EXTRACTION OF LEAD (II) IONS FROM WASTE SOLUTIONS AND WASTEWATER BY ELECTROCHEMICAL METHOD

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Abstract. The problem of extracting heavy and non-ferrous metals from spent solutions of galvanic production is of great importance from the point of view of capturing metals valuable for the national economy and neutralizing industrial wastewater.

Existing methods of extracting lead from spent solutions and wastewater mainly involve the addition of reagents. These methods have some disadvantages: economic unprofitability; does not meet modern environmental requirements; additional pollution with ions and the formation of poorly soluble compounds and the labor intensity of extracting metals from them.

Close to the method proposed by us in technical essence is the use of volume-porous flow electrodes (VPFE) made of carbon fibrous materials. The disadvantage of this method is the high cost of electrodes associated with the use of carbon fibrous materials.

The most advantageous seems to be the electrochemical method proposed by us using lump electrodes with a developed surface. The proposed work presents the results of electrolysis of solutions with an initial lead concentration of 200 mg/l on lump graphite electrodes. The experiments were conducted in a flow mode on bulk lump graphite electrodes in an electrolytic cell. An experimental setup was used to purify waste solutions from lead ions using an electrochemical method with the use of piece electrodes with a developed surface. The electrolyzer setup consists of two glass vessels and an electrolyzer with lump electrodes, which are the cathode, and the graphite rod serves as the anode. The thickness of the lump electrode layer was changed depending on the experimental conditions within 0.5-3 cm.

Key words: extraction; electrolyze; lead (II) ions; graphite electrodes.

Introduction

A significant increase in the lead content in the environment (including surface waters) is associated with coal combustion, the use of tetraethyl lead as an antiknock agent in motor fuel, and the removal of lead into water bodies with wastewater from ore processing plants, some metallurgical plants, chemical plants, mines, etc. Significant factors in reducing the concentration of lead in water are its adsorption by suspended substances and deposition with them in bottom sediments. Among other metals, lead is extracted and accumulated by hydrobionts.

Lead is found in natural waters in a dissolved and suspended (sorbed) state. In dissolved form, it occurs in the form of mineral and organomineral complexes, as well as simple ions, in an insoluble form - mainly in the form of sulfides, sulfates and carbonates.

In river waters, the concentration of lead varies from tenths to units of micrograms per 1 dm3. Even in water bodies adjacent to areas of polymetallic ores, its concentration rarely reaches

tens of milligrams per 1 dm3. Only in chloride thermal waters does the concentration of lead sometimes reach several milligrams per 1 dm^3.

Lead is an industrial poison that can cause poisoning under unfavorable conditions. It enters the human body mainly through the respiratory and digestive organs. It and its compounds are dangerous not only because of their pathogenic effect, but also because of the cumulative therapeutic effect [1, 2], high accumulation coefficient in the body, low rate and incompleteness of excretion with waste products. It is eliminated from the body very slowly, as a result of which it accumulates in the bones, liver and kidneys [3, 4].

Lead suppresses many enzymatic processes in the body. With lead intoxication, serious changes occur in the nervous system, thermoregulation, blood circulation and trophic processes are disrupted, the immunobiological properties of the body and its genetic apparatus change [5].

The limiting indicator of lead harmfulness is sanitary and toxicological. The maximum permissible level of lead is 0.03 mg/dm^3 [6].

Tetraethyl lead. It enters natural waters due to its use as an antiknock agent in motor fuels of watercraft, as well as with surface runoff from urban areas. This substance is highly toxic and has cumulative properties.

The content of tetraethyl lead in water bodies for domestic, drinking, cultural, domestic and fishery purposes is not permitted [6].

Pollution with heavy metals can destroy all life in natural waters and in biological treatment facilities for municipal wastewater under certain conditions. It should also be noted that it is important to capture heavy metals and other components from waste solutions in order to reduce the specific removal of salts from the electrolyte in order to increase their efficiency.

For many industries, the problem of extracting metals from solutions in which the concentration of heavy metal ions does not exceed units of grams per liter is relevant.

During electrolysis, the solution is purified from metal ions, and valuable metals are also extracted in the form of products. But, as is known, electrochemical processes are heterogeneous, i.e. the reduction reaction occurs only on the surface of the cathode, so the process is ineffective. In addition, at a low concentration of metal ions in the waste solutions, the main part of the current will be spent on a side unnecessary process – the release of hydrogen gas [7].

In this regard, there is a need to develop effective methods for cleaning water bodies, since the previous, existing methods cannot be considered perfect in modern conditions. One of the main directions in the creation of new waste-free and environmentally friendly technologies for the disposal of waste solutions and waste water and the extraction of heavy non-ferrous metal ions from them may be the use of electrochemical methods using volumetric-porous electrodes, including lump (powder) electrodes with a highly developed surface 7-10]. The use of such electrodes is notable for the fact that the costs are minimal; the processes are practically reagent-free [11].

Materials and research methods

To conduct electrolysis in a flow mode, a conductive graphite plate with small holes is placed at the bottom of the electrolyzer. Lump graphite electrodes with a diameter of 0.2-0.25 cm, which are poured onto the plate, were used as a cathode. The height of the lump electrode layer varies depending on the electrolysis conditions within the range from 0.5 to 3.0 cm. A graphite rod located in the upper part of the electrolyzer served as an anode. The analyzed solution containing heavy metal ions was passed at a given speed through a layer of lump electrodes. The distance between the front surface of the cathode and the graphite anode is 50 mm. Electrolysis was carried out at a cathode current density of 50-550 A/m^2.

The content of heavy metal ions in the analyzed solution before and after the experiments was determined by the polarographic method on an oscillographic polarograph brand PO-5122. Depending on the wave height on the polarograph, the metal content is found using the formula [38]:

$$C_{Me} = (h_x \cdot C_{cт})/h_{cт} \tag{1}$$

where, C_{Me} – concentration of heavy metals in the test solution, g/l; h_x, $h_{cт}$ – readings during polarography of the test and standard solutions; $C_{cт}$ – concentration of heavy metals in the standard solution, g/l. The degree of purification of the solution from heavy metal ions was calculated using the formula:

$$\alpha\,(\%) = (C_{Me(1)} - C_{Me(2)} / C_{Me(1)}) \cdot 100 \tag{2}$$

Here $C_{Me(1)}$ is the concentration of the metal in the analyzed solution, g/l (before the experiment); $C_{Me(2)}$ is the concentration of the metal after electrolysis, g/l.

To calculate the current efficiency, using Faraday's law, we calculate the mass of lead ions that theoretically passed into the solution:

$$m_{теор.} = I \cdot \tau \cdot q \tag{3}$$

where, I – current strength, A; τ – electrolysis time, hour; q – electrochemical equivalent, g/A·hour.

The power yield was calculated using the formula:

$$\text{power yield} = m_{practical} / m_{theory} \cdot 100\% \tag{4}$$

Results and Discussion

The influence of such factors as current density (i, A/m^2), solution flow rate (V, ml/h), size of lump electrodes (l, cm), thickness of the lump electrode layer (*, cm), and initial concentration of lead ions ([Pb(II)], g/l) on the degree of lead extraction was studied.

Wastewater containing lead ions is passed at a certain speed through the layer of the lump electrode.

The studies were based on the purification of waste solutions from lead ions by their electrolytic reduction on a lump graphite cathode to an elemental state, according to the reaction:

$$Pb^{2+} + 2e \rightarrow Pb^0 \tag{5}$$

The following process takes place at the anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4\bar{e} \tag{6}$$

Studies of the effect of current density (Table 1) on the degree of solution purification from lead (II) ions were conducted within the current density range from 50 A/m^2 to 550 A/m^2. With an increase in current density, the degree of lead extraction at 150 A/m^2 reaches 98%, a further increase in current density leads to a decrease in the degree of metal extraction to 95%.

Table 1 – Effect of current density (i, A/m^2) on the degree of lead extraction (*,%), (V_{flow} = 150 ml/hour, [Pb^{2+}]$_{init.}$ = 200 mg/l; l = 0.1 cm; d = 0.1 cm; δ = 0.5 cm)

i, A/м^2	50	150	250	350	450	550
α, %	85.5	98.0	97.2	97.2	96.3	95.0

The maximum degree of metal extraction is achieved when the entire volume of the electrode operates in the mode of the limiting diffusion current. A decrease in the degree of lead

(II) extraction with an increase in current density can be explained by an increase in the competitive process – hydrogen evolution.

The curve showing the dependence of the degree of extraction on the change in the solution flow rate passes through a maximum. This phenomenon can be explained by the fact that with an increase in the flow rate, the solution layer expands, mass transfer increases and, accordingly, the limiting current density. Further, at even higher flow rates, lead (II) ions do not have time to be reduced on the electrodes, and this leads to a sharp decrease in the degree of metal extraction from the solution.

With an increase in the initial concentration of lead in the solution (Fig. 1) from 0.5 g/l to 3.5 g/l, the degree of lead extraction at 2.0 g/l reaches its maximum (97%), at high concentrations its decrease is observed. As we assume, at the cathode, due to the discharge of hydrogen ions, an increase in the pH of the solution is observed in the near-cathode space, and lead ions form hydroxide according to the reaction:

$$Pb^{2+} + OH^- \rightarrow Pb(OH)_2 \downarrow \tag{7}$$

If we take into account the presence of oxygen in the electrolyte, then the following reaction may occur:

$$2Pb + O_2 + H_2O \rightarrow 2Pb(OH)_2 \downarrow \tag{8}$$

The released white precipitate of lead hydroxide at high concentrations of lead slows down the process of metal extraction on the surface of lump electrodes. Increasing the concentration of HNO_3 in the electrolyte reduces the degree of lead extraction, due to the good solubility of the released lead in the electrolyte. For example, in the process of electrolysis without HNO_3, the degree of lead extraction is 90%.
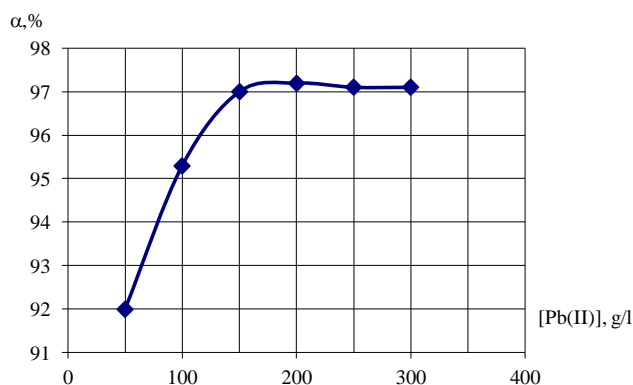

Figure 1 – Effect of the initial concentration of lead ions [Pb(II), g/l] on the degree of lead extraction (α%), I = 150 A/m^2; V$_{init.}$ = 200 ml/hour; l = 0.1 cm; d=0,1 см; δ=0,5см

Increasing the acid concentration from 5 g/l to 30 g/l, the degree of lead extraction decreases from 60% to 35%.

The effect of the electrode material on the electrolysis process is also considered. The maximum degree of extraction is observed on the graphite electrode (98%), and on the lead electrode this figure reached 67.7%, on the copper electrode – only 44%.

When studying the effect of the size of lump electrodes, it turned out that a high degree of extraction is achieved when using pieces with a diameter of 0.1 cm and a length of 0.1 cm; it should be noted that on small powder electrodes, lead extraction decreases. Apparently, when

passing the solution through very fine graphite powder, the powder particles stick together, i.e. they are characterized by agglomeration and the reaction surface of the electrodes decreases.

With an increase in the layer thickness of the lump graphite electrode to 3.0 cm, as can be seen from Figure 2, the degree of lead extraction reaches 99.2% already at a layer thickness of 0.5 cm, then it decreases. In the volume of large lump electrodes, when a cathode potential is applied, zones of anodic polarization may occur; this is explained by the formation of a clot of particles that acquire the functions of a bipolar electrode. Zones of maximum polarization and electrically inactive zones may also occur. In the absence of lump electrodes, the degree of lead extraction does not exceed 15%. Under optimal conditions (i = 150 A/m^2; V = 150 ml / h; δ = 0.5 cm; l = 0.1 cm), the degree of lead extraction reached 99.4%. It should be noted that if the initial solution is passed through several such electrolyzers, the degree of lead extraction will be even higher. The precipitated lead can be separated from the electrode by burning the graphite electrode.
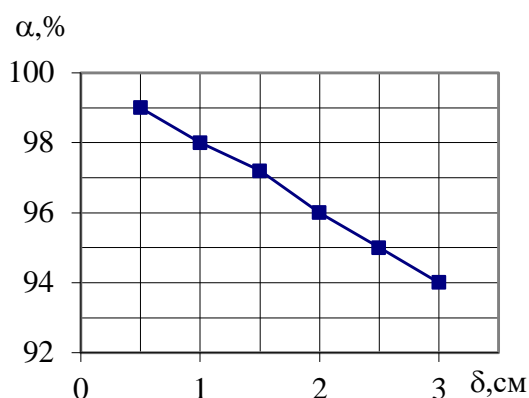

Figure 2 – Effect of electrode layer thickness (δ, cm) on the degree of lead extraction (α%), I = 150 A/m^2; [Pb^{2+}]$_{init.}$ = 200 mg/l; V$_{init.}$ = 200 ml/hour; l = 0.1 cm; d = 0.1 cm

Thus, waste water or waste solutions can be almost completely purified from lead ions using piece electrodes. Waste water purification problems can be solved using electrochemical methods. These methods are simple, easy to use, almost reagent-free and cost-effective.

Conclusion

The features of lead (II) ion extraction from waste solutions and mine waters on lump electrodes with a developed surface were studied. The results of the study showed that the use of lump electrodes can significantly increase the degree of solution purification compared to flat electrodes.

The influence of various electrochemical parameters on the process of lead (II) ion reduction on lump electrodes was studied and optimal conditions were established (i = 125-175 A/m^2; V = 125-175 ml / h; δ = 0.5 cm; l = 0.1 cm), and the degree of lead extraction from the solution reached 99.4%.

It was shown that the degree of lead extraction from lead-containing solutions can be increased to 99.9%. A basic scheme for extracting metal ions from waste solutions on lump electrodes is proposed.

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ИЗВЛЕЧЕНИЕ ИОНОВ СВИНЦА (II) ИЗ СТОЧНЫХ ВОД ЭЛЕКТРОХИМИЧЕСКИМ МЕТОДОМ

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Аннотация. Проблема извлечения тяжелых и цветных металлов из отработанных растворов гальванического производства имеет большое значение с точки зрения улавливания ценных для народного хозяйства металлов и нейтрализации промышленных сточных вод. Существующие методы извлечения свинца из отработанных растворов и сточных вод в основном предполагают добавление реагентов. Эти методы имеют ряд недостатков: экономическая нерентабельность; не соответствует современным экологическим требованиям; дополнительное загрязнение ионами и образование малорастворимых соединений, и трудоемкость извлечения металлов из них. Близким к предложенному нами способу по технической сути является использование объемно-пористых проточных электродов, изготовленных из углеродных волокнистых материалов. Недостатком данного способа является высокая стоимость электродов, связанная с использованием углеродных волокнистых материалов. Наиболее выгодным представляется предложенный нами электрохимический метод с использованием кусковых электродов с развитой поверхностью. В предлагаемой работе представлены результаты электролиза растворов с начальной концентрацией свинца 200 мг/л на кусковых графитовых электродах. Эксперименты проводились в проточном режиме на объемных кусковых графитовых электродах в электролизере. Экспериментальная установка использовалась для очистки отработанных растворов от ионов свинца электрохимическим методом с использованием штучных электродов с развитой поверхностью. Электролизерная установка состоит из двух стеклянных сосудов и электролизера с кусковыми электродами, которые являются катодом, а графитовый

стержень служит анодом. Толщина слоя кускового электрода изменялась в зависимости от условий эксперимента в пределах 0,5-3 см.

Ключевые слова: экстракция; электролиз; ионы свинца (II); графитовые электроды.

ЭЛЕКТРОХИМИЯЛЫҚ ӘДІСПЕН АҒЫНДЫ СУЛАРДАН ҚОРҒАСЫН (II) ИОНДАРЫН АЛУ

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Аннотация. Гальваникалық өндірістің пайдаланылған ерітінділерінен ауыр және түсті металдарды алу мәселесі халық шаруашылығы үшін құнды металдарды ұстау және өнеркәсіптік ағынды суларды бейтараптандыру тұрғысынан үлкен маңызға ие. Қалдық ерітінділер мен ағынды сулардан қорғасынды алудың қолданыстағы әдістері негізінен реагенттерді қосуды қамтиды. Бұл әдістердің бірқатар кемшіліктері бар: экономикалық тиімсіздік; қазіргі экологиялық талаптарға сәйкес келмейді; иондардың қосымша ластануы және ерімейтін қосылыстардың түзілуі және олардан металдарды алудың күрделілігі. Техникалық тұрғыдан біз ұсынған әдіске жақын – көміртекті талшықты материалдардан жасалған көлемді кеуекті ағынды электродтарды пайдалану. Бұл әдістің кемшілігі – көміртекті талшықты материалдарды пайдаланумен байланысты электродтардың жоғары құны. Ең тиімдісі – осы ұсынған электрохимиялық әдіс, беті дамыған электродтарды қолдану. Ұсынылған жұмыста кесек графит электродтарында қорғасынның бастапқы концентрациясы 200 мг/л болатын ерітінділердің электролизінің нәтижелері келтірілген. Тәжірибелер электролизердегі көлемді графит электродтарында ағынды режимде жүргізілді. Эксперименттік қондырғы қорғасын иондарынан қалдық ерітінділерді электрохимиялық әдіспен, беті дамыған электродтарды қолдана отырып тазарту үшін қолданылды. Электролизер қондырғысы екі шыны ыдыстан және катод болып табылатын электродтары бар электролизерден тұрады, ал графит таяқшасы анод ретінде қызмет етеді. Кесек электрод қабатының қалыңдығы эксперимент жағдайына байланысты 0,5-3 см аралығында өзгерді.

Түйін сөздер: экстракция; электролиз; қорғасын (II) иондары; графит электродтары.