb_3O_4. Every 10 minutes, a sample of the solution was taken, which was later analyzed for the presence of Pb (IV) compounds. The results given in Fig. 2 show that the saturated concentration of plumbates in the solution is established in less than an hour and at a temperature of 60 ºC and is equal to (75±5)×10^{-5} mol/dm^3 (solubility of plumbates in water is about 10^{-16} mol/dm^3).

So, it was established that PbO_2 is not completely deposited on the anode. A small part of Pb (IV) dissolves in the electrolyte and, after accumulating to a saturated concentration, begins to settle on the surfaces of the equipment in the form of brick-red bottom deposits.

As established by E. Dzhafarov [16], the formation of bottom sediments begins after the flow of 5–6 A·h/dm^3 of electricity. At the same time, in our previous experiments, it started already after passing through the solution of 1.5–2 A·h/dm^3 of electricity. After a detailed analysis of our actions, it became clear that, unlike E. Dzhafarov, who prepared the solution and fed it with the help of freshly obtained plumbum (II) hydroxide ($Pb(OH)_2$), we used commercial PbO of the Pro Analysi (p.a.) brand as a plumbum-containing substance, which had been stored in the research laboratory since 1995. The analysis showed that this reagent contains (1.313±0.003)×10^{-3} mol/kg of Pb (IV) compounds. The reason for the appearance of traces of Pb (IV) in PbO has been clarified.

PbO that is freshly tempered at a temperature of 600 ºC, as analytical measurements show, contains Pb (IV) compounds in a concentration at the method limit of sensitivity (0.005±0.003×10^{-3} mol/kg). However, mechanical processing (grinding in a mortar) activates the oxidation process of PbO (Fig. 3).

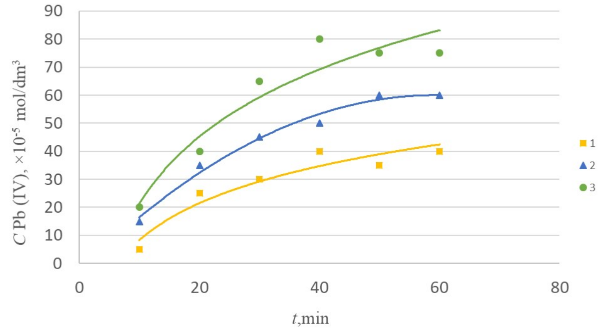

Fig. 2. Kinetics of dissolution of plumbates in an alkaline complex electrolyte at different temperatures:
1 – 20 ºC; 2 – 40 º C; 3 – 60 º C

Fig. 3. Mechanical activation of PbO oxidation

a b

Fig. 4. Freshly tempered (b) and grinded for 10 minutes (a) PbO

Fig. 4 shows a comparison of PbO that is freshly tempered and grinded for 2 minutes.

The kinetics of increasing the concentration of Pb (IV) in PbO during mechanical processing of the latter was studied. It was established that the oxidation of PbO occurs up to a certain limit (Fig. 5). This can be explained by the easy oxidation of the surface of PbO crystals and the difficulty of further oxidation of the deep layers of the oxide.

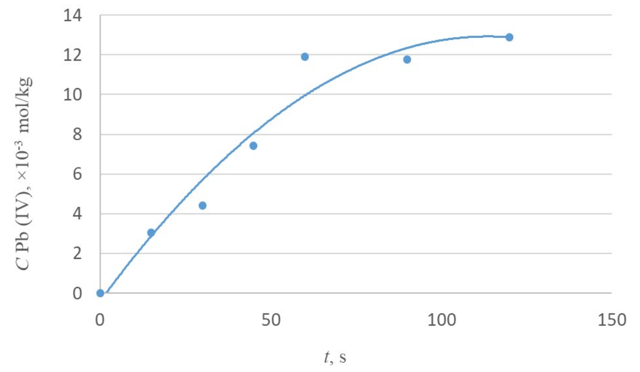

Fig. 5. Kinetics of accumulation of Pb (IV) during mechanical processing of PbO

Thus, it has been proven that during transportation, packaging and storage of PbO, compounds of Pb (IV) accumulate in it every time the powder is poured. Analytical measurements show that, for example, the reagent PbO of the Pro Analysi (p.a.) brand, which was stored in the chemical laboratory of the Institute of Mechanical Engineering Problems of the National Academy of Sciences of Ukraine, contained 1.4×10^{-3} mol/kg. Reactive PbO in the laboratory of the Department of Electrochemistry of NTU "KhPI" (Pro Analysi (p.a.)) – 1.38×10^{-3} mol/kg Pb (IV), and technical plumbum for the production of paints – 1.8×10^{-3} mol/kg Pb (IV).

The result of the thermodynamic calculation that is shown below confirms the energy efficiency of the oxidation reaction of PbO to oxide of intermediate oxidation state Pb_3O_4 at room temperature.

$$6PbO + O_2 = 2Pb_3O_4; \quad \Delta G(20\ ^\circ C) = -52.12 \text{ кJ/mol.}$$

When dissolving in the electrolyte during its feeding with PbO instead of freshly deposited hydroxide, Pb (IV) compounds significantly accelerate the onset and increase the rate of formation of bottom deposits during the electrodeposition of PbO_2 from alkaline electrolytes.

During the electrodeposition of PbO_2 in previous experiments, a large amount of metallic plumbum sponge was formed on the cathode. This meant the loss of plumbum in the solution and the need for accelerated feeding of the electrolyte with PbO. Thus, the consumption of the reagent for feeding the electrolyte doubles, and in addition, a large amount of waste is formed – sponge metal plumbum, which is difficult to recycle. To avoid this, separation of the cathode space from the anode space using an anion exchange membrane was used, with the simultaneous filling of the anode chamber with NaOH solution of the appropriate concentration. It was also noticed that the process of bottom sediments formation begins much faster.

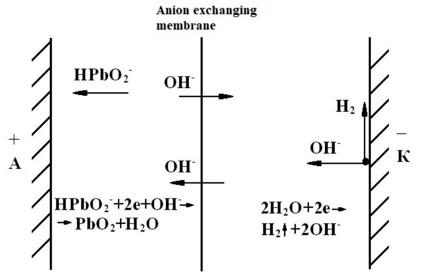

Fig. 6. Scheme of mass transfer processes in a cell with a separated catholyte

The process of accumulation of Pb (IV) compounds during the electrodeposition of PbO_2 was studied. For the purity of the experiment, a buffer cathode chamber, separated from the anolyte by an anion exchange membrane, was formed. This chamber was filled with a 2.5 mol NaOH solution.

Transfer processes in a cell with a separate cathode chamber are schematically shown in Fig. 6.

Freshly precipitated $Pb(OH)_2$, which was guaranteed not to contain Pb (IV) compounds, was used for the preparation and feeding of electrolytes. The current density in all cases was 200 A/m^2, and the anode area was 10^{-3} m^2. The volume of the solution in the cell was 250 cm^3. After each hour of electrolysis, a sample of the electrolyte was taken together with the suspended sediment and analyzed for Pb (IV) content. For comparison, control experiments were carried out without the use of an anion exchange membrane and a buffer cathode chamber.

The results of the study of the Pb (IV) compounds accumulation kinetics in an alkaline complex electrolyte both with the participation of the cathodic reduction process and without it are shown in Fig. 7.

So, as can be seen, the contribution of the cathodic process to the reduction of Pb (IV) compounds is very significant. A saturated concentration of plumbates is reached, and the formation of bottom sediments begins after the passage of 0.45 A·h/dm^3 of electricity during the separation of the cathode. If the cathodic process is involved in the reduction of Pb (IV) compounds, bottom deposits are formed, in full accordance with the data of E. Dzhafarov, after the flow of 5.7–5.8 A·h/dm^3 of electricity.

The process of accumulation in an alkaline complex solution of Pb (IV) compounds when the cathode is separated by a membrane is subject to the dependence (5)

$$m=KQ, \tag{5}$$

where K=1.063×10^{-2} mol/F is the coefficient in the equation for the accumulation of Pb (IV) compounds.

In the course of the experiments, it was noticed that the cathode deposit is formed in the form of large lamellar crystals of the dendritic type with dimensions (1–2)×(1–2) mm. It had a relatively low bulk density (1500–1600 kg/m^3), its crystals were covered with a thin yellowish layer of $Pb(OH)_2$. It is assumed that since the electrolyte is constantly saturated with $Pb(OH)_2$, when plumbate ions are restored on the surface of the cathode, a thin layer of the solution becomes oversaturated with Pb (II) compounds. An excess amount of plumbite precipitates from the solution on the surface of metal plumbum on the cathode in the form of $Pb(OH)_2$, passivating the active surface of the metal. The next experiment, conducted with an electrolyte undersaturated with plumbum (the concentration of Pb (II) compounds was 0.5 eq/dm^3) showed (Fig. 8) that the concentration of plumbate increases during electrolysis, but much slower than in a solution saturated with plumbum, and reaches a maximum at the level of 6×10^{-4} mol/dm^3 with a flow of 4 A·h/dm^3. After that, the concentration of Pb (IV) begins to decrease, which can be explained by the reduction of Pb (IV) compounds on the active surface of metallic plumbum. When the cathode space is separated from the main volume of the solution, the nature of the dependence is almost the same as when the electrolyte is saturated with PbO (K=1,069×10^{-2} mol/F).

It is extremely difficult to feed the electrolyte with freshly precipitated $Pb(OH)_2$ in industrial conditions. The real process of production of anodes at the enterprise should provide the electrolyte with PbO for feeding. This will plumbum to additional accumulation of plumbates in the electrolyte. Considering the fact that the concentration of Pb (IV) compounds in the PbO reagent was determined by us, the increase in the concentration of Pb (IV) compounds in the electrolytes was calculated (Fig. 9) according to the assumption of 100% anodic and cathodic current outputs of the processes of PbO_2 and Pb (metallic plumbum on the cathode) electrodeposition.

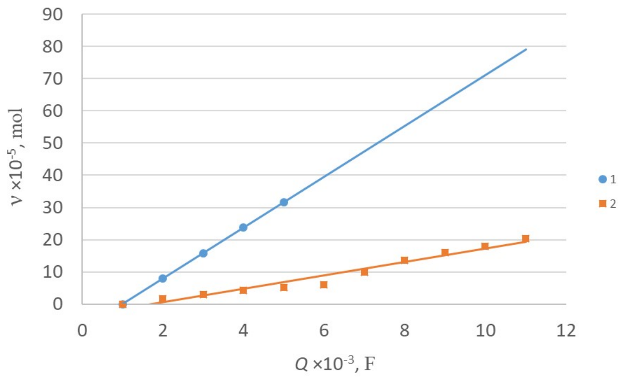

Fig. 7. Kinetics of the Pb (IV) compounds accumulation in an alkaline complex electrolyte, v, mol:
1 – with separation of the cathode space;
2 – without separation of the cathode space

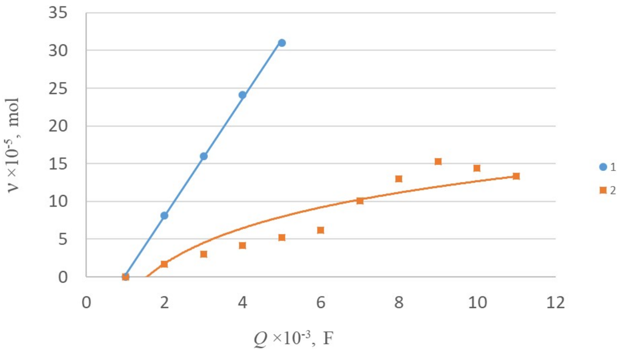

Fig. 8. Kinetics of accumulation of Pb (IV) compounds, v, mol, in a complex electrolyte with a concentration of Pb (II) compounds of 0.5 eq/dm^3:
1 – with separation of the cathode space;
2 – without separation of the cathode space

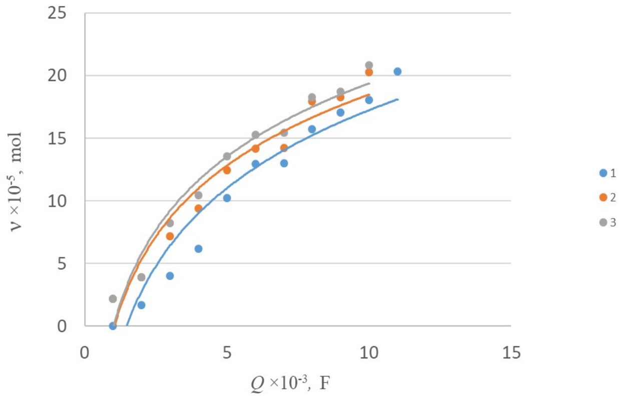

Fig. 9. Kinetics of accumulation of Pb (IV) compounds in a complex electrolyte without separation of the cathode space, v, mol:
1 – preparation and feeding of $Pb(OH)_2$;
2 – preparation on PbO, feeding of $Pb(OH)_2$;
3 – preparation and feeding of PbO

In reality, the increase in the concentration of plumbates due to feeding the solution with commercial PbO will be stepwise in accordance with the loading of successive portions of the reagent into the electrolyte.

For the next calculation of the electrodeposition process of PbO_2, it was necessary to study the effect of feeding the solution with commercial PbO without taking into account the cathodic reduction of plumbate. Such studies were carried out, and their results are shown in Fig. 10.

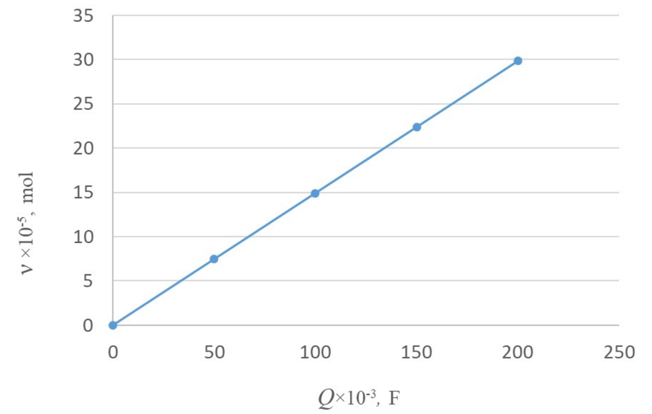

Fig. 10. Kinetics of accumulation of Pb (IV) compounds in a complex electrolyte with separation of the cathode space, v, mol from the electricity quantity Q, F

The dependence of the mass of plumbate formed in the electrolyte on the quantity of electricity that passed through it is in this case subject to the equation

$$m=C_0+KQ, \quad (6)$$

where C_0 is the concentration of plumbates that accumulate in the electrolyte when it is prepared from commercial PbO.

Accordingly, the constant in equation (6) is equal to the complex electrolyte K=1.072×10^{-2} mol/F.

As it can be seen, the use of commercial PbO instead of freshly deposited $Pb(OH)_2$ in the complex electrolyte to feed the solution significantly accelerates the accumulation of Pb (IV) compounds and reaching the solubility limit (75×10^{-5} mol/dm^3), after which the formation of bottom sediments begins.

The operation of the PbO_2 electrodeposition process with continuous maintenance of the concentration of Pb (II) compounds at the level of 0.5 mol/dm^3, as well as at any other level, except for the saturated concentration, is very difficult in industrial conditions. Therefore, it is necessary to spatially separate the processes of anodic deposition of PbO_2 and reduction of dissolved Pb (IV) compounds, and distribute them in different devices.

Feeding of the electrolyte with reactive PbO instead of freshly deposited $Pb(OH)_2$ and the use of a silicate additive to improve the mechanical and technological properties of the cathodic plumbum deposit additionally inhibits the reduction of plumbates at the cathode. Based on this, it is proposed to restore plumbate in the electrolyte by immersion in a solution of metallic plumbum.

To calculate the entire process of electrodeposition, it was necessary to study the kinetics of the reduction of Pb (IV) compounds on metallic plumbum.

Further experiments to study the kinetics of reduction of Pb (IV) compounds on the surface of metallic plumbum were carried out on a special plant. 250 cm^3 of the studied solution was poured into a glass beaker with a capacity of 0.3 dm^3, and under thermostatic conditions (60 ºC) it was brought to a state saturated with Pb (IV) compounds. The concentration of Pb (IV) compounds in the solution was measured. After that, the solution was separated from the Pb_3O_4 precipitate. Pre-prepared plates cut from metallic plumbum foil with a total area of 30 cm^2 were immersed in the solution. Preparation consisted of mechanical cleaning from the oxide layer, degreasing with gasoline, drying, etching in 1% nitric acid solution for 3 minutes and thorough rinsing with water. After every hour of the experiment, a sample of 25 cm^3 was taken and the concentration of Pb (IV) compounds was measured. The selected 25 cm^3 samples were compensated with the same amount of the mixture of the input solution and the solution saturated with plumbates in order not to change the concentration of plumbates in the reaction volume.

It is assumed that the reduction of Pb (IV) on the surface of metallic plumbum is a classical heterogeneous process that is subject to the equation (7)

$$\frac{dm}{d\tau}=-KSC\,, \quad (7)$$

where m is the Pb (IV) mass, mol; C is the Pb (IV) concentration, mol/m^3; τ is the time since the start of the process, hours; K is the reduction process rate constant, m/h; S is the surface of metallic plumbum, m^2; V is the solution volume, m^3.

$$\frac{VdC}{d\tau} = -K'SC\,; \tag{8}$$

$$\frac{dC}{d\tau} = -K'\frac{S}{V}C\,. \tag{9}$$

Equation (9) is amenable to the distribution of variables and analytical solution

$$\frac{dC}{C} = -K'\frac{S}{V}d\tau\,; \tag{10}$$

$$\ln\frac{C}{C_0} = -K'\frac{S}{V}\tau\,; \tag{11}$$

$$C = C_0 e^{-K'\frac{S}{V}\tau}, \tag{12}$$

where C_0 is the initial concentration of plumbates, mol/m^3.

The results of three parallel experiments on the kinetics of reduction of Pb (IV) compounds are shown in Fig. 11.

According to the experimental data obtained by us, the rate constant of the plumbate reduction reaction in the complex electrolyte for the electrodeposition of PbO_2 was calculated. According to equation 3.7, this constant K' is equal to 0.9673×10^{-2} m/h.

The constants determination in the processes of accumulation and reduction of plumbates made it possible to calculate the required ratio of the surfaces of the anode and metallic plumbum immersed in the solution for the reduction of plumbates. According to equation (5)

$$m = KQ\,.$$

Let's transform this equation into a differential form

$$\frac{dm}{dQ} = K\,; \tag{13}$$

$$\frac{dm}{iS_A d\tau} = K\,; \tag{14}$$

$$\frac{dm}{d\tau} = KiS_A\,, \tag{15}$$

where i is the anodic current density, A/m^2, to obtain an unstressed deposit it is 200 A/m^2; S_A is the anode surface area, m^2.

At the same time according to equation (7)

$$\frac{dm}{d\tau} = -K'S_{Pb}C\,,$$

where S_{Pb} is the surface area of metallic plumbum immersed in the solution, m^2; C is the plumbate concentration, mol/m^3.

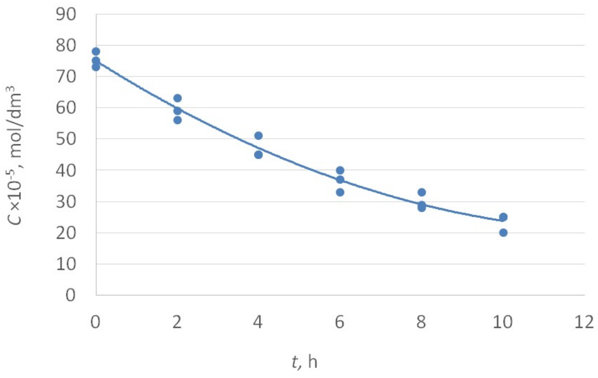

Fig. 11. Kinetics of the reduction of Pb (IV) compounds in a complex electrolyte on the active surface of metallic plumbum

Equating the rates of plumbate formation and reduction, the following equation is obtained

$$KiS_A = K'S_{Pb}C\,. \tag{16}$$

From this we derive the criterion of stability of the solution

$$\frac{S_{Pb}}{S_A} = \frac{Ki}{K'C}\,. \tag{17}$$

For a complex electrolyte when fed with freshly deposited $Pb(OH)_2$ and commercial PbO, taking into account the need to maintain the concentration of plumbate in the solution equal to half of the saturated (37×10^{-5} mol/dm^3), the ratio of the metallic plumbum and anode areas is 5.94 and 5.99, respectively, including the surface of the cathode deposit.

Thus, we have developed a method of preventing the formation of bottom deposits during the electrodeposition of PbO_2 from alkaline electrolytes, which consists in immersing metallic plumbum in the electrolyte, on the surface of which plumbates are reduced to plumbites, which then participate in the electrodeposition process PbO_2.

Results and their discussion

The developed method of reduction of Pb (IV) compounds accumulated in the complex electrolyte for electrodeposition of PbO_2 made it possible to significantly extend its service life and, thus, eliminate the main drawback of this technology. However, other disadvantages of alkaline electrolytes remained unchanged – a relatively low current density (100–200 A/m^2), which significantly increases the duration of the process of obtaining thick coating layers, as well as the gradual carbonation of free alkali CO_2 from the air, which, with the accumulation of sodium carbonate, makes further use of the solution impossible. Thus, to obtain a thick coating of PbO_2, it was deposited from a nitrate electrolyte on a pre-deposited layer of a thin coating from an alkaline complex electrolyte. The deposition of the main layer of PbO_2 took place at high current densities (500–1000 A/m^2). A laboratory sample of the anode (Fig. 12), which was subjected to resource tests on the plant shown in Fig. 1, was obtained.

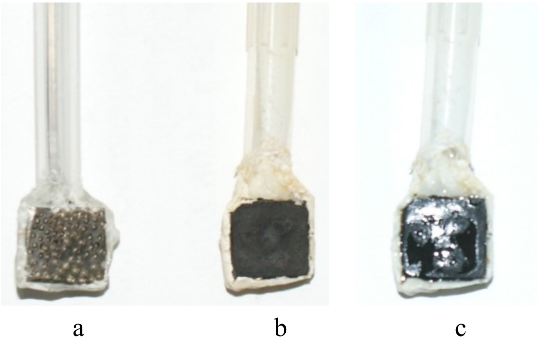

Fig. 12. Samples of anodes:
a – titanium base for anode obtaining;
b – the same base with a manganese dioxide protective sublayer;
c – finished anode with PbO_2 coating, which has a metallic luster

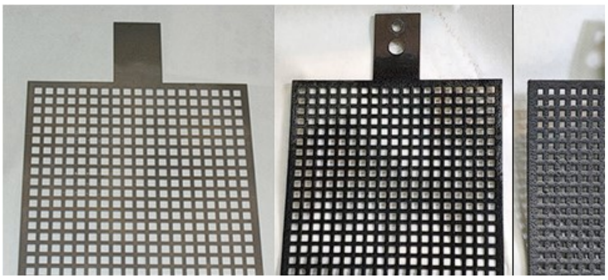

Fig. 13. Titanium base for plant anode (a), MnO_2 sublayer (b) and finished anode with 3 mm PbO_2 coating (c)

The indicated anode was tested at a current density of 2000 A/m^2, which is 20 times higher than the working current densities for the electrochemical water treatment process, for 1450 hours in a mixed solution of sodium sulfate and chloride with a concentration of 1 eq/dm^3, respectively. The destruction of the anode surface and the growth of the anode potential were not noted.

After ascertaining the anodic resistance, anodes for a plant electrolyzer with the size of the working part of 180×180 mm were obtained (Fig. 13).

The process of de-ironing and neutralization of sulfides in highly mineralized mine water was tested during the processing of an experimental batch of water from the "Rodina" mine by PJSC "Kryvyi Rih Iron Ore Plant" with a volume of 15 dm^3. The composition of this water is given in Table 1.

Table 1. Water composition of the "Rodina" mine, PJSC "Kryvyi Rih Iron Ore Plant"

Ionic composition, mg/dm^3								Mineralization, g/dm^3
Ca^{2+}	Mg^{2+}	Na^+	Cl^-	SO_4^{2-}	HCO_3^-	Fe_{gen}	S^{2-}	
1392.4	567.3	30004	46661	4562.1	732.9	30.3	17.2	83.92

Such water was subjected to electrochemical treatment in a rectangular stainless bath with a capacity of 16 dm^3. Processing was carried out on one anode with a symmetrical arrangement of two stainless steel cathodes. The distance between the cathodes and the anode was 20 mm, the current density was 300 A/m^2. The redox potential was continuously measured in the solution. Mine water was intensively mixed with a propeller stirrer. In the course of electrolysis, there was a gradual increase in the redox potential. Electrolysis was carried out until the solution potential reached +726 mV.

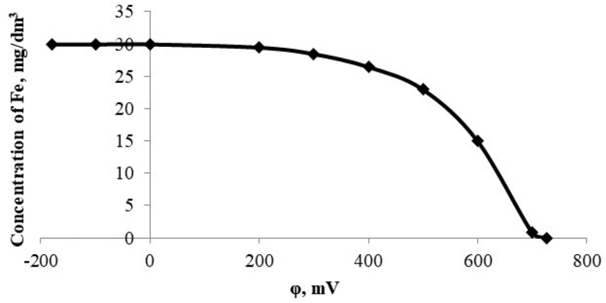

Fig. 14. Changes in the concentration of soluble iron compounds with an increase in the redox potential φ of mine water during electrolysis

The duration of electrolysis was 2.5 hours. The initial redox potential was -200 mV. When reaching rare potential -100; 0; 200; 300; 400; 500; 600; 700; 726 mV, a sample of the solution was taken, filtered through a "blue ribbon" filter and analyzed for the content of Fe2+ ions. The dependence of the concentration of dissolved iron compounds on the redox potential is shown in Fig. 14.

Subsequently, the obtained mine water was subjected to deep processing to obtain 115 g of Na_2SO_4, 1154 g of NaCl, 60 g of calcium-magnesium sludge and 14 l of condensate with an electrical conductivity of 2 µS/cm, suitable after purification for use as feed water for TPP boilers. During the experiment, the destruction of the surface of the active PbO_2 coating was not noted.

Thus, a stable inert anode, which does not contain noble metals and can be used not only in water treatment processes, but also in other electrochemical processes for wastewater treatment, obtaining chlorates, perchlorates and persulfates, as well as in the processes of obtaining galvanic coatings and cleaning galvanic effluents, including at significant concentrations of chromate and nitrate ions under the condition of continuous anodic polarization, was obtained.

Conclusions

A method of obtaining stable inert anodes based on titanium with an active PbO_2 coating that do not contain noble metals and their compounds has been developed. With their use, experimental extraction of iron compounds and sulfides from the water of the "Rodina" mine of PJSC "Kryvyi Rih Iron Ore Plant" was carried out. Deep processing of iron-free water from the mentioned mine was carried out to obtain condensate suitable for the production of feed water for the thermal power industry.

The developed anodes significantly expand the scope of application of electrochemical processes. They can be used for water treatment in thermal power generation, wastewater treatment of various mineral and organic composition, chemical-technological processes for oxidants obtaining, etc.

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Метод отримання металоксидних анодів, що не містять благородних металів

В. Г. Михайленко, О. В. Антонов, О. І. Лук'янова, Є. Ф. Лук'янов, О. Є Хінєвіч, Т. С. Вітковська

Інститут проблем машинобудування ім. А. М. Підгорного НАН України,
61046, Україна, м. Харків, вул. Пожарського, 2/10

У гірничо-промислових регіонах України утворюється велика кількість шахтних і кар'єрних вод, які внаслідок високої мінералізації не можуть бути скинуті у природні гідрографічні об'єкти без глибокої переробки, включаючи й демінералізацію. Більшість таких вод суттєво забруднена концентратами сульфідів і розчинених сполук феруму (заліза), що заважають їх подальшій очистці. У той же час об'єкти теплоенергетики, розташовані в даних регіонах, споживають для своїх потреб значну кількість дефіцитної питної води. Глибока переробка шахтних і кар'єрних вод дозволяє очистити їх й отримати живильну воду для тепломереж, котлів ТЕС і ТЕЦ. Розроблено спосіб одержання стійких інертних анодів на основі титану з активним покриттям PbO_2, які не містять благородних металів та їх сполук. Спосіб полягає у захисті титану від пасивації оксидною плівкою шляхом нанесення термічним шляхом покриття з MnO_2, а пізніше нанесення на основу з цим покриттям тонкого шару PbO_2 з лужного комплексного електроліту, який містить 2,5 моль/дм^3 NaOH, 0,6 моль/дм^3 ЕДТА, добавку етиленгліколю й є насиченим PbO. Основний шар покриття завтовшки 3–5 мм наноситься з нітратного електроліту, до складу якого входить $Pb(NO_3)_2$ 1 моль/дм^3, $Cu(NO_3)_2$ 0,4 моль/дм^3, $Al(NO_3)_3$ 0,2 моль/дм^3 і добавка желатина. Описано спосіб продовження строку експлуатації лужного електроліту шляхом відновлення сполук Pb (IV) при контактуванні з активною поверхнею металевого плюмбуму. Проведені ресурсні випробування цього аноду протягом 1400 годин довели його стійкість при обробці розчинів, що містять суміш натрій сульфату й натрій хлориду. На основі цього аноду розроблено й експериментально апробовано технологію електрохімічного знезалізнення шахтних вод і вилучення з них сульфідів перед демінералізацією. Дана технологія є єдино можливим способом безреагентного знезалізнення й вилучення сульфідів із вод з високою мінералізацією. Такі аноди значно розширюють сферу застосування електрохімічних процесів. Вони можуть застосовуватися не лише для водопідготовки в теплоенергетиці, а й для очищення стічних вод різного мінерального й органічного складу, хіміко-технологічних процесів отримання окисників тощо.

***Ключові слова**: інертні аноди, PbO_2, MnO_2, вилучення феруму та сульфідів, водопідготовка, очищення шахтних та кар'єрних вод.*

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