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FORMATION OF SELENIUM POWDERS IN CATHODE REDUCTION OF SELENITE IONS IN COPPER (II) HYDROCHLORIC ACID SOLUTION

Abstract. The work presents the results of the study of cathode reduction of selenium (IV) ions in hydrochloric acid medium in the presence of Cu (II) ions. The following electrolysis parameters were studied: concentrations of hydrochloric acid and copper (II) ions. In the course of the studies, it has been found that an increase in cathode current density and hydrochloric acid concentration leads to a decrease in the current yield of selenium powder. This exposure to hydrochloric acid is due to the fact that the formed copper monovalent ions are complexed with chlorine ions of type CuCl_n^{n-} , where the number "n" increases with an increase in the concentration of hydrochloric acid and, accordingly, this leads to a decrease in the reducing capacity of cuproions. The effect of copper (II) ion concentration has a positive effect on the current output of the powder formation of the investigated element. This is due to the increase in the concentration of intermediate products - monovalent copper ions.

It should be noted that under all optimal electrolysis conditions, little colloidal selenium powder is observed in the near-cathode space, due to the monovalent ions involved in the reaction. At high cathode current densities, partial formation of copper selenide is also observed. This is because freshly formed selenium and copper powder interact with each other to form metal selenide. Thus, the cathodic reduction of tetravalent selenium in hydrochloric acid solutions in the presence of divalent copper ions to form selenium powders was first investigated. It has been shown that an increase in copper (II) ion concentrations leads to an increase in the current yield of selenium powder and an increase in hydrochloric acid concentration leads to a decrease. The proposed "red-ox" Cu (II) - Cu (I) system allows electrocatalytic reduction of selenite ion to form ultradisperse selenium powders.

Key words: selenium, powder, recovery, selenite ion, copper (II).

Introduction. Selenium is a constant companion of many sulfide ores and concentrates of heavy and non-ferrous metals, isomorphic replacing sulfur, due to its high chemical activity, is present in raw materials, usually as selenides and in some cases as elemental [1]. The main industrial significance are sulfide deposits. The selenium content in sulfides ranges from 7 to 110 g / t. Global selenium reserves are estimated at ~90 thousand tons for copper deposits. Selenium is also found, for example, in coal and crude oil (from 0.5 to 12 ppm), as well as in seawater (4 ppm), which increases its global reserves by 80-90 times, but these resources are not currently involved in industrial turnover. It seems that in order to implement this technology, there must be a significant increase in selenium prices. The main industrial sources of selenium are slurries formed during electrolytic treatment of copper anodes. Copper slurries contain 5-25 % selenium in the form of compounds with noble metals. The main producers of selenium are countries such as Japan, Canada, Europe, the United States, China, Mexico and Russia [2].

The presence of a wide range of related metals and chemical elements in selenium-containing industrial products implies a variety of processing methods.

To date, the main amount of selenium (up to 90 %) is extracted from the electrolyte slurries of copper and Nickel production, which has led to the emergence of a large number of technological studies in this direction.

Under the guidance of Professor A. Bayeshov, numerous works were carried out and the electrochemical properties of selenium were studied in more detail [3-4]. It is shown that it is possible to

obtain selenium powder from tetravalent selenium ions when polarized by a cathode pulse current, and that it is possible to restore selenium (VI) anions in the presence of "red-ox" systems Ti (III)-Ti (IV), Cr (II)-Cr (III) and Fe (II)-Fe (III).

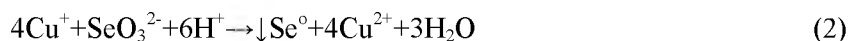
The standard potential (E^0) of the Cu (I) - Cu (II) system in hydrochloric acid solution is -0.54 V, and the potential of the Se-Se (IV) system is 0.77 V. This indicates that monovalent copper ions chemically reduce tetravalent selenium ions to an elementary state, while copper (I) ions are oxidized to a divalent state.

The divalent copper ions present in the solution at low cathode current densities are also reduced stepwise and mainly to the monovalent state by reaction:



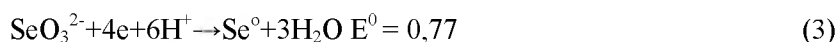
which can participate in the reaction of reducing selenite ions to elemental powdered selenium by reaction (2).

The monovalent copper ions formed by the reaction (1) according to the potentials of the above-mentioned redox systems Cu (I) - Cu (II) and Se-Se (IV), in the cathode space as well as in the volume of the solution, will enter into the chemical reaction of reducing selenium ions (IV):



at the same time, dispersed selenium powders of red-brown color are formed.

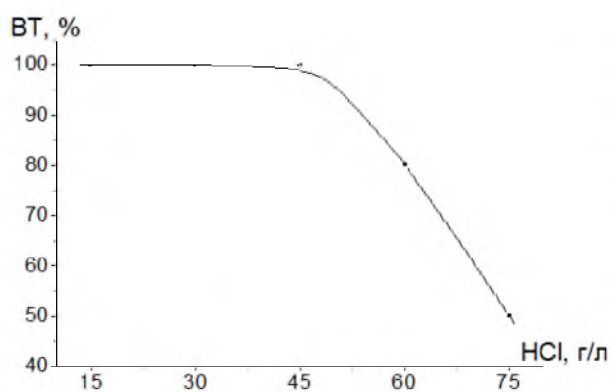
There is also a direct cathode reduction of Selenite ions at the cathode:



Experimental part. In this paper, the experiments were performed in an electrolyzer with a volume of 50 ml, the electrode spaces are not separated. A titanium plate was used as the cathode. The current yield of selenium powder was calculated by the weight of the resulting powder.

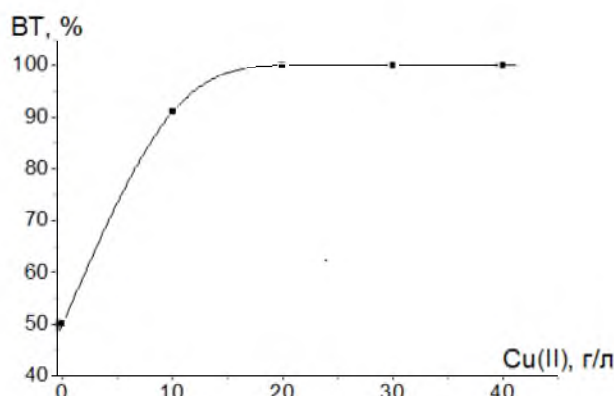
As can be seen from figure 1, increasing the concentration of hydrochloric acid leads to a decrease in the current output of the formation of selenium powder. This effect of hydrochloric acid is due to the fact that the formed ions of monovalent copper bind in a complex with chlorine ions of the CuCl_n^{n-} -type, where the number "n" increases with increasing concentration of hydrochloric acid and, accordingly, this leads to a decrease in the reducing ability of cuproions by reaction (2). All this in total leads to a decrease in the current output of the formation of selenium powder.

As can be seen from figure 2, with an increase in the concentration of divalent copper ions in the solution, the cathode yield of the selenium powder formation current increases. This is due to an increase in the concentration of intermediate products - monovalent copper ions.



$\text{Cu}^{2+} = 40 \text{ g/l}$; $\text{Se(IV)} = 10 \text{ g/l}$; $i = 50 \text{ A/m}^2$; $\tau = 30 \text{ min}$; $t = 20 \text{ }^\circ\text{C}$

Figure 1 – Effect of hydrochloric acid concentration on the current output of selenium powders formation



$\text{HCl} = 30 \text{ g/l}$; $\text{Se(IV)} = 10 \text{ g/l}$; $i = 50 \text{ A/m}^2$; $\tau = 30 \text{ min}$; $t = 20 \text{ }^\circ\text{C}$

Figure 2 – Dependence of the current output of selenium powders formation on the concentration of copper (II) chloride

Results and discussion. When the solution temperature increases from 20 to 60 $^\circ\text{C}$, the current output of selenium powder formation has a maximum current output of 100 %.

It should be noted that in all optimal conditions of electrolysis in the cathode space, a small amount of colloidal selenium powder is observed, this is due to the participation in the reaction of monovalent ions formed by the chemical reaction (1) and (2). At high cathode current densities, partial formation of copper selenide is also observed.

This is due to the fact that freshly formed selenium and copper powders interact with each other to form metal selenide:



Thus, for the first time, the cathode reduction of tetravalent selenium in hydrochloric acid solutions in the presence of divalent copper ions with the formation of selenium powders was studied. It is shown that an increase in the concentration of copper (II) ions leads to an increase in the current yield of selenium powder formation, and an increase in the concentration of hydrochloric acid leads to a decrease. The proposed "red-ox" Cu (II) - Cu (I) system allows electrocatalytically restoring selenite ions to form ultrafine selenium powders.

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**МЫСТЫҢ (II) ТҰЗ ҚЫШҚЫЛДЫ ЕРІТІНДІСІНДЕ
СЕЛЕНИТ-ИОНДАРДЫ КАТОДТЫ ҚАЛПЫНА КЕЛТІРУДЕ
СЕЛЕН ҰНТАҚТАРЫН ҚАЛЫПТАСТЫРУ**

Аннотация. Жұмыста Cu (II) иондарының қатысуы негізінде тұзды қышқылды ортада селен иондарын катодтық қалпына келтіруді зерттеу нәтижелері ұсынылған. Электролиздің мынадай параметрлері зерттелді: ерітіндінің температурасы, тұз қышқылы мен мыс (II) иондарының концентрациясы. Зерттеу барысында тұз қышқылының концентрациясы артатындықтан, селен ұнтағының пайда болу тоғының шығымы төмендейтіні айқындалды. Тұз қышқылының мұндай әсері бірвалентті мыстың түзілетін иондары CuCl_n^{n-} типті хлор-иондармен кешенге байланыстырылуына қатысты, мұнда «n» саны тұз қышқылының концентрациясының ұлғаюы негізінде өседі және тиісінше, бұл купроиондардың қалпына келтіру қабілетінің төмендеуіне әкеледі. Мыс (II) иондары концентрациясының әсері зерттелетін элемент ұнтағының пайда болу тоғына оң әсер етеді. Бұл аралық өнімдер, яғни, мыстың бір валентті иондарының концентрациясының ұлғаюына байланысты.

Айта кететін болсақ, электролиздің барлық оңтайлы жағдайларында катодтық кеңістікте селен коллоидты ұнтағының шамалы мөлшері байқалады, бұл бір валентті иондар реакциясына қатысуға байланысты. Токтың жоғары катодты тығыздығы кезінде мыс селенидінің жартылай түзілуі байқалады. Бұл жағдай селен мен мыс ұнтағы бір-бірімен өзара әрекеттесін, металл селенидінің пайда болуына әкеледі.

Түйін сөздер: селен, ұнтақ, қалпына келтіру, селенит-ион, мыс (II).

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**ФОРМИРОВАНИЕ ПОРОШКОВ СЕЛЕНА ПРИ КАТОДНОМ ВОССТАНОВЛЕНИИ
СЕЛЕНИТ-ИОНОВ В СОЛЯНОКИСЛОМ РАСТВОРЕ МЕДИ (II)**

Аннотация. В работе представлены результаты исследования катодного восстановления ионов селена (IV) в солянокислой среде в присутствии ионов Cu (II). Изучены следующие параметры электролиза: температура раствора, концентрации соляной кислоты и ионов меди (II). В процессе проведения исследований установлено, что увеличение концентрации соляной кислоты приводит к снижению выхода по току образования порошка селена. Такое воздействие соляной кислоты обусловлено тем, что образующиеся ионы одновалентной меди связываются в комплекс с хлор-ионами типа CuCl_n^{n-} , где число «n» возрастает с

увеличением концентрации соляной кислоты и, соответственно, это приводит к снижению восстановительной способности купроионов. Влияние же концентрации ионов меди (II) положительно сказывается на выходе по току формирования порошка исследуемого элемента. Это связано с увеличением концентрации промежуточных продуктов – одновалентных ионов меди.

Следует отметить, что во всех оптимальных условиях электролиза в прикатодном пространстве наблюдается незначительное количество коллоидного порошка селена, это связано с участием в реакции одновалентных ионов. При высоких катодных плотностях тока также наблюдается частичное образование селенида меди. Это связано с тем, что свежобразованный порошок селена и меди взаимодействуют друг с другом с образованием селенида металла.

Ключевые слова: селен, порошок, восстановление, селенит-ион, медь (II).

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REFERENCES

[1] Zhong L., Cao Y., Li W., Xie K., Pan W.P. Selenium speciation in flue desulfurization residues // Journal of Environmental Sciences. 2011. Vol. 23. 1. P. 171-176. DOI: 10.1016/S1001-0742(10)60390-7.

[2] Naumov A.V. A survey of the world market for selenium and tellurium (the economic of selenium and tellurium) // Russ. J. Non-Ferr. Metals. 2006. Vol. 47, N 4. P. 18-26.

[3] Bayeshov A., Ivanov N., Myrzabekov B. Electrochemical behavior of Selenium as part of Composite Electrode in Sulfuric Acid Medium // Journal of Advances in Chemistry. 2014. Vol. 7. N 3. P. 1378-1385. DOI: <https://doi.org/10.24297/jac.v7i3.2373>

[4] Bayeshov A., Kadirbayeva A.S., Bayeshova A.K., Zaykov Y.P. Formation of copper powders by anode and cathode half-periods of industrial alternating current // NAS RK's news. Geology and Technical Science Series. 2018 N 6. P. 73-79. DOI: 10.32014/2019.2518-170X.70