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Direct reduction of selenite-ions from a hydrochloric acid solution of copper (II) chloride with selenium powder formation

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Abstract. Research article presents an electrochemical method for obtaining selenium powder from compounds of 4-valent selenium in the presence of copper (II) ions. The electrolysis was carried out in an electrolytic cell with an unseparated interelectrode space in a hydrochloric acid solution containing copper chloride, where a copper electrode was used as the anode and a titanium electrode as the cathode. Cu (I) – Cu (II) redox pair potential difference was used as a reducing agent. Ultrafine selenium powder formation as a result of the chemical reduction of selenium (IV) ions by copper (I) ions obtained by anodic dissolution, as well as by the interaction of copper (II) ions with an anode was shown. Results of our study were presented, showing the influence of electrolysis conditions, current density, temperature of medium, acid concentration and copper (II) ion concentration during electrolysis on selenium formation current output, shape and size of the resulting powder. Study results demonstrate selenium powder formation with a very high current efficiency.

Key words: selenium, powder, copper, electrolysis, cathode, anode, micrograph.

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Introduction

Currently, selenium is widely used in the field of non-ferrous, ferrous metallurgy and machinery. Only a small amount of casting cast steel will allow the formation of fine granular steel, which prevents defects in the steel casting and provides high resistance to it. Magnesium-manganese alloy adds anti-corrosion properties of selenium alloy [1-3]. Selenium is also widely used as semiconductor in electrical engineering. But in this case, the cleanliness of the selenium is of great importance.

The selenium powder has increased its use. So, as additives to some of the stainless steel grades, the selenium improves their mechanical processing properties and prolongs the durability of the process. Another useful area of the powder canola is ceramic and glass production. Depending on the size of the

selenium, glass products give them a variety of colorful colors. Coloured glass products are widely used in the colour filters function in the colour alert system. This property of selenium is well-known in the engineering and chemical industries and has long been the main consumer of the selenium [1].

There are different methods of separating selenium from aqueous solutions. One of the known methods is the method of extracting powder by chemical reducing the selenium compounds (IV) [3]. Sulfur (IV) dioxide gas is used as a defibrer. At this point, the reaction is as follows: $H_2SeO_3 + 2SO_2 + H_2O \rightarrow Se^0 \downarrow + 2H_2SO_4$.

Preservation and use of sulfur dioxide gas (IV) causes a number of difficulties. At the same time, the work with toxic gas sulfur dioxide should be carried out in specially equipped sealed installations and must be strictly controlled by the fact that the amount

of toxic gas in the workplace does not exceed the high concentration without harm (0.02 milligram/liter). The selenium obtained on the basis of the above method should be gradually purified by processes of distillation. Due to these problems, this method is not widely used in production.

Known methods for extracting the selenium hexafluoride compound used for the removal of net selenium by reduction (at 60 ° C with potassium, sodium and lithium at 500 ° C) with alkali metal at 100 ° C, with arsenic at 180 ° C and silicon at 250 ° C [4, 5]. However, such methods are also produced in the gas environment and require high temperatures. This makes the technology more economically ineffective, complicating the process of the process.

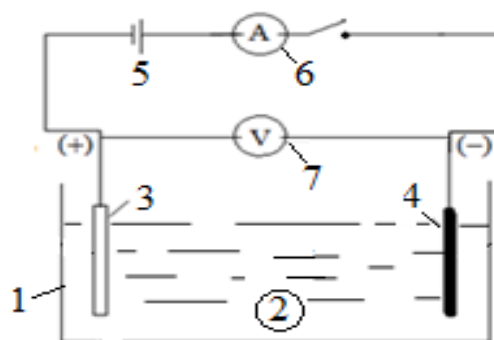
Certain reducing agents that adversely affect the environment or sophisticated equipment are used in selective methods used for selenium removal. As a result, many methods are economically or ecologically inefficient and can not be implemented at the production scale. In this regard, the research and analytical work aimed at increasing the efficiency of use of the method of extraction and reduction of ecological harm is one of the most important issues.

Methods

One of the most important methods for extracting selenium powders is electrochemistry methods in silicene cathodes [6-10]. Usually these methods use variable valent metal ions. Depending on the large differences in the oxidation-reduction potentials, the reduction of the selenium ions by using the Ti (III) -Ti (IV), Cr (II) -Cr (III) and Fe (II) -Fe (III) systems in the aqueous solution. This was mentioned in the scientific works of a professor Bayeshov A. B. [1, 7-10]. However, the oxidation-reduction catalytic systems were used only for the reduction of six valence selenium ions. The proposed scientific work suggests the method of obtaining selenium powder by reduction of selenium ions (IV) from aqueous solutions. The oxidation-reduction system of the copper Cu (I) -Cu (II) was used as the defibrillator. As known from a reference [11], the standard potential of Cu (I) -Cu (II) in the hydrochloric acid solution is +0,54 Volt, and the potential of Se-Se (IV) is + 0,77 Volt. As we have seen, the copper (I) ion, which has the potential to negate potential, reduces oxidative erythane (IV), which has the potential of positive potassium and gives rise to selenium powder.

In electrolysis, copper (II) chloride solution with hydrochloric acid, the electrode space with a volume of 50 ml was carried out in an unlit electrolysis device.

Electrodes are connected to a DC source, as anodes - copper and cathode - titanium plates (Figure 1).



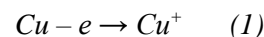
1 - Electrolysis device; 2 - Electrolyte (Se (IV) + HCl + CuCl₂); 3 - copper anode; 4 - titanium cathode; 5 - DC power source; 6 - ammeter; 7 - voltmeter.

Figure 1 The principal scheme of electrolyser used to obtain selenium powder

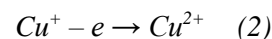
Results

In the solution (15-60 g / l) HCl (5-20 g / l) of Cu (II) and 10 g / l Se (IV) in various ($i = 50-200 \text{ A/m}^2$) current density, electrolysis was carried out in a half an hour and the current flows (CF) of the selenium powders were calculated and its electron-microscopic image was captured. In each of the electrolysis parameters, the powder was analyzed and the chemical composition and form of the powder were determined and the results were obtained.

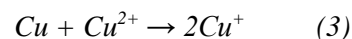
One valence copper ion formed during anode dissolution of a copper electrode and it passes step by step. [10]:



and



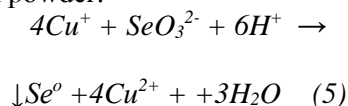
During electrolysis, low-current densities formed by reactions 1, 2, and copper (II) in electrolyte interact with copper anodes, form additional copper (I) ions:



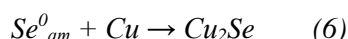
Copper (II) ions contained in the electrolyte are gradually reduced to copper (I) ions on the cathode surface. One valence copper ion is an intermediate product:



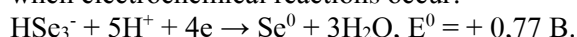
One valence copper ions, formed as a result of the above reactions, react with selenium ions and form selenium powder:



The results of the study showed that copper electrode in acetic acid copper (II) solution was coated with one valence copper ion based on reaction 3 and chemical deformation of the metal. As a result, the copper (I) ion that has been dissolved in the solution is formed as a result of reaction 5 with the selenium (IV) ion incorporating the solution into a solution of selenium powder. Since the formed atomic tributary is very active, copper anelite may also be formed by reacting with copper anode:



It should be noted that the amount of copper saline formed is relatively low. Electrolysis occurs when electrochemical reactions occur:

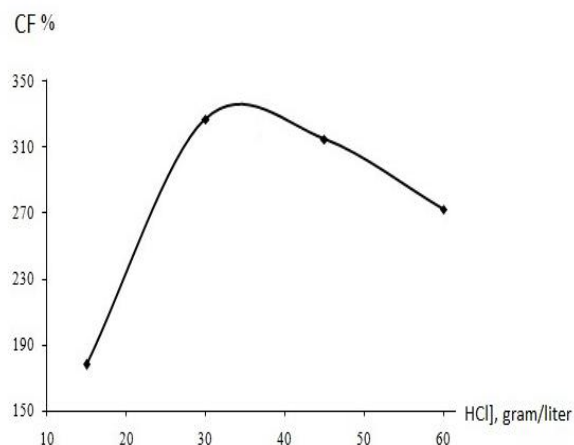


In addition, oxidized copper (II) ions form copper (I) ions by reaction 4 on the cathode surface. This, in turn, suppresses selenium (IV) ions on the surface of the cathode and in this region and forms additional selenium powder.

Discussion

In a stable situation (20 g/l Cu (II), 10 g/l Se (IV), $i = 200 \text{ A/m}^2$, $t = 20 \text{ C}^\circ$, $\tau = 0,5$) the amount of hydrochloric acid content in the electrolyte increases from 178% to 327% in the CF when growing from 15 gram/liter to 30 gram/liter concentration. It should be noted that in the known sulfuric acid solution [12], the stability of one valence copper ions is low, and in ionic acid solution it improves ion stability, as shown in Figure 2, the rate of formation of one valence copper ions based on 4-reactions increases with the increase of concentration of hydrochloric acid. Accordingly, the copper (I) ions precipitating in the solution, reduce oxides of selenium (IV) and increase the selenium powder. When the acid concentration is further increased by 60 gram/liter, the CFs decrease from 315 to 272.4% (Figure 2). The copper (I) ions formed by high concentrations of hydrochloric acid known in the references [12, 13, 14] form complex compounds such as chloride complexes:

$CuCl + nCl^- \rightarrow CuCl_{n+1}^{n-}$, where n - increases depending on the acid concentration. The number of chloride ions in the complex increases. At the same time, the complex ion charge also increases, accordingly the activity of the copper (I) ions decreases and the decomposable property decreases and the amount of powdered selenium powder is reduced. In subsequent studies, the influence of the concentration of copper (II), previously added to the electrolyte composition of Tselinol powder, was investigated. The results of the study are shown in Figure 2.



Cu (II) - 20 gram/liter, Se (IV) - 10 gram/liter, $i = 200 \text{ A/m}^2$,
 $t = 20 \text{ C}^\circ$, $\tau = 0,5 \text{ hour}$

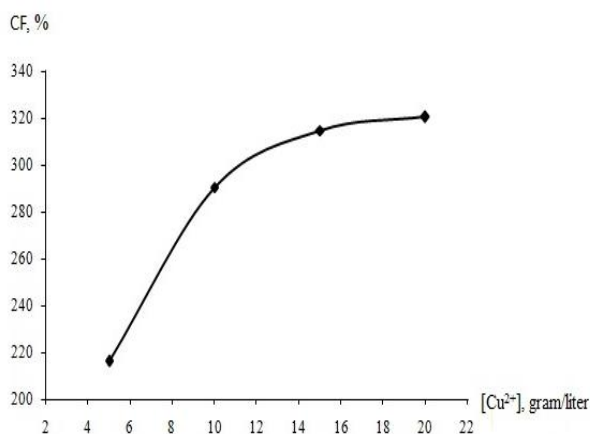
Figure 2 The effect of hydrochloric acid concentration on CF of selenium powder

As you can see from the picture, the value of CFs increased due to the concentration of copper (II) ions added to the electrolyte. The concentration of copper (II) in the electrolyte increased from 5 gram/liter at concentration to 20 gram/liter, CF increased from 216% to 320%. As mentioned above, the copper (II) ions are reacted to reaction 4 on the surface of the cathode to the copper (I) ions and, in addition, copper (I) ions are formed as a result of reaction 3, which reduces the ionic content of the selenium (IV) to the elementary state (reaction 5). In this regard, there is a sharp increase in CF of selenium powder formation. The result obtained without electrolysis, copper (II) ions being preheated electrolyte corresponds to the lowest result of the above data.

The effect of electrode density on electrode was investigated. The following figure 4 shows a decrease in CF when the current density increases.

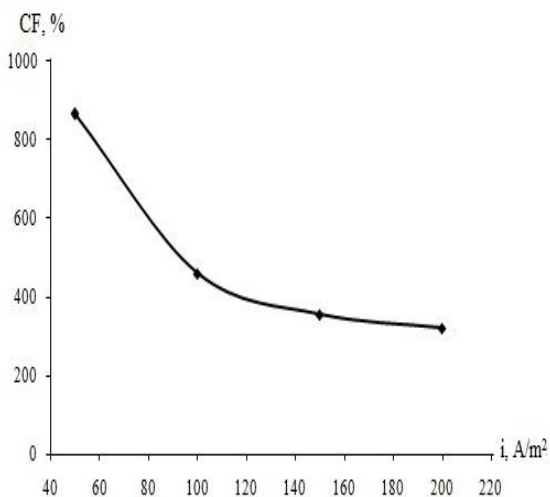
The current density of the electrodes changes the electrode potential in the Tafel equation. The potential of the copper electrode increases the density of the current with a considerable positive value. The shift of the electrode to the positive potential increases the ability of reaction 2 to increase the velocity of one valence copper ions formed at the first stage with two valence states. Accordingly, the value of CF decreases.

This phenomenon also occurs on the cathode surface and in the cathode area. In the high current density, the titanium electrode potential in the Tafel equation shifts to the negative value. In this case, the stability of the intermediate single valence ions decreases and they quickly pass to the metal state. These phenomena reduces the value of CFs generated by selenium powders.



HCl - 30 gram/liter, Se (IV) - 10 gram/liter, $i = 200 \text{ A/m}^2$, $t = 20 \text{ C}^\circ$, $\tau = 0,5 \text{ hour}$

Figure 3 Influence of copper (II) ion concentration in the electrolyte composition of selenium powder to CF



Cu (II) - 20 gram/liter, HCl - 30 gram/liter, Se (IV) - 10 gram/liter, $t = 20 \text{ C}^\circ$, $\tau = 0,5 \text{ hour}$

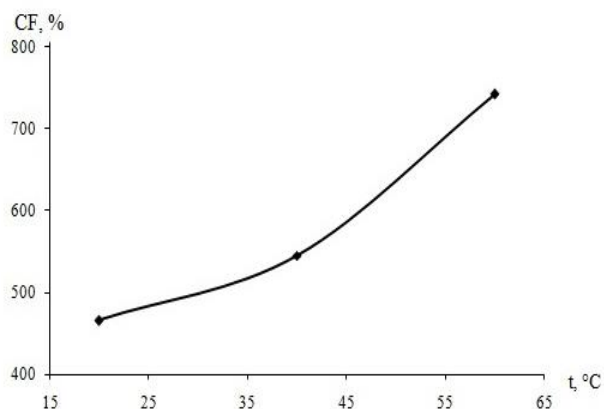
Figure 4 Influence of selenium powder on CF in electrodes density

The effect of temperature on selenium powder formation in CF was investigated. When the temperature increased from 20 C° to 60 C° , CF increased from 466% to 742% (Figure 5).

When the electrolyte temperature rises, the copper (I) ions of copper anode increases with the direct dissociation activity (reaction 1, 2), resulting in the formation of copper (I) ions, increasing the selenium powder content. Accordingly, there is a direct rise in temperature relative to the formation of powders in CF.

The powder was tested and the elemental analysis was performed during the above-mentioned parameters (Table 1). As a result of the analysis, the content of the powder contained in the sample was about 71 - 88.5 %. The copper content in the powder was 9,34 - 24,07 %. According to the analysis, the powder also contains copper selenium as well as pure selenium.

The formation of copper saline can be explained by the reaction 6. The microscopic images of the powders obtained are shown in Figure 6, the average size is 0.102 - 0.236 μm , it looks like the spheroid forms.

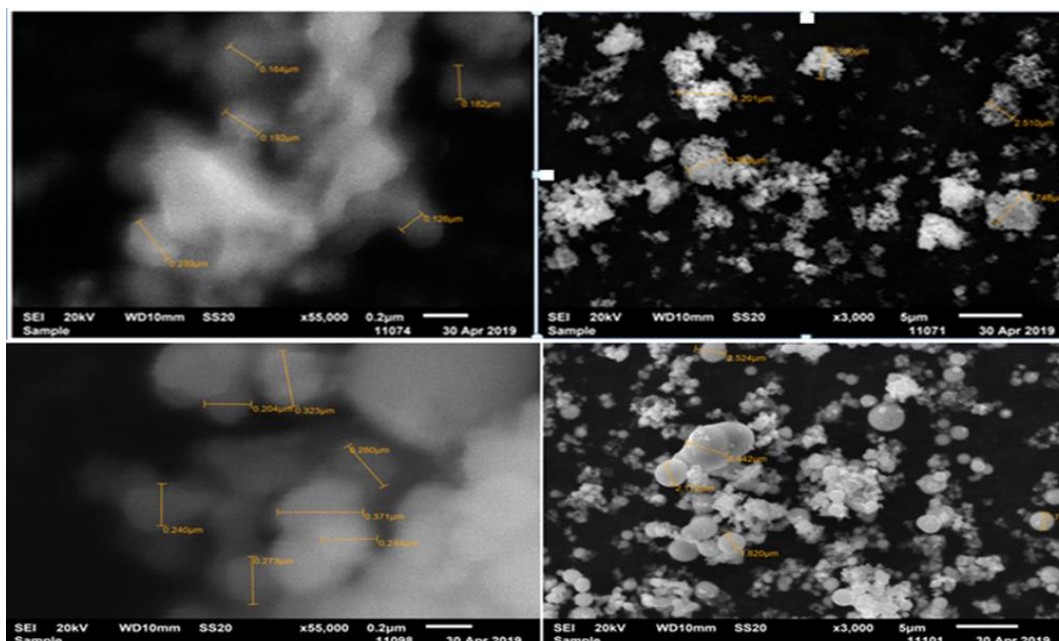


Cu (II) - 20 gram/liter, HCl - 30 gram/liter, Se (IV) - 10 gram/liter, $i = 100 \text{ A/m}^2$, $\tau = 0,5 \text{ hour}$

Figure 5 Influence of electrolyte temperature on selenium powder formation on CF

Table 1 Электролиз арқылы алынған ұнтаққа жүргізілген элементтік талдау нәтижесі

Experiment №	Electrolysis parameters				The result of the analysis				
	$i_0, \text{ A/m}^2$	[Cu ²⁺], gram/liter	[HCl], gram/liter	$t, \text{ C}^\circ$	O, %	Si, %	Cl, %	Cu, %	Se, %
1	200	10	30	20	1.99	0.08	3.47	9.34	85.12
2	50	20	30	20	1.01	0.17	3.75	24.07	71.00
3	200	20	60	20	0.77	0.05	0.88	11.17	87.13
4	200	20	30	60	0.44	0.13	1.44	9.43	88.5



Cu (II) - 20 gram/liter, HCl - 30 gram/liter, Se (IV) - 10 gram/liter, $i = 100 \text{ A/m}^2$, $\tau = 0,5 \text{ hour}$

Figure 6 Selenium powder microorganisms

Conclusion

At the present time, many products in the processing of rare and non-ferrous metals are packed with intermediate products and waste. Subsequently, separation of valuable substances from them is accompanied by acidic solution containing selenium ions. Removal of residual acid in the form of powder from the solution is still one of the unresolved issues. Our results show that saline acid can be obtained from copper (II) by removing selenium ions (IV) ions at anode, cathode, and electrolyte with very high current flow and can be used for selenium powders. It was discovered that copper selenium powders were formed. Anode and cathode on the surface show that when a large number of valence copper ions are

formed, they diffuse in the electrolyte volume and that there is an additional generation of selenium powders in the entire solution.

The proposed method is characterized by its simplicity of equipment and low environmental hazard because it is normally operated outdoors.

Acknowledgement

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Селенит иондарының қышқылды мыс (II) хлориді ерітіндісінде селен ұнтақтарын түзе тотықсыздануы

Баешов Ә.Б., Маханбетов А.Б.

Түйіндеме. Мақалада селеннің төрт валентті қосылыстарынан мыс (II) иондары қатысында селен ұнтағын алудың электрохимиялық әдісі ұсынылды. Электролиз, мыс (II) хлориді қосылған тұз қышқылы ерітіндісінде, электрод кеңістіктері бөлінбеген, мыс аноды мен титан катодынан тұратын электролизерде жүргізілді. Тотықсыздандырғыш ретінде Cu (I)-Cu (II) тотығу-тотықсыздану жүйесіндегі потенциалдар айырымы

пайдаланылды. Анодтық еру барысында және мыс (II) иондарының анодпен әрекеттесуі барысында түзілетін мыстың бір валентті иондары селен (IV) иондарын химиялық тотықсыздандырып, ультрадисперсті селен және кей жағдайларда мыс селенидінің ұнтағын түзетіндігі көрсетілді. Электролиз кезінде селеннің түзілуінің ток бойынша шығымына, түзілген ұнтақ формасына және розміне электролиз параметрлерінің – ток тығыздығының, ерітінді температурасының, тұз қышқылы концентрациясының және мыс (II) иондарының концентрацияларының әсерлері зерттеліп нәтижелері келтірілді. Зерттеу нәтижелері селен ұнтақтарының өте жоғары ток бойынша шығыммен түзілетіндігін көрсетті.

Түйін сөздер: селен, ұнтақ, мыс, электролиз, катод, анод, микросурет.

Восстановление селенит-ионов в хлоридно-кислом растворе меди (II) с образованием порошков селена

Башов А.Б., Маханбетов А.Б.

Аннотация. В статье представлен электрохимический метод получения порошка селена из соединений селена (IV) в присутствии ионов меди (II). Электролиз проводили в солянокислом растворе в присутствии хлорида меди, электролизере с неразделенными пространствами, где в качестве анода использовали медный, а в качестве катода -титановый электроды. Процесс восстановления протекает из-за разницы потенциалов в окислительно-восстановительной системе Cu (I)-Cu (II). Показано, что при анодном растворении и взаимодействии ионов меди (II) с анодом образуются ионы меди (I), которые химически восстанавливают ионы селена (IV) с образованием ультрадисперсных порошков селена. Приведены результаты, полученные при исследовании влияния таких параметров электролиза, как плотность тока, температура среды, концентрации ионов меди (II) и кислоты на выход по току образования селена при электролизе. Результаты проведенных исследований показали, что образуются порошки селена с высокими выходом по току.

Ключевые слова: селен, порошок, медь, электролиз, катод, анод, микрофотография

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