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Obtaining of lead (II) sulfate by polarization of bipolar lead electrodes with alternating current

The process of electrolysis using bipolar lead electrodesat polarization by alternating current of industrial frequency (50 Hz) in sulfuric acid solutions was studied for the first time. It is shown that the oxidation of lead to the bivalent state on all monopolar and bipolar electrodes takes place in the anode half-period of alternating current. Next, the anode half-period is replaced by a cathode half-period, then the lead electrode becomes a cathode and hydrogen is released on its surface. Lead (II) ions react with sulfate anions in the near-electrode space to form lead (II) sulfate. It was found that the total loss of electrode mass increases with increasing current density up to 1200–1400 A/m^2, and in the region of 2000 A/m^2 — significantly decreases, which is associated with increased adverse reactions.In the interval of experiment duration 0.5–2 hours the total loss of electrode mass increases. However, after 2 hoursthis value remains almost constant. Apparently, lead (II) sulfate begins to be accumulating on the electrodes and interfere with the dissolution process. It was found that when using bipolar electrodes, the mass of lead (II) sulfate is about 2.4 times greater at the same current strength than when conducting electrolysis with only two monopolar electrodes.

Keywords: lead, bipolar electrode, electrolysis, alternating current, oxidation, anodic half-period, sulfuric acid.

Introduction

Lead (II) sulfate is used in the paint industry as additives in the manufacture of minium [1; 771] for filling the cells of a lead-acid battery plates [2; 519], in the synthesis of certain acids as a necessary component of technological processes, and also performs the role of a stabilizer in the production of plasticized PVC [3, 4]. Obtaining of lead (II) sulfate is usually carried out [1; 771, 5; 322] by precipitation from soluble salts of divalent lead (nitrate, acetate) with sulphuric acid.

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$$

The authors of article [6] proposed a method for obtaining lead (II) sulfate by electrochemical dissolution of lead electrode in sulfuric acid during polarization by alternating current of industrial frequency of 50 Hz. In this case, one electrode is a metallic lead and titanium is used as the second electrode. Electrolysis is carried out at a current density of 1500 A/m^2 on lead electrode and 8000–12000 A/m^2 on a titanium electrode. The highest current outputs are observed at current densities at the lead electrode equal to 3000 A/m^2 and reach 53.5 %.

The proposed method has certain disadvantages, which include the fact that the formation of lead (II) sulfate occurs on only one lead electrode in the anode half-cycle of alternating current, as a result of which the productivity of the process is low.

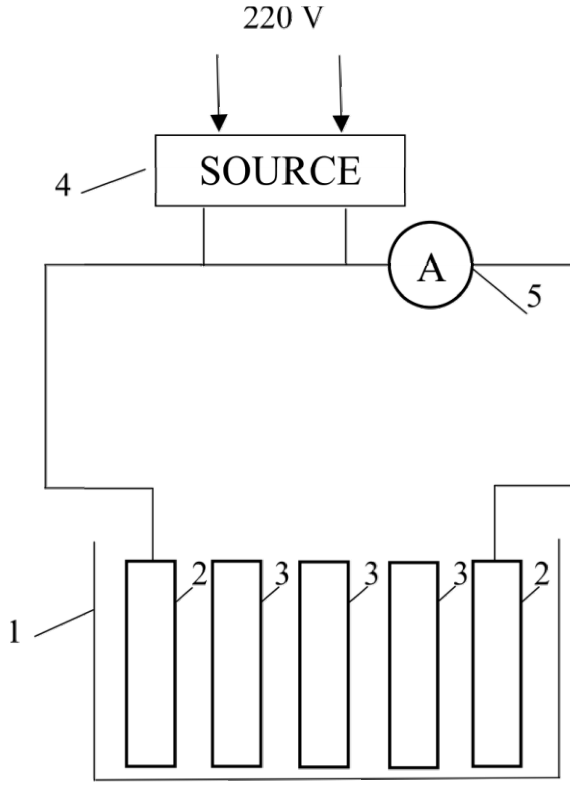
In addition, at high current densities, lead oxidation reactions may occur with the formation of lead oxides, which can contaminate the resulting product. Besides, the use of titanium causes possible contamination of the reaction product with titanium ions, since it is known that during alternating current polarization, titanium also passes into solution [7]. The process of formation of lead (II) sulfate as a result of oxidation of lead sulfide with hydrogen peroxide solution was studied by the authors [8]. It is established that the yield of the product (lead (II) sulfate) and its purity depend on the amount of oxidant.

In connection with the demand in a number of technological processes, the development of new methods for producing lead sulfate seems to be an urgent problem. The aim of our work is to develop a method for producing lead (II) sulfate by electrolysis with polarization by alternating current using bipolar electrodes and, in this regard, to analyze literature sources covering the issues of bipolar electrode connection.

Experimental technique

The unit shown in Figure 1 was used for the research. The unit consists of an electrolyzer (1) in which two extreme monopolar (2) and three (3) bipolar lead electrodes are installed. The electric current of the required power is supplied through SOURCE (MATRIX of single-phase TDGC-1 1 KVA, 4A), the magnitude of current measured by the ammeter (laboratoryA-meterE538). Lead plates of C-1 grade were used as electrodes, electrolyte solutions were prepared from sulfuric acid of chemically pure grade. The electrolysis was carried out with polarization by alternating current of industrial frequency (50 Hz). Two electrodes were attached to the current source, located closer to the wall of the electrolyzer, which are conventionally called «terminal». Between them three more electrodes were installed vertically and parallel to each other. The distance between them was equal to 1.4 cm. Surface area of all electrodes were the same and equal to 12.5 cm^2. The electrolyzer was made of plexiglass and had a rectangular shape.

The electrodes were placed in such a way that there were no large gaps between the side walls of the electrolyzer and the electrodes. Before the experiment, the lead electrodes were thoroughly cleaned with sandpaper, washed with water and treated with alcohol. After electrolysis, the electrode mass loss was determined by weighing.



1 — electrolyzer; *2* — monopolar electrodes; *3* — bipolar electrodes;
4 — adjustable electric source; *5* — ammeter

Figure 1. Schematic diagram of the installation for the obtaining of lead (II) sulfate by electrochemical method

The effect of the current density and duration of the experiment on the mass loss of lead electrodes was studied.As a result of electrolysis in the electrode spaces in the solution, the interaction of lead ions with sulfate ions occurred with the formation of lead (II) sulfate, which in the form of a white precipitate fell to the bottom of the cell. After the experiment, the electrolyte was filtered, the precipitate was separated from the solution, washed with water and dried. The sediment was identified by x-ray fluorescence, x-ray phase and elemental analysis methods.

Results and discussion

As it is known from the literature [9; 178, 10], anodic polarization of lead in an aqueous solution of sulfuric acid may result in the following electrode reactions:

1) oxidation of metallic lead to a divalent state followed by the formation of lead (II) sulfate:

$$Pb + SO_4^{2-} - 2e^- \rightarrow PbSO_4 \qquad E^0 = -0.356\ V; \qquad (1)$$

2) oxidation of divalent ions of lead to a tetravalent state with the formation of lead dioxide:

$$PbSO_4 + 2H_2O - 2e^- \rightarrow PbO_2 + SO_4^{2-} + 4H^+ \qquad E^0 = +1.685\ V; \qquad (2)$$

3) direct oxidation of metallic lead to tetravalent state:

$$Pb + 2H_2O - 4e^- \rightarrow PbO_2 + 4H+ \qquad E^0 = +0.66\ V;$$

4) release of oxygen:

$$2H_2O - 4e^- = O_2 + 4H^+ \text{ (in acidic solutions)} \qquad E^0 = +\ 1.229\ V;$$

5) the possible discharge of ions SO_4^{2-} with the formation of acid:

$$SO_4^{2-} - 2e^- \rightarrow S_2O_8^{2-} \qquad E^0 = +\ 2.01\ V.$$

Of the several possible reactions at the anode, first of all, the one that requires the lowest energy costs, i.e. a reaction with more negative potential, i.e. a reaction (1), should occur. It was found [11; 339] that a fairly dense porous layer of lead sulfate is formed on the surface of the lead electrode. After a certain time, the reaction (2) takes place, i.e. the formation of lead dioxide, the reaction of the formation of lead sulfate completely stops, although the supply of metallic lead has not been used upyet. Passivation occurs when the thickness of the lead sulfate layer is about 1 μm.

In contrast to the known methods of electrolysis, our experiments were carried out under the influence of alternating current of industrial frequency using bipolar electrodes.

It is known [12; 35] that electrolyzers with mono- and bipolar inclusion of electrodes in the DC circuit are used in electrochemistry. In a monopolar circuit, all electrodes of the same sign are connected to the corresponding pole of the current source. In this case, the current passing through one electrode, in accordance with the law of parallel connection of conductors is equal to the total current divided by the number of electrodes. The voltage that occurs between a pair of electrodes of the opposite sign is equal to the total voltage on the electrolyzer.

In the bipolar scheme of inclusion of electrodes, the current is supplied only to the terminal electrodes, which are monopolar electrodes. All other electrodes located between the terminal monopolar electrodes have no current leads and work as bipolar — one side of the electrode is the cathode, and the other is the anode. Through each cell of the bipolar electrolyzer all the current coming from an external current source passes and the total voltage is equal to the product of the voltage on one cell by the number of cells. It is noted [13] that when sufficient voltage is applied to the solution in which the bipolar electrode (BPE) is immersed, oxidation and reduction reactions occur on the opposite sides of the BPE.Since no direct electrical contact with a current source is required to activate redox reactions, large electrode arrays can be controlled by only one DC source or even a battery in an electrochemical circuit. The wireless aspect of the BPE also allows for electrosynthesis and screening of new materials for a wide range of applications.Additionally, the bipolar connection of the electrodes allows the movable electrodes, called microswitch to move freely in the solution.Practical application of bipolar electrodes is widespread in water electrolysis [14; 39, 15; 97, 126]. The advantages of electrolyzers with bipolar electrodes are compact design, there is no need to supply current to each electrode, the ability to impose high voltages.Advantages of electrolyzers with bipolar electrodes are compact design, no need to supply current to each electrode, the ability to impose large voltages.

Known literature sources [16] present the results on study using bipolar electrodes and show that the effective removal of fluoride ions from water occurs when the electrodes are bipolar.

In addition, in the review [17], the authors note the prospects for the use of bipolar electrodes, using the expression «bipolar electrochemistry». They stress that this method of electrolysis has attracted new interest in the last two decades, due to the use in several fields — from materials science to sensing and so on.

The same review presents new examples of the use of the bipolar connection, focused on the sensing of electrotransplantations, the electrodeposition and the use of graphene as a bipolar electrode.

The authors of [18] demonstrated that bipolar electrode coupling can be used for high-performance corrosion tests covering a wide range of potentials in one experiment, and that this, combined with rapid image analysis, is a simple and convenient way to verify the corrosion properties of conductive materials.

Interesting studies have been carried out in the work of the authors [19]. They show that the rotation of the bipolar electrode in a constant electric field between the supply electrodes causes an alternating bipolar current with alternating current frequency, which depends on the rotation speed.

It should be noted that the use of bipolar connection of electrodes in direct current polarization is described in the known literature sources.

In this report, we present the results of the use of bipolar connection of lead electrodes at polarization by alternating current of industrial frequency. In this regard, we note: it was previously shown [20; 43, 21] that when metals are polarized by alternating current, the anode half-period of the alternating current is quickly replaced by the cathode half-period. In this regard, oxidation processes can occur in the anode half-cycle.

But at the same time, changing the direction of the alternating current does not favor the flow of all possible anode processes. Consequently, in the case of alternating current polarization of lead in the anode half-period, the reaction first proceeds, which has a more negative potential, i.e. oxidation of lead to the divalent state:

$$Pb^0 - 2e^- \rightarrow Pb^{2+}$$

Then, in a matter of seconds, the anode half-cycle is replaced by the cathode half-cycle, i.e. the lead electrode becomes the cathode and hydrogen is released on its surface:

$$2H^+ + 2e^- \rightarrow H_2$$

Bivalent lead ions formed in the near-electrode space interact with sulfate anions. Due to the low value of the solubility product ($1, 6\cdot10^{-8}$) [22; 739] lead (II) sulfate precipitates to the bottom of the electrolyzer:

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$$

Bubbles of hydrogen release carry crystals of lead sulfate formed from the electrode surface. The described processes are periodically repeated with a change in the direction of the current depending on its frequency, i.e. in our case 50 times per second. It becomes possible to purposefully proceed with the formation of lead sulfate (II). Moreover, when using bipolar electrodes, the oxidation reaction of lead occurs on those electrodes that are not directly connected to the current source. In the cathode half-cycle, the reduction of lead ions to the elemental state does not occur, since this reaction proceeds with a high overvoltage.

We have studied the effect of current density on the mass loss of lead electrodes during alternating current polarization in the presence of bipolar electrodes. As shown in Table 1, the mass loss of monopolar and bipolar electrodes increases with increasing current density to 1200–1400 A/m^2, and significantly decreases in the region of 2000 A/m^2, which is associated with increased adverse reactions. Terminal monopolar electrodes are conventionally designated 2^1 and 2^2, bipolar electrodes located between them — 3^1, 3^2 and 3^3.

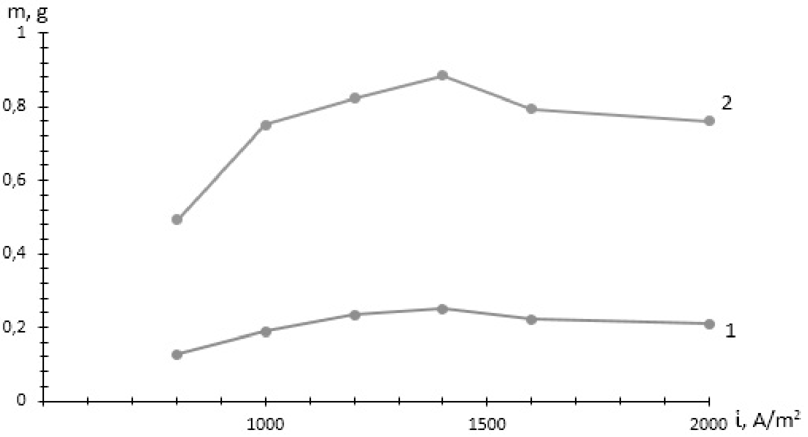
Table 1

Effect of current density on the mass loss of monopolar and bipolar lead electrodes during alternating current polarization ($C(H_2SO_4)$ = 150 g/l; τ = 0.5 hour)

Magnitude of mass loss	Current density, A/m^2					
	800	1000	1200	1400	1600	2000
Δm (2^1)	0.1272	0.1892	0.2348	0.2512	0.2214	0.2095
Δm (3^1)	0.0813	0.1406	0.1413	0.1411	0.1402	0.1344
Δm (3^2)	0.0675	0.0928	0.0959	0.0952	0.0822	0.0811
Δm (3^3)	0.0914	0.1371	0.1368	0.1485	0.1236	0.1208
Δm (2^2)	0.1244	0.1912	0.2125	0.2487	0.2257	0.2136
Σm		0.7509	0.8213	0.8847	0.7931	0.7594

Figure 2 graphically shows the dependence of the mass loss of one monopolar electrode — 2^1 and the total decrease in the mass of the electrodes from the current density. We note that the values of the mass loss of monopolar and bipolar electrodes are quite close to each other, in this regard, these values are not graphically reflected, but are given in detail in Table 2.

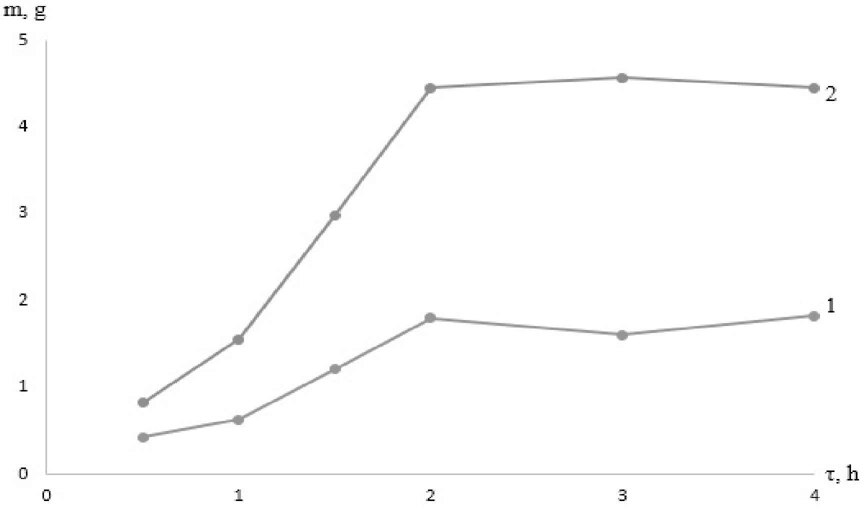
As shown in Table 1, the dissolution process of the electrodes is intense at a current density of 1200–1400 A/m^2, the rate of electrochemical dissolution is reduced at 2000 A/m^2, as the reverse process.



$C(H_2SO_4)$ = 150 g/l; τ = 0.5 hour

Figure 2. Dependence of the mass loss of one monopolar (2^1) electrode (curve 1) and the total mass loss of all electrodes (curve 2) on the current density on the electrodes

The study of the effect of the duration of the experiment showed that in the range of 0.5–2 hours the total mass of lead ions transferred to the solution increases (Fig. 3, curve 2). However, after 2 hours the mass remains almost constant. Apparently, the resulting lead sulfate begins to accumulate on the surface of the electrode and prevent the process of dissolution of the metal electrode. Table 2 shows the values of the mass loss of monopolar and bipolar lead electrodes depending on the duration of electrolysis.



1 — in electrolysis with monopolar electrodes; *2* — in electrolysis with bipolar electrodes;
i = 1200 A/m^2; $C(H_2SO_4)$ = 150 g/l

Figure 3. Dependence of the total mass of lead ions (*m*, g), passed into the solution of the duration of the experiment

The results of the experiments show that the mass loss of two monopolar (terminal) electrodes have similar values. Also, the values of the mass loss of two bipolar electrodes located next to the terminal monopolar ones are quite close, although their values are slightly lower than the mass loss of the two extreme monopolar electrodes. Nevertheless, in the case of dissolution of each monopolar and each bipolar electrode, it is noticeable that after 2 hours the mass loss remains practically unchanged. Note that the Table shows the values of the mass loss of all electrodes, and the Figure shows only the curve of the total mass loss of all electrodes (monopolar and bipolar) and for comparison shows the curve of the mass loss of only one monopolar electrode.

Table 2

Effect of the duration of the experiment on the dissolution of monopolar and bipolar electrodes in sulfuric acid during industrial alternating current polarization, $i = 1200$ A/m^2, $C(H_2SO_4) = 150$ g/l

Magnitude of mass loss	Electrolysis duration, hour					
	0.5	1	1.5	2	3	4
Δm (2^1)	0.2348	0.4112	0.8255	0.9748	0.9684	0.9538
Δm (3^1)	0.1413	0.2939	0.5584	0.8283	0.9148.	0.8481
Δm (3^2)	0.0959	0.1771	0.2011	0.8108	0.8871	0.7811
Δm (3^3)	0.1368	0.2921	0.5546	0.8384	0. 8916	0.8943
Δm (2^2)	0.2125	0.3811	0.8369	0.9961	0.9088	0.9783
Σm	0.8213	1.5554	2.9765	4.4484	4.5707	4.4556

In order to show the advantages of using bipolar electrodes, experiments with two monopolar electrodes were conducted separately. A comparison of the results of electrolysis carried out using two electrodes and electrolysis using five electrodes showed that during electrolysis using two monopolar and three bipolar electrodes, the oxidation of lead in sulfuric acid with the formation of lead sulfate is intensified more than 2.4 times. Table 3 shows the results of the process of dissolution of lead electrodes in bipolar compounds (5 electrodes in total) and in monopolar (2 electrodes in total) compounds under industrial alternating current polarization.

Table 3

Comparison of the total mass that passed into the solution in experiments with 5 electrodes and 2 electrodes

Electrolysis duration, hour	0.5	1	1.5	2	3	4
Σm (in the experience with 5 electrodes)	0.8213	1.5554	2.9765	4.4484	4.5707	4.4556
Σm (in the experience with 2 electrodes)	0.43	0.6315	1.2101	1.7997	1.6037	1.825
n	1.91	2.46	2.46	2.47	2.85	2.41

Note. Table «*n*» shows how many times more dissolved lead electrode using five electrodes compared to the experience with two lead electrodes.

In our experiments the prospects of bipolar connection of electrodes at polarization by industrial alternating current with frequency of 50 Hz are shown. The rapid change of the current direction on the electrodes noted above contributes to the fact that lead oxidation reactions stop at the first stage and the phenomenon of electrode passivation is practically not observed due to the formation of electrically conductive oxide compounds directly on the electrode surface.

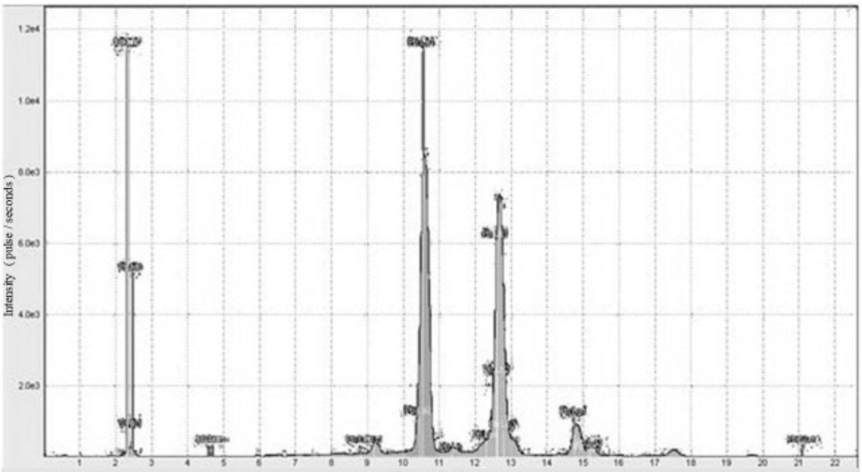


Figure 4. X-ray Fluorescence analysis of lead (II) sulfate obtained by using bipolar electrodes during alternating current polarization

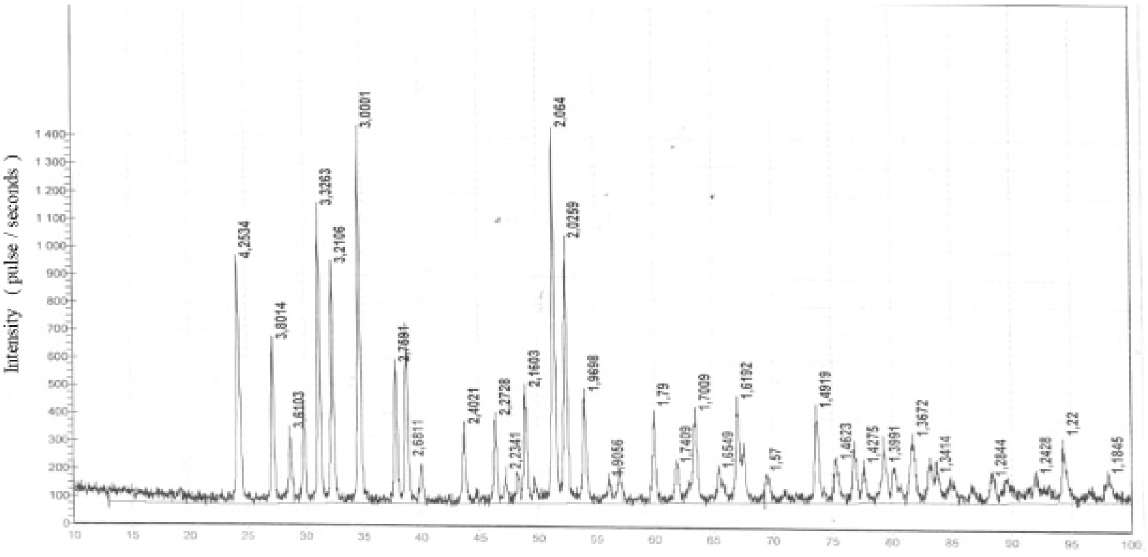


Figure 5. Diffractogram of lead (II) sulfate obtained by using bipolar electrodes during alternating current polarization

The composition and purity of the resulting lead (II) sulfate were determined by x-ray fluorescence, elemental and x-ray phase analysis methods (Fig. 4 and 5). It is shown that all the reflexes of the x-ray belong to lead (II) sulfate, i.e. to $PbSO_4$, the ratio of the elements allow us to judge the production of lead sulfate $PbSO_4$ of high purity.

Conclusions

Thus, this article presents a number of literature data on the electrochemistry of lead and bipolar connection of electrodes. For the first time, the process of dissolution of bipolar lead electrodes under alternating current polarization with an industrial frequency of 50 Hz was studied. It was found that when using BPE, the mass of the resulting lead (II) sulfate is approximately 2.4 times greater at the same current strength in the electrochemical circuit than during electrolysis with only two monopolar electrodes.

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Биполярлы қорғасын электродтарын айнымалы токпен поляризациялау арқылы қорғасын (II) сульфатын алу

Алғаш рет өндірістік жиіліктегі (50 Гц) айнымалы токпен поляризациялау арқылы күкірт қышқылы ерітінділерінде биполярлы (БПЭ) қорғасын электродтарын пайдаланумен электролиз процесі зерттелді. Айнымалы токтың анодты жартылай периодында қорғасынның екі валентті күйге дейін барлық монополярлы және биполярлы электродтарда тотығатыны көрсетілді. Содан кейін анодты жартылай период катодты жартылай периодқа ауысады, демек, қорғасын электроды катод қызметін атқарады және оның бетінде сутек бөлінеді. Екі валентті қорғасын иондары электрод аумағындағы кеңістікте сульфат-аниондарымен әрекеттеседі де, қорғасын (II) сульфаты түзіледі. Қорғасын электродтарының массасының азаю мөлшеріне ток тығыздығының әсері зерттелді. Электродтардың массаларының жиынтықты түрде азаю мөлшері ток тығыздығын 1200–1400 А/м^2-ге дейін арттырғанда көбейетіні, ал 2000 А/м^2 аумағында — айтарлықтай төмендейтіні көрсетілген, бұл қосымша реакциялардың жылдамдығының артуына байланысты. Тәжірибе ұзақтығының 0,5–2 сағат аралығында электродтар массасының азаю мөлшері артады. Бірақ 2 сағаттан кейін — бұл шама тұрақты қалыпқа түседі. Мұның себебі, электродтар бетінде қорғасын (II) сульфаты жинақталады да, еру процесіне кедергі келтіре бастайды деп болжауға болады. БПЭ қолданған кезде түзілген қорғасын (II) сульфатының массасы екі монополярлы электрод қолданып жүргізген электролизбен салыстырғанда, бірдей ток күшінде, жуық шамамен 2,4 есе артық екені анықталды.

Кілт сөздер: қорғасын, биполярлы электрод, электролиз, айнымалы ток, тотығу, анодтық жартылай период, күкірт қышқылы.

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Получение сульфата свинца (II) при поляризации биполярных свинцовых электродов переменным током

Впервые изучен процесс электролиза с использованием биполярных (БПЭ) свинцовых электродов при поляризации переменным током промышленной частоты (50 Гц) в растворах серной кислоты. Показано, что в анодном полупериоде переменного тока протекает окисление свинца до двухвалентного состояния на всех монополярных и биполярных электродах. Далее анодный полупериод сменяется катодным полупериодом, тогда свинцовый электрод становится катодом и на его поверхности выделяется водород. Ионы свинца (II) взаимодействуют с сульфат-анионами в приэлектродном пространстве с образованием сульфата свинца (II). Установлено, что суммарная убыль массы электродов возрастает с увеличением плотности тока до 1200–1400 А/м^2, а в области 2000 А/м^2 — заметно уменьшается, что связано с усилением побочных реакций. В интервале продолжительности опыта 0,5–2 ч суммарная убыль массы электродов увеличивается. Однако после 2-х ч эта величина практически остается постоянной. По-видимому, сульфат свинца (II) начинает накапливаться на электродах и препятствовать процессу растворения. Установлено, что при использовании БПЭ масса сульфата свинца (II) больше примерно в 2,4 раза при одинаковой силе тока, чем при проведении электролиза только с двумя монополярными электродами.

Ключевые слова: свинец, биполярный электрод, электролиз, переменный ток, окисление, анодный полупериод, серная кислота.

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