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STUDY OF THE BEHAVIOR OF ARSENIC IN COPPER ELECTROLYTE

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In industrial wastewater, arsenic is most often present in the trivalent state. An analysis of existing purification methods shows that in all cases, with a few exceptions, the most complete removal of arsenic is observed from solutions in which it is in the pentavalent state. This is explained by the significantly lower solubility of arsenates of heavy and alkaline earth metals compared to the corresponding arsenites. The chemical oxidation of As(III) in the following systems was studied: As(III)-H_2SO_4-H_2O, As(III)-$MeSO_4$-H_2O, As(III)–H_2SO_4–$MeSO_4$–H_2O (where Me is Cu, Ni, Co, Mn, Zn). The influence of temperature, the amount of transition metal ions, the duration of the experiment, and the concentration of sulfuric acid on the degree of transition of As(III) to As(V) was studied. The effect of catalytic oxidation of As(III) in sulfuric acid solutions was discovered. The maximum degree of oxidation of trivalent arsenic (55-60%) is observed when transition metal salts are introduced into an arsenic solution in the presence of a platinum plate. It has been established that the nature of the studied transition metal salts (Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}), process duration and temperature do not have a significant effect on the degree of As(III) conversion. The results obtained largely explain the predominance of pentavalent forms of arsenic in production solutions of non-ferrous metallurgy.

Keywords: copper electrolyte, arsenic, transition metals, catalytic role, instant oxidation effect, activated oxygen.

МЫС ЭЛЕКТРОЛИТІНДЕГІ МЫШЬЯКТІҢ КҮЙІН ЗЕРТТЕУ

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Өнеркәсіптік ағынды суларда мышьяк көбінесе үш валентті күйде болады. Қолданыстағы тазарту әдістерін талдау барлық жағдайларда, бірнеше ерекшеліктерді қоспағанда, мышьяктың ең толық жойылуы оның бес валентті күйде болатын ерітінділерден байқалатынын көрсетеді. Бұл ауыр және сілтілі жер металдарының арсенаттарының сәйкес арсениттермен салыстырғанда айтарлықтай төмен ерігіштігімен түсіндіріледі. Жүйелердегі As(III) химиялық тотығуы: As(III)-H_2SO_4-H_2O, As(III)-$MeSO_4$-H_2O, As(III)-H_2SO_4-$MeSO_4$-H_2O (мұндағы Me - Cu, Ni, Co, Mn, Zn). As(III)-тің As(V)-ке өту дәрежесіне температураның, өтпелі металл иондарының мөлшерінің, тәжірибенің ұзақтығының және күкірт қышқылының концентрациясының әсері зерттелді. Күкірт қышқылы ерітінділеріндегі As(III) каталитикалық тотығуының әсері ашылды. Үш валентті мышьяктың максималды тотығу дәрежесі (55-60%) өтпелі металл тұздарын платина пластинасының қатысуымен мышьяк ерітіндісіне енгізгенде байқалады. Зерттелетін өтпелі металл тұздарының табиғаты (Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}), процестің ұзақтығы мен температурасы As(III) түрлену дәрежесіне айтарлықтай әсер етпейтіні анықталды. Алынған нәтижелер түсті металлургияның өндірістік ерітінділерінде мышьяктың бес валентті түрлерінің басым болуын көптеп түсіндіреді.

Түйін сөздер: мыс электролиті, мышьяк, өтпелі металдар, каталитикалық рөл, лезде тотығу эффектісі, белсендірілген оттегі.

ИССЛЕДОВАНИЕ ПОВЕДЕНИЯ МЫШЬЯКА В МЕДНОМ ЭЛЕКТРОЛИТЕ

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В промышленных сточных водах мышьяк присутствует чаще всего в трехвалентном состоянии. Анализ существующих способов очистки показывает, что во всех случаях за небольшим исключением, наиболее полное удаление мышьяка наблюдается из растворов, в которых он находится в пятивалентном состоянии. Объясняется это значительно меньшей растворимостью арсенатов тяжелых и щелочноземельных металлов по сравнению с соответствующими арсенитами. Исследовано химическое окисление As(III) в системах: As(III)-H_2SO_4-H_2O, As(III)-$MeSO_4$-H_2O, As(III)–H_2SO_4–$MeSO_4$–H_2O (где Me - Cu, Ni, Co, Mn, Zn). Изучено влияние температуры, количества ионов переходных металлов, продолжительности опыта, концентрации серной кислоты на степень перехода As(III) в As(V). Обнаружен эффект каталитического окисления As(III) в сернокислых растворах. Максимальная степень окисления трехвалентного мышьяка (55-60%) наблюдается при введении в мышьяковый раствор солей переходных металлов в присутствии платиновой пластинки. Установлено, что природа изученных солей переходных металлов (Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}), продолжительность процесса и температура не оказывают существенного влияния на степень превращения As(III). Полученные результаты во многом объясняют факт преобладания пятивалентных форм мышьяка в производственных растворах цветной металлургии.

Ключевые слова: медный электролит, мышьяк, переходные металлы, каталитическая роль, эффект мгновенного окисления, активированный кислород.

Introduction. In hydrometallurgical methods for producing non-ferrous metals, the electrorefining process is characterized by the accumulation of impurities in the electrolyte, one of which is arsenic. Depending on the type of production, arsenic in aqueous solutions can be in various forms. In the presence of free sulfide ions in water, arsenic is present in the form of anions of thiosalts AsS_2^-, AsS_3^{3-} and AsS_4^{3-}, in other cases - in the form of oxygen-containing molecules and anions. The form of existence of arsenic in aqueous solutions depends on its valency [1-2].

According to literature data [3, 4], during electrorefining of copper, 60-80% of arsenic passes from the anode into the electrolyte, the rest goes into sludge. The distribution of arsenic between the electrolyte and sludge, as well as the form of its presence in the solution, depends on the composition of the electrolyte and the electrolysis mode. For example, the presence of As and Sb of different valencies in the electrolyte leads to the precipitation of antimony-arsenic (Sb^{3+}-As^{5+}) and antimony-arsenic (Sb^{5+}-As^{3+}) precipitation. An increase in the total content of impurities in the electrolyte leads to an increase in the electrical resistance of the solution and its viscosity, an increase in electricity consumption, a decrease in current efficiency and an increase in the content of harmful impurities in the cathode metal. Therefore, blister copper, as the main raw material of the copper electrorefining process, determines the composition of the electrolyte during electrolysis. An increase in the content of impurities such as nickel, arsenic and antimony leads to the production of defective copper or copper of low grades.

During the processing of technogenic arsenic-containing materials by hydrometallurgical methods, a large proportion of arsenic goes into solution in trivalent form. Practice and research show that arsenic in copper electrolyte is mainly pentavalent. For effective purification and precipitation of sparingly soluble iron arsenates, it is necessary to oxidize arsenic (III) ions to the pentavalent state [5]. If we take into account that during electrochemical oxidation, metallic arsenic forms arsenic trioxide [6, 7], then elucidating the reasons for this fact is an interesting problem.

The relevance of these studies is due to the need to remove arsenic from the technological process of non-ferrous metal production in an environmentally safe form, taking into account their subsequent storage or disposal. Such forms are arsenates, where arsenic is pentavalent.

Materials and methods. To obtain information about the behavior of arsenic in a copper electrolyte, the chemical oxidation of As(III) was studied in the following systems: As (III)-H_2SO_4-H_2O, As (III)-$MeSO_4$-H_2O, As(III)–H_2SO_4–$MeSO_4$–H_2O (where Me - Cu, Ni, Co, Mn, Zn). Trivalent arsenic was introduced into the studied systems in the form of sodium arsenite (0,011 gEq/l) and solid trioxide. The influence of temperature, the amount of transition metal ions, the duration of the experiment, and the concentration of sulfuric acid on the degree of transition of As(III) to As(V) was studied. Experiments were carried out with air blowing., Oxidation of As(III) in solutions, where dissolved oxygen was previously removed by blowing with an inert gas (argon), was also studied.

The oxidation process was carried out as follows: solutions of sulfuric acid and transition metal sulfates were introduced into a vessel with a $NaAsO_2$ solution, and the contents were stirred with a magnetic stirrer for a certain time. Air and argon were supplied into the solution under pressure while stirring.

To avoid the presence of atmospheric oxygen in the reaction zone, the experiments were carried out under sealed conditions with constant argon purging. Reagents for this purpose were preliminarily prepared in a box using transition metal salts that were twice recrystallized and dried in an argon atmosphere.

Quantitative determination of As(III) was carried out by amperometric titration.

We discovered the fact of instantaneous oxidation of As(III) in small quantities (up to 10%) when various amounts of sulfuric acid are added to the working solution. In this case, the content of sulfuric acid does not change in all experiments, i.e. the oxidation of arsenic (III) occurs with the participation of dissolved oxygen, and the fact of the instantaneous transformation of part of As(III) into As(V) is due to the catalytic nature of the process. The ability of H_2SO_4 to increase the rate of “spontaneous” oxidation of arsenic in solutions is indicated by the author of the work [8].

The effect of catalytic oxidation of As(III) is observed in all experiments when introducing transition metal salts into an arsenic solution. Moreover, in As(III)-$MeSO_4$-H_2O systems the degree of conversion reaches 25%.

It should be noted that in the systems As(III)-H_2SO_4-$MeSO_4$-H_2O (where Me - Cu, Ni, Co, Mn, Zn), the amount of instantly oxidized arsenic increases, and no significant dependence on the nature of the salt (among those studied) is observed (Table 1). The degree of transition of As(III) to As(V) depends on the concentration of metal ions and reaches its maximum at a molar ratio of Me:As(III) above (6÷9):1. Based on data [9] on the solubility of oxygen in aqueous solutions, it was determined that about 60-80% of dissolved oxygen is involved in the process of catalytic oxidation of trivalent arsenic.

The duration of the process and temperature do not play a significant role. This is evidenced by the following experimental data: within 6 hours after instant oxidation, the transition of As(III) to As(V) in the As(III)-H_2SO_4-H_2O system was about 6-7%, and in a solution, for example, containing 0,1 gEq/l of copper sulfate, the degree of conversion at temperatures of 22^0C, 40^0C and 60^0C was 34.5%, 34.8% and 36%, respectively. The results of experiments on the oxidation of As(III) in the presence of ions of other transition metals under study are relatively close to these data.

Table 1 - The degree of conversion of As(III) (%) in a sulfuric acid medium in the presence of transition metal ions and an adsorbing surface (Pt plate) when blown with air

($\overset{ucx}{C^{NaAsO_2}}$ = 0,011 gEq/l, $C^{H_2SO_4}$ = 0,12 gEq/l, t = 60^0C, τ = 3 hours)

Me	Concentration $C^{Me^{2+}} \cdot 10^{-2}$ gEq/l	Effect of catalytic oxidation, %	Oxidation state of As(III) in the presence of the ion Me^{2+}, %
-	-	4,21	29
Cu	4,8	21,4	51,9
	7,8	33,5	60,2
	9,8	33,8	60,1
Ni	4,8	32,9	49,4
	7,8	34,9	58,2
	9,8	34,9	57,7
Co	4,8	33,6	54,1
	7,8	31,7	58,6
	9,8	32,1	58,7
Mn	4,8	30	52,5
	7,8	30,8	55,3
	9,8	30	55
Zn	4,8	33,9	50,8
	7,8	34,8	55,2
	9,8	30,5	54,9

Our experiments have shown that blowing air through solutions has such a weak effect on the oxidation process in the systems under study that even for 3 or more hours, air bubbling both in the As(III)-H_2SO_4-H_2O system and in the system As(III)-H_2SO_4-$MeSO_4$-H_2O did not lead to significant oxidation of As(III). Varying the temperature in the range of 20-60^0C did not have a significant effect on the progress of the process.

In experiments with air blowing, the oxidation process of As(III) can be intensified at the liquid-solid interface due to the sorption of oxygen on it. In addition, the interface is an integral element of the copper electrorefining process, which to some extent brings the experimental conditions closer to production ones. We tested the effect of a platinum plate immersed in the reaction zone on the oxidation of As(III). This metal has the ability to adsorb oxygen on its surface and oxidation on such a surface occurs with the participation of oxygen from platinum oxides [10], according to the scheme:

$$AsO_3^{3-} + PtO[O] \rightarrow AsO_4^{3-} + PtO$$

Initially, the As(III)-H_2SO_4-H_2O system was studied with air blowing in the presence of a Pt plate. At the same time, at the initial moment, the oxidation of As(III) is a fairly intense process, which slows down over time. Thus, at a temperature of 21^0C in 2 hours the degree of conversion was 26,7%, and in the next 1,5 hours it increased by only 2%. Increasing the temperature of the working solution to 60^0C allowed us to speed up the process. In this case, the same amount of As(III) - 26.7% transforms into As(V) in 0,5 hours, and subsequent oxidation takes a long time.

Another factor that had a significant impact on the oxidation of As(III) in the presence of a Pt plate was the introduction of transition metal ions (Cu, Ni, Co, Mn, Zn) into the working solution, the ability of which to reversibly bind and activate oxygen is well known [11]. The highest degree of transition of As(III) to As(V) was recorded at a temperature of 60^0C. Within 3 hours, the percentage of conversion of trivalent arsenic reaches 55-60%, where the effect of catalytic oxidation is about 30-35%. These results (Table 1) are further evidence of the participation of atmospheric oxygen in the process of catalytic oxidation of As(III) in the presence of some transition metal ions. The importance of iron, copper and zinc ions in the oxidation of arsenic was also confirmed in works [12-14].

Therefore, if the presence of oxygen in the reaction zone is eliminated, the oxidation of As(III) should be practically absent. For this purpose, we conducted experiments with preliminary blowing of argon through a $NaAsO_2$ solution and a sulfuric acid solution of $MeSO_4$ (where Me is Cu, Ni, Co, Mn, Zn) before mixing them. The experiments were carried out at a temperature of 60^0C and constant bubbling with argon with stirring. Within 3 hours, we observed a slight decrease in the concentration of As(III), which was about 5%. In our opinion, the observed phenomenon is explained by the fact that blowing argon does not contribute to the complete removal of oxygen bound in the active complex. In our opinion, the activation of oxygen by transition metal ions occurs in the process of hydrolysis of these ions and complex formation. Thus, in an aqueous solution of $CuSO_4$, hydrated ions $[Cu(H_2O)_4]^{2+}$ are able to attach an oxygen molecule O_2 as a weak ligand, promoting its activation. Based on this, solutions of sulfuric acid and transition metal salts were prepared in an inert environment-box. Purge of trivalent arsenic solution with argon began 0,5 hour before mixing the solutions and was carried out throughout the experiment. Under the conditions of this experiment, the percentage of oxidation was 0,5% within 3 hours. Those. Despite a slight decrease in the degree of As(III) conversion under these conditions, we were not able to completely eliminate the presence of oxygen in the system.

The catalytic role of transition metal ions in the oxidation of arsenic is also evidenced by the results of our studies of the behavior of solid arsenic trioxide in sulfuric acid solutions in the presence of Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+} ions (Table 2). The dissolution of As_2O_3 in sulfuric acid solutions is a slow process with simultaneous oxidation of As^{3+} to As^{5+} in the liquid phase. As can be seen from Table 2, the influence of transition metal ions on the oxidation of solid arsenic trioxide is very significant. The degree of transition of As^{3+} to As^{5+} increases with increasing temperature of the reaction mixture.

Table 2 - Degree of conversion of As_2O_3 (%) in a sulfuric acid medium in the presence of transition metal ions (Me^{2+}) ($m^{As_2O_3}$ = 0,30 g, $C^{H_2SO_4}$ = 0,12 gEq/l, C_{Me2+} = 0,10 gEq/l, V = 50 ml, τ = 3 hours) depending on the temperature when blowing air

Temperature, ^{o}C	Degree of As_2O_3 conversion in the presence of Me^{2+}, %					
	-	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}	Zn^{2+}
20	0,04	14,9	13,6	14,1	13,5	12,8
40	0,084	26,4	23	24,9	24,8	21,1
60	0,12	58,2	54,9	56,4	56	52,1

Conclusions. Thus, the stage of the transition of arsenic from the trivalent to the pentavalent state occurs with the participation of atmospheric oxygen and occupies a central place in the process of anodic oxidation of elemental arsenic in sulfuric acid solutions in the presence of Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+} ions, and the nature of the studied transition metal salts does not have a significant effect on the degree of As(III) conversion. This property of some transition metal ions to catalytically oxidize As(III) was used by us later in the development of new methods for processing copper electrolyte with transition metal compounds with the removal of arsenic in the form of arsenates. In practice, preliminary introduction of transition metals into arsenic-containing solutions will allow the arsenic to be maximally converted into the pentavalent state, which will ensure their effective purification with the removal of arsenic in an environmentally safe form.

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