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**Комплексное
Использование
Минерального
Сырья**

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**Complex
Use of
Mineral
Resources**

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Concentration of rare-earth elements by sorption from sulphate solutions

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Abstract. Constantly increasing demand for rare-earth elements contributes to the involvement in the production of ore processing waste, the content of not extracted REE in which is quite large. One of the types of such waste is man-made mineral formations from the processing of phosphate uranium ores, which serve as raw materials for the production of REE concentrate at SARECO LLP. The technology for producing a concentrate includes the following redistribution: opening of raw materials cleaning of productive solutions from impurities; obtaining a concentrate on rare earth elements. One of the main disadvantages of this technology is the coprecipitation of almost 30% REE with ferrous cake when cleaning the most productive solution from impurities. To extract the rare earth elements ferrous cake is leached with sulphuric acid. The article studies the process of sorption from both model solutions that are similar in composition to the productive leaching of ferrous cake and directly from the productive ones, with the aim of further combining the resulting eluates with solutions supplied to precipitate REE. Considerable attention has been paid to disrupt by ammonium salts.

Key words: rare-earth elements, technogenic mineral formations (TMF), ferrous cake, sorption, desorption.

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Introduction

In connection with the recently increased demand for rare-earth elements, one of the urgent problems is the expansion of the list of raw materials that can be used as feedstock. The question of the use of waste production of rare and rare earth elements containing fairly high concentrations of unrefined REEs is being considered. One type of such waste is man-made mineral formations (TMF) from the processing of phosphate uranium ores, the content of which is the amount of REE is 5.0%.

Currently, REE concentrate is obtained from this raw material at SARECO LLP [1]. In the process of cleaning productive solutions obtained by leaching the raw material, ferrous cake is formed, with which a significant amount (up to 30%) of rare-earth elements co-precipitates. Ferrous cake is leached

twice with sulphuric acid to further extract REE. The consequence of combining the obtained solutions with the productive one after purification from impurities is an increase in the cost of oxalic acid for precipitating REE concentrate. When combining these solutions with the original producers - the material flows entering the filtering increase, which complicates the already problematic filtering unit. In this regard, we have studied the method of pre-concentration of rare-earth elements by sorption from solutions of leaching of ferrous cake.

Research methodology

The model solutions with La concentration - 0.75 g/dm³ (solution No. 1), model with concentration, mg/dm³ were used as initial solutions: La - 98.2; Y - 89.6; Dy - 58.0; Fe³⁺ - 101.4 (solution No. 2) And

leaching yielding ferrous cake of the following composition, mg/dm³: La - 98.2; Ce - 103.1; Dy - 58.0; Er - 27.2; Eu - 3.9; Gd - 65.4; Ho - 13.1; Lu, 5.1; Nd, 132.1; PR - 41.3; Sm - 34.6; Tb - 9.9; Tm - 4.7; Y - 89.6; Yb - 26.6; \sum REE - 712.8; Fe³⁺ - 4.01 g/dm³. When the ferric iron is reduced to the divalent state, according to the method [2], its concentration in the productive solution decreases and amounts to Fe³⁺ - 101.4 mg/dm³.

Sorption of lanthanum from model solutions was carried out in a static mode with the ratio S: L = 1: 500 for 8 hours, and productive in dynamic conditions in a 25 cm³ column at a speed of 50 cm³ / hour. In the course of the research, Sorbents KU-2-8n, C-100 "Purolite", Lewatit S1567, MTC-1600 "Purolite" were used. Rare-earth elements from the resin phase were eluted with ammonium sulphate and ammonium nitrate solutions in a static mode at an S: L ratio = 1: 50.

Methods of analysis

The quantitative content of rare-earth elements was determined on an atomic emission spectrometer with an inductively coupled plasma Optima 8300DV.

The results of researches

At the first stage, experiments were carried out on the sorption extraction of lanthanum (solution No. 1) From the model solution in order to select an ion exchange for subsequent studies. The results are shown in Figure 1, from which it can be seen that REE is more actively used from ion exchangers used, for example, lanthanum, absorbs KU-2-8n sulfo cation exchange. In subsequent studies, sulfonic cation exchange KU-2-8n was used for the sorption of REE.

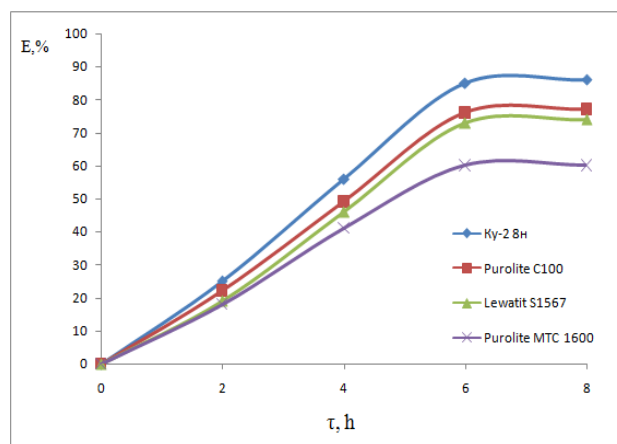


Figure 1 Lanthanum sorption from model solutions

From literary sources and our own experience it is known that ferric ions are the most negatively

affected by the process of sorption of rare earth elements. Earlier, we studied the behaviour of iron and its influence on the sorption of REE in binary systems Ln³⁺ - Fe³⁺ [3] with the same concentration of components. Considering that ferric iron is the main impurity in productive solutions from leaching of ferrous cake, we investigated its effect on the REE sorption from the model solution (solution No. 2), in which the concentration of rare-earth elements correlates with the concentration in the productive ones. The content of ferric iron, as indicated above, in the model solution is equal to its residual concentration in the productive solution after reduction to the bivalent state. The rare-earth elements in the model solution are represented by lanthanum, dysprosium and yttrium. Lanthanum and dysprosium were selected as typical representatives of the subgroups of light and heavy REE, and yttrium, as a specific representative of rare-earth metals, having no f-orbits. Sorption was carried out in static conditions, according to the method indicated above. Kinetic sorption curves are presented in Figure 2.

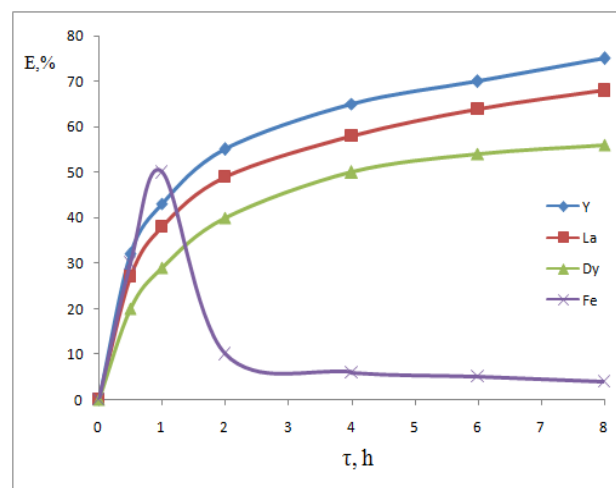
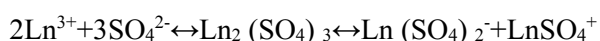


Figure 2 Sorption of rare-earth elements and iron from model solutions

As follows from the figure, the degree of sorption of rare earth elements gradually increases with time and decreases in the series Y - La - Dy. This dependence is associated with the magnitude of the ionic radius of rare-earth elements and their concentration. Iron during the first hour of the process is actively sorbed by the cationite, during the next two hours the speed of the process decreases sharply and remains almost constant. Thus, during the sorption of rare-earth elements in the presence of iron, the latter is actively sorbed at the beginning of the process, then the rate of sorption of rare-earth elements, which displace iron, increases. The process of ion exchange is characteristic not only for sorption, but also desorption. In the literature, there is information about the desorption of rare earth

elements by acids, salts, compounds, forming complexes with REE [4-7]. Previously, we studied the desorption process with sulphuric acid; it was shown that elution of rare-earth elements proceeds quite effectively with sulphuric acid with a concentration of 200 g/dm³. However, ammonium salts are of particular interest as eluates. In the literature, this issue gives considerable attention. For example, there is an ambiguous opinion regarding the use of ammonium sulphate. In literature [8], data on the study of the possibility of using (NH₄)₂SO₄ for desorption of lanthanides are given. It has been established that extraction of REE from the phase of cation exchanger KU-2-8n with a solution containing 30 wt. % (NH₄)₂SO₄, under dynamic conditions, is very effective. The degree of desorption of the sum of REEs in the described experiments reaches 87.1%. Other authors [9] indicate the difficulty of elution of REE with ammonium sulphate. The difficulties are due to the characteristic feature of the sulphates of rare-earth elements to form metastable supersaturated solutions. Equilibrium in such systems can occur for a long time and is described by the following equation:



The concentration shift of other ions in the solution certainly affects the equilibrium shift. For example, the presence of NH₄⁺ ions lowers the solubility of the resulting REE sulphates. In the resulting eluates, the source authors of references [9, 12] observed the formation of precipitates of the composition Ln₂(SO₄)₃ · 8H₂O. At a high concentration of eluent, crystallization began already in the layer of cation exchange, which made the desorption process difficult.

At this stage, we investigated the possibility of desorption of rare-earth elements by ammonium salts - sulphate and nitrate. To study the desorption process, the KU-2-8N ion exchange was pre-saturated with lanthanum from model solution No. 1. The content of lanthanum in the resin was 0.0027 Mol/g.

Further, a series of experiments on the desorption of lanthanum with ammonium sulphate solutions of different concentrations (g/dm³: 100, 200, 250, 300, 400) was carried out. Elution was carried out in a static mode, with a ratio of S: L = 1:50, room temperature and contact time of 120 minutes.

The obtained solutions after desorption were very unstable. The formation of fine crystalline precipitation was observed. An unequivocal conclusion was made about the unacceptability of using ammonium sulphate as eluent of rare-earth elements. Ammonium nitrate desorption was studied under conditions similar to ammonium sulphate.

Figure 3 shows the dependence of the degree of elution of lanthanum on the concentration of ammonium nitrate.

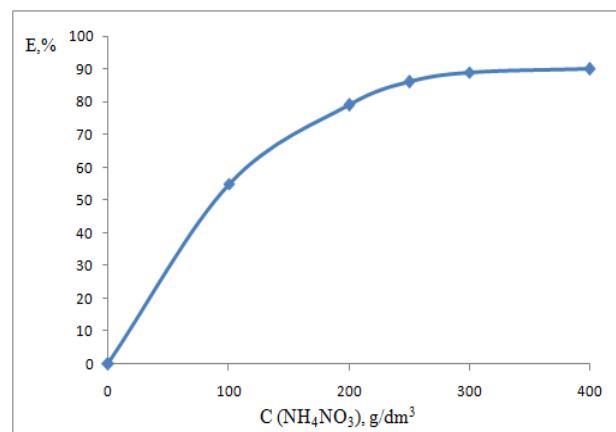


Figure 3 Dependence of changes in the degree of elution of lanthanum on the concentration of ammonium nitrate

From the figure it follows that the value of the degree of elution of lanthanum increases sharply with an eluent concentration of 300 g/dm³ and then varies slightly, desorption with ammonium nitrate is advisable to keep the solution with a concentration of 300 g/dm³. Further, in the course of research, the dependence of the degree of elution of REE, using lanthanum, as an example, from the cation exchange KU-2-8-n solution of ammonium nitrate with a concentration of 300 g/dm³ on the phase contact time was studied. The results are presented in Figure 4.

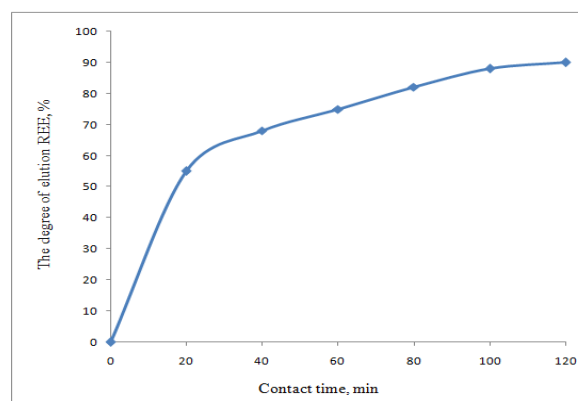


Figure 4 Change in the degree of elution of lanthanum from the phase of cation exchanger KU-2-8-n in time

Thus, from the conducted studies and the obtained results, it follows that the REE sulfonic cation exchange KU-2-8n absorbs most effectively from the tested ion exchangers. It is advisable to conduct the elution from the sulfocationite phase with a solution of ammonium nitrate with a concentration of 300 g/dm³. The sorption rate of individual REEs depends on both their ionic radius and concentration.

Conclusions

In order to determine the prospects of sorption concentration of rare-earth elements from solutions from leaching of ferrous cake, in the first stage, the ion exchange was chosen for REE sorption. The study of the sorption of lanthanum ionites KU-2-8n, C-100 "Purolite", Lewatit S 1567, MTC-1600 "Purolite" found that the lanthanum suffocation exchange KU-2-8n was more efficiently absorbed among the studied. The study of sorption from a model solution, in which the content of individual REE and iron correlates with the productive one, showed a decrease in the degree of sorption in the series Y-La-Dy, which is associated with the ionic radius of rare-earth elements and their concentration. The iron present in the solution is actively sorbed at the beginning

of the process (it can give figures from and to), then the rate of sorption of REE, which displace iron, increases.

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Күкірт қышқылды ерітінділерден, сирек кездесетін элементтерді сорбциямен концентрлеу

Кенжалиев Б. К., Суркова Т.Ю., Есімова Д.М.

Түйіндеме. Сирек кездесетін элементтер сұранысының куннен-кунге өсуі, кен қалдықтарын қайта өңдеу өндірісіне мүмкіндік береді, демек бөлінбеген СКЭ үлестері анағұрлым жоғары. Осындай қалдықтардың біріне, фосфатты уран кендерін қайта өңдегенде пайда болатын техногенді минеральды түзілімдер (ТМТ), яғни бастапқы шикізат ретінде «SARECO» ТОО-ғы СКЭ концентратын алу жатады. Концентрат алудың технологиясы, келесідей: бастапқы шикізатты ашу; өнімді ерітінділерді кірмелерден тазалау; сиреккездесетін элементтердің концентрациясын алу бөлімдерінен тұрады. Бұл технологияның негізгі кемшіліктерінің бірі, кірмелерден өнімді ерітіндіні тазартқан кезде темірлі кекпен бірге 30 % бірге шөгіледі. Сирек кездесетін элементтерді қайтадан бөліп алған жағдайда, темірлі кекті күкірт қышқылымен шаймалайды. Мақалада, СКЭ концентратын тұндыруға жөнелтетін, әрі арықарай ерітіндімен бірге элюаттарды алу мақсатында, темірлі кекті шаймалағандағы өнімнің құрамына жақын модельді ерітіндімен және тікелей өнімнің сорбциялық үрдісі зерттелінді. Десорбцияда, аммоний тұздарына аса көңіл бөлінді.

Түйінді сөздер: сирек кездесетін элементтер, техногенді минеральды түзілімдер (ТМТ), темірлі кек, сорбция, десорбция.

Концентрирование редкоземельных элементов сорбцией из сернокислых растворов

Кенжалиев Б. К., Суркова Т.Ю., Есімова Д.М.

Аннотация. Постоянно увеличивающийся спрос на редкоземельные элементы способствует вовлечению в производство отходов переработки руд, содержание не извлеченных РЗЭ в которых достаточно велико. Одним из видов таких отходов являются техногенные минеральные образования от переработки фосфатных урановых руд, которые служат исходным сырьем для получения концентрата РЗЭ на ТОО «SARECO». Технология получения концентрата включает следующие процессы: вскрытие исходного сырья; очистка продуктивных растворов от примесей; получение концентрата редкоземельных элементов. Одним из основных недостатков данной технологии является соосаждение почти 30% РЗЭ с железистым кеком при очистке продуктивного раствора от примесей. Для доизвлечения редкоземельных элементов железистый кек выщелачивают серной кислотой. В статье изучен процесс сорбции как из модельных растворов, близких по составу продуктивным от выщелачивания железистого кека так и непосредственно из продуктивных, с целью дальнейшего объединения получаемых элюатов с растворами, поступающими на осаждение концентрата РЗЭ. Уделено значительное внимание десорбции солями аммония.

Ключевые слова: редкоземельные элементы, техногенные минеральные образования (ТМО), железистый кек, сорбция, десорбция.

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Leaching of gold-containing ores with application of oxidation activators

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Abstract: The Article presents the results of studies conducted to process gold-bearing rocks from one of the fields in Kazakhstan. We studied a phase of the chemical and mineral composition of the ore using semi-quantitative X-ray fluorescent, chemical (assay), electron raster and rational (phase) analysis. We found that the test sample contained 1.4 g/t Au and 0.14 g/t Ag. The granulometric analysis showed that the main gold (36.51%) was concentrated in a class of -2.5 +1.25 mm size, with 1.42 g/t gold content. The main components of the initial sample composition were quartz 38.9%, albite 20.3%, pyrite 5.8%. We studied the gravity recovery possibility of gold-bearing ore using laboratory equipment, i.e. Knelson KS-MD 3 centrifugal concentrator. We obtained a gold-containing concentrate with 6.04 g/t gold content on a centrifugal concentrator with extraction of 52.65%, and 0.82 g/t gold in gravity tailings under the one-stage recovery flow sheet. We determined the optimal leaching parameters for the recovery products (gravity concentrates and gravity tailings) using various oxidation activators. The gold recovery degree was 77.3% with direct gravity concentrate cyanidation, and 85.7% with preliminary oxidation using calcium hypochlorite increasing the gold recovery degree by 8.4%, when leaching the gravity tailings using calcium hypochlorite -73.1%, sodium peroxide - 75.6%, Ascor oxidation activator (AS-45102) - 71.9%.

Key words: gold-bearing rock, leaching, gravity concentrates, gravity tailings, recovery, oxidation activator.

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Introduction

Modern and highly efficient technologies for their recovery are required due to the depletion of alluvial gold and silver deposits and the use of raw materials with a low content of valuable components and complex composition during the processing [1]. These ores are characterized with the presence of free, very fine gold uniformly distributed in the ore [3]. There are three main ways to process raw materials depending on the mineralogical composition of the ores and the size of gold in them:

gravity concentration; flotation recovery; gold leaching with pre-oxidation [4]. Cyanides forming highly soluble complexes of gold and silver are now widely used to leach gold-bearing ores and concentrates [5]. An active search for alternative cyanide reagents and ways to intensify the precious metals recovery process from ores has been conducted within recent years due to the cyanidotoxicity and the complex composition of the feedstock [2].

One of the important issues in the gold ore treatment is the pre-oxidation of the sulphide part for more complete

gold recovery. The use of oxidation activators, such as sodium peroxide and calcium hypochlorite, promotes the gold leaching from refractory sulphide raw materials. The implementation of the intensive cyanidation process for gravity concentrates and gravity tailings in the presence of activator reagents enables to increase the efficiency of gold-bearing rocks processing significantly.

The purpose of this study is to develop a method to leach gravity concentrate and gravity tailings using various oxidation activators.

Experiment and discussion of the results

We used a representative sample of the original ore from one of the deposits in Kazakhstan. A chemical analysis was carried out using a mass spectrometry method with the help of Varian Optical Spectroscopy Instruments atomic absorption spectrometer with an inductively coupled plasma. The research results showed the following elemental composition in %: 1.95 Fe; 0.46 S; 0.19 Cu; 0.52 Zn; 0.033 As; 1.45 ° C; 1.6 g/t Au, 0.14 g/t Ag.

It was found under the rational analysis results (Table 1) that 46.43% gold was found in this sample in a bound form, in association with sulfides, 25.0% in intergrowths and 25.0% in visible fine-dispersed native form (native gold).

X-ray phase analysis was performed using a D8-ADVANCE BRUKER X-ray diffractometer. X-ray phase analysis data (Table 2, Figure 1) of the sample showed that the main components of the initial sample phase composition were quartz 38.9%, albite 20.3%, pyrite 5.8%.

The electron microscopic analysis of ore (Figure 2) was performed using an electron scanning microscope with a JEOLJXA-8230 electron probe microanalyzer (JEOL, Japan). It follows from the results obtained that gold, and the silver, iron, sulphur carbon are present in the sample microstructure. The form of gold grains is lamellar, irregular, isometric.

Table 1 Results of rational (phase) analysis of the original ore sample.

Gold Forms in Tailing	Gold distribution	
	g/t	%
Free gold with a clean surface at 90% class minus 0.071 mm	0.35	25.0
Gold in intergrowths (cyanidable)	0.35	25.0
Gold associated with sulphides	0.65	46.43
Gold in minerals and quartz insoluble in nitrohydrochloric acid	0.05	3.57
Total gold	1.4	100.0

Table 2 X-ray phase analysis of the original ore

Наименование	Formula	%
Quartz, syn	SiO ₂	38.9
Albite (heattreated)	Na(AlSi ₃ O ₈)	20.3
Riebeckite	Na ₂ (Fe ²⁺ ₃ Fe ³⁺ ₂)Si ₈ O ₂₂ (OH) ₂	9.7
Clinochlore 1M1a	Mg _{2.5} Fe _{1.65} Al _{1.5} Si _{2.2} Al _{1.8} O ₁₀ (OH) ₈	7.3
Pyrite, arsenian	Fe(S _{0.99} As _{0.01}) ₂	5.8
Calcite	Ca(CO ₃)	4.6
Dolomite	CaMg(CO ₃) ₂	4.2
Orthoclase	(K _{.88} Na _{.10} Ca _{.009} Ba _{.012})(Al _{1.005} Si _{2.995} O ₈)	3.9
Muscovite 2M1, syn	KAl ₃ Si ₃ O ₁₀ (OH) ₂	3.2
Clinoptilolite	(Na _{.K} .Ca) ₂₋₃ Al ₃ (Al _{.Si}) ₂ Si ₁₃ O ₃₆ ·12H ₂ O Na _{4.12} Si ₃₆ O ₇₂ (H ₂ O) _{23.12}	2.3

Table 3 Results of the gold distribution by size class

Size classes, mm	Classes yield %	Gold content, g/t	Gold distribution %
-2.5+1.25	36.0	1.42	36.51
-1.25+0.8	19.0	1.5	20.36
-0.8+0.5	13.6	1.59	15.45
-0.5+0.25	13.6	1.2	11.66
-0.25+0.1	14.6	1.3	13.56
-0.1+0.071	2.2	1.1	1.73
-0.071	1.0	1	0.71
Total	100.0	1.4	100.0

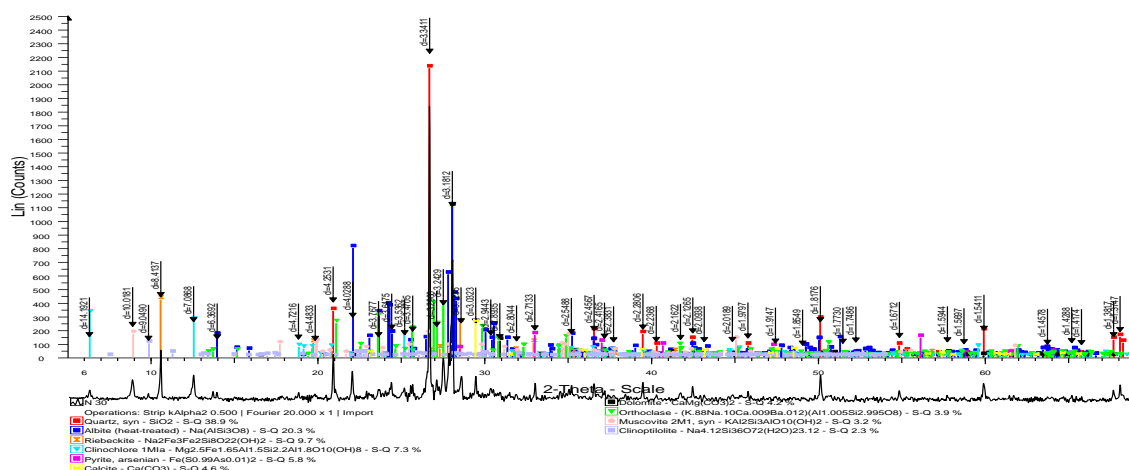


Figure 1 The results of x-ray phase analysis of ore samples

It was revealed under the results of the particle size analysis that the main ore fractions were represented by a particle size of $-2.5 +1.25$ and $-1.25 +0.8$ mm; the yield was 36.51 and 20.36%, respectively (Table 3).

Thus, the physical and chemical studies of the original ore showed that the gold content in the ore sample was 1.4 g/t, including 46.43% of gold in a bound form in association with sulphides, 25.0% in intergrowths, and 25.0% of the visible fine-grained native form (native gold). The phase composition was mainly represented by quartz - 38.9%, albite - 20.3%, pyrite - 5.8%. According to the particle size analysis, the main ore fractions were represented by a particle size of $-2.5 +1.25$ and $-1.25 +0.8$ mm, the yield was 36.51 and 20.36%, respectively.

Gravity recovery is widely used to process gold ores.

The method of gravity concentration using centrifugal concentrators is one of the effective gravitational recovery methods for gold-bearing ores enabling to extract free not only large, medium and fine, but also thin and dusty gold from ores.

We carried out gravity recovery tests using ore with a particle size of 85% of the 0.071 mm class (Table 4).

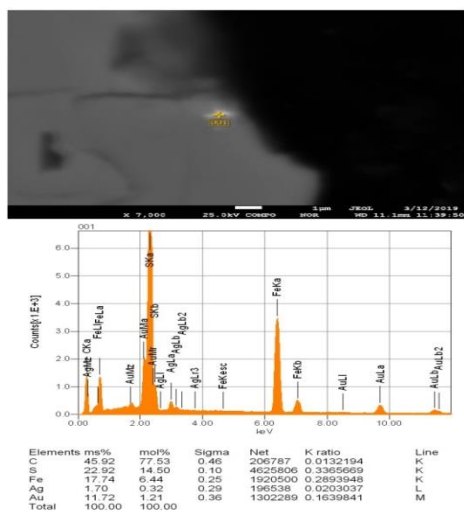


Figure 2 Electron-microscopic analysis of ore

Gravity recovery was carried out using a 3-inch Knelson KS-MD 3 centrifugal concentrator.

Selection of the gravity concentration mode for the ore sample:

Gravity recovery parameters:

- Centrifugal acceleration 60 G;
- Fluidising water flow rate 3.5 l/min;
- Solids intake 0.5-0.6 kg/min;
- Fluidising water excessive pressure 15 kPa;
- Solids content in the pulp supplied to the gravity concentration, 25-30%.

Table 4 Results of the original ore gravitational recovery

Product Name	Yield		Au content, g/t	Au recovery, %
	г	%		
Concentrate	558	13.95	6.04	52.65
Tailings	3442	86.05	0.82	43.75
Total	4000.0	100.0	1.4	100.0

Under the gravitational recovery results of the ore specified in the Table, the yield of gold-bearing concentrate was 14% with gold content - 6.04 g/t and gold recovery was 52.65%, gravity tailings contained 0.82 g/t.

We leached the concentrates and gravity recovery tailings by direct cyanidation, as well as using oxidizing agents: calcium hypochlorite ($\text{Ca}(\text{ClO})_2$), sodium peroxide (Na_2O_2), and Ascor oxidation activator (AS-45102). It should be noted that the preliminary oxidation studies considered in scientific papers [11–14] showed high efficiency of the reagents used.

Cyanation products were subject to atomic absorption and assay (cake) analysis methods. We studied the cyanidation dynamics (with direct cyanidation and in the presence of oxidizing agents), controlled the sodium cyanide concentration and the pulp pH during the tests. The cyanide leaching parameters and results are shown in Tables 5-6.

Table 5 Gravity concentrate cyanidation mode

Parameter	Unit of measurement	Value
Grain size	mm	
W:Tratio = (1:3)	g/ml	100:300
Cyanide concentration	%	0.1
Cyanation duration	h	24
Температура	°C	22
With air supply		+
Medium value	pH	11.2 – 11.5

It follows from the data in Tables 5 and 6 that the process conditions (Table 5) enable to achieve 77.3% gold recovery from the concentrate during direct cyanidation and with 90% particle size of 0.071 mm

class, as well as with 0.1% sodium cyanide concentration, 85.7% for cyanidation with preliminary oxidation with calcium hypochlorite, i.e. ore pre-oxidation contributes to an increase in the gold recovery degree by 8.4%. A method was proposed to process the refractory gold-bearing ore from the Kazakh deposit based on the studies conducted.

Table 6 Results of gravity concentrate cyanidation tests

Names	Parameters	
	Test 1	Test2
Sample weight, g	70	70
Solution volume, ml	280	280
NaCN concentration, %	0.1	0.1
pH	10.7	11.03
Duration, h	24	24
Type of oxidizer, g		1.0 Ca(ClO) ₂
With air supply	+	+
Au content in the initial conc. under assay analysis, g/t	6.04	6.04
Au content in cake, g/t	1.37	0.86
Au recovery rate from cake, %	77.3	85.7

Conclusion

Thus, the best leaching parameters for gravity tailings were obtained by preliminary oxidation with such reagents as Na₂O₂ and Ca(ClO)₂, i.e. 75.6% and 73.1%, respectively, and pre-oxidation increased the gold recovery degree by 8.4% when leaching gravity concentrate indicating the sulfide oxidation efficiency. The maximum gold recovery degree of gravity concentrate was 85.7%.

A method was proposed to process the refractory gold-bearing ore from the Kazakh deposit based on the studies conducted.

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Байытылған өнімдерді тотықтырғыш қосып шаймалап алтынды бөліп алу

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Түйіндеме. Мақалада Қазақстанның алтынқұрамды шикізатты өңірлерінің зерттеу нәтижелері келтірілген. Сынама алынып кендердің фазалық құрамы зерттелді. Жартылай сандық рентгендік флуоресцентті, химиялық (талдау), электронды-растрлық және рационалды (фазалық) талдауды қолдану арқылы кендердің химиялық және минералды құрамы берілген. Сынақ үлгісінде 1,4 г/т Au және 0,14 г/т Ag бар екендігі анықталды. Гранулометриялық талдау көрсеткендей, алтынның негізгі бөлігі (36,51%) мөлшері -2,5 +1,25 мм мөлшерінде шоғырланған, алтын мөлшері 1,42 г/т. Бастапқы сынаманың негізгі фазалық құрамы кварц - 38,9%, альбит - 20,3%, пирит - 5,8%. Рентгендік флуоресцентті талдау нәтижелері бойынша кремний сынамадағы басымдыққа ие екендігі анықталды. Зертханалық құрал-жабдықтарды пайдалана отырып, алтыннан алынған кендерді гравитациялық байыту мүмкіндігі: Центрифугалық центрифугалаушы Knelson KS-MD 3 бір сатылы байыту схемасына сәйкес, алтынның құрамында 6,04 г/т болатын центрифугалық концентраторда 52,65%, гравитациялық қалдықтарда - 0,82 г/т алтын мөлшерін құрады. Байыту өнімдерінің оңтайлы шаймалау параметрлері (гравитациялық концентрат және гравитациялық қалдықтар) түрлі тотығу активтендіретін реагенттерді пайдаланып көрсетілген. Ең жоғары көрсеткіштер гравитациялық концентраттың тікелей цианидтеу кезінде алтын өндіру дәрежесі 77,3% құрады; кальций гипохлоритімен алдын-ала тотықтырумен 85,7%, ол алтын өндіру дәрежесін 8,4% -ға арттырады. Гравитациялық қалдықтарды шаймалау кезінде кальций гипохлоритін пайдалану арқылы - 73,1%, натрий пероксиді 75,6%, AS-45102 - 71,9% құрайды.

Түйін сөздер: алтынқұрамды шикізат, шаймалау, гравитациялық концентрат, гравитациялық қалдықтар, алу, тотығу активатордар.

Извлечение золота выщелачиванием продуктов обогащения с применением окислителя

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Аннотация. В статье приведены результаты исследований переработки золотосодержащего сырья одного из месторождений Казахстана. Изучены фазовый химический и минеральный составы руды с применением рентгенофлуоресцентного полуколичественного, химического (пробирного), электронно-растрового и рационального (фазового) анализов. Установлено, что в исследуемой пробе содержится 1,4 г/т Au и 0,14 г/т Ag. Гранулометрический анализ показал, что основная масса золота (36,51 %) сосредоточена в классе крупности -2,5 +1,25 мм, при содержании золота 1,42 г/т. Основные компоненты фазового состава исходной пробы - кварц 38,9 %, альбит 20,3 %, пирит 5,8 %. Изучена возможность гравитационного обогащения золотосодержащей руды

с использованием лабораторного оборудования: центробежного концентратора Knelson KC-МД 3. По одностадийной схеме обогащения на центробежном концентраторе получен золотосодержащий концентрат с содержанием золота 6,04 г/т при извлечении 52,65 %, в хвостах гравитации содержится 0,82 г/т золота. Показаны оптимальные параметры выщелачивания продуктов обогащения (гравитационного концентрата и хвостов гравитации) с применением различных реагентов-активаторов окисления. При прямом цианировании гравитоконцентрата степень извлечения золота составило 77,3 %, с предварительным окислением гипохлоритом кальция 85,7 %, что повышает степень извлечения золота на 8,4 %, при выщелачивании хвостов гравитации с применения гипохлорита кальция -73,1 %, пероксидом натрия - 75,6 %, активатора окисления Ascog (AS-45102) - 71,9 %.

Ключевые слова: золотосодержащее сырье, выщелачивание, гравитационный концентрат, хвосты гравитации, извлечение, активатор окисления.

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Physical and chemical researches of nickel-cobalt concentrates made from wastes of heat-resistant nickel alloys

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Abstract. The wastes of rhenium-containing heat-resistant nickel alloys (HRNA) contain 50-75% of Ni, 3-15% of Co. While electrochemical processing of the wastes of the HRNA up to 80-90% of Re, Ni and Co passes into the solutions, and a small part of them remains in the anode slurry. The remaining part of the metals from the slurry is chemically dissolved into the solution. After electrochemical treatment of wastes and chemical dissolution of slurry the solutions are combined and Re is extracted from them. The Ni – Co concentrate was precipitated (until a pH of 8–9 was established, at a temperature of 40 °C, by intensive stirring for 1 h) from the raffinate (g/dm³: 14.26 Ni; 2.48 Co) after the extraction of Re by NaOH (500 g/dm³) solution. Physical and chemical studies of the concentrate using X-ray fluorescent, X-ray phase, thermogravimetric and X-ray methods showed that it contains the following phases, wt. %: 62.6 Na₂SO₄; 37.4 Ni₂(NO₃)₂(OH)₂ • 2H₂O and Co(OH)₂. Washing the concentrate from sodium by water at L:S = 10: 1 ratio allowed reducing its mass (~ 2.4 times), reducing the content of sodium, increasing the content of Ni (from 15.68 to 37.55 %) and Co (from 1.89 to 4.48%). When the concentrate is annealed in the temperature range of 300-400 °C, the processes of dehydration of the hydroxides of Ni and Co and their transition to the oxide forms occur. The resulting concentrate can be sent for further processing in order to extract non-ferrous metals from it or used to produce some ferroalloys.

Key words: wastes of HRNA, raffinate, Ni-Co concentrate, precipitation, washing, annealing.

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Introduction

Nowadays, the general metal production faces an obstacle in the efficient and integrated use of secondary raw materials that is becoming

increasingly important both world wide and in the Republic of Kazakhstan.

Heat-resistant alloys have been widely used as a special type of structural materials in recent years, connected with the development of various

areas of technology. Heat-resistant nickel-based alloys are of particular importance, which include rare and trace elements: rhenium, tungsten, molybdenum, tantalum, niobium, hafnium. Such alloys are widely used in the aerospace industry, nuclear and thermal power, mechanical engineering and petrochemistry [1].

Now the world has accumulated a large amount of the wastes of heat-resistant nickel alloys (HRNA) in the form of scrap parts, with expired service life. The high cost of heat-resistant nickel alloys containing expensive metals (rhenium, tantalum, cobalt, etc.), required to solve the problem of efficient and complex processing of these materials.

Current technologies for the processing of wastes of HRNA can be divided into 4 groups:

- direct pyrometallurgical wastes processing [2];
- oxidative-thermal technologies [3, 4];
- hydrochemical technologies [5, 6];
- electrochemical technologies [7, 8].

Electrochemical methods are often suggested to use for the lump scraps based on the anodic dissolution of the material under the direct or alternating currents transferring either rhenium or a nickel alloy base into solution with the rhenium concentration in the anode slurry [9-10].

Analysing scientific, technical and patent literature has resulted in the present increasing interest of researches in the field of integrated processing of HRNA wastes due to the growing amount of such wastes, which is a valuable secondary raw material.

HRNA generally contain from 50 to 75 wt. % of nickel, from 3 to 15 wt. % of metals such as cobalt, chromium and, aluminum if required, as well as from 1 to 10 wt. % of one or several elements of tantalum, niobium, tungsten, molybdenum, rhenium, platinum, and hafnium series [11].

Therefore, it is also of interest to extract other valuable non-ferrous and rare metals in terms of integrated processing of HRNA wastes along with the expensive rhenium. This is especially true of the metals are quite large contained in the alloy. Here such metals are nickel and cobalt. An integrated processing of HRNA will allow to obtain compounds of these valuable non-ferrous metals. Due to the nature of the HRNA, which determines their resistance to the effects of various kinds, the extraction of valuable metals from the wastes of these alloys presents considerable difficulties.

There is no processing of such secondary raw materials in Kazakhstan. However, a well-known company for the rhenium and its compounds production from sulfur wash-acid of the copper production of RSE Zhezkazganredmet is currently

seeking additional raw material sources of rhenium. In this regard, the company has shown interest in wastes of rhenium-containing HRNA.

The Institute of Metallurgy and Ore Beneficiation JSC of the Republic of Kazakhstan has developed a method for the electrochemical processing of large-volume of rhenium-containing HRNA wastes in the sulfuric acid solutions [12-16]. At this, up to 80-90% of rhenium, nickel and cobalt go into solutions, and a small part of them remain in the anode slurry. To extract the remaining rhenium, nickel and cobalt in the slurry, the anode slurry is sent for chemical dissolution [15]. The resulting solutions after electrochemical processing of wastes and chemical dissolution of anodic slurry are combined and the rhenium is extracted from them [12-13, 16]. Nickel and cobalt remain almost completely in the raffinate sulphate solution after extraction of rhenium, their content may be depending on the composition of the raw material and the conditions of its processing, on average, g / dm³ 16,85-25,74 Ni; 2.48-3.74 Co.

A wide range of methods of nickel and cobalt deposition from the solutions into a common nickel-cobalt concentrate, for example, sulfides [17-18], but most often they are precipitated from acidic solutions by alkali [12, 16].

This paper presents the results of physical and chemical studies of nickel-cobalt concentrates obtained from the products of electrochemical break-down of HRNA wastes.

Testing

From the sulphate raffinates are left after extraction of rhenium and containing significant amounts of nickel and cobalt, these metals were precipitated into a concentrate using alkali.

The deposition processes were carried out in a thermostated cell (Figure 1) with stirring using a mechanical stirrer using an adjustable speed.



Figure 1 - Laboratory setup for Ni-Co concentrate deposition

The chemical and phase composition of raffinates and processing products (filtrate, service water, Ni-Co concentrate before and after washing) was determined using X-ray fluorescence (spectrometer with wave dispersion Axios PANalytica), X-ray phase diffractometer (D8 Advance diffractometer (BRUKER), radiation Cu. K α); chemical (atomic emission spectroscopy Optima 2000 DV, USA, Perkin Elmer), infrared spectroscopic (FTIR spectrometer Thermo Nicolet Avatar 370 FTIR Spectrometer), thermal (STA 449 F3 Jupiter, the results were processed using the NETZSCH Proteus software) methods of analysis.

Testing procedure for the Ni-Co raffinate concentrate deposition. A saturated blue raffinate (Figure 2a) containing g/dm³ Ni — 14.260; Co - 2,481; Re - 0.102; Mo - 0.121; W — 0.012; Al = 1.810; Cr - 2.212 (95.06 g/dm³ of acidity). A predetermined raffinate volume (1 dm³) was poured into a thermostated cell (Figure 1), the process temperature was maintained at 40 °C, and with continuous stirring at a speed of 700 rpm, a precipitator — NaOH solution (500 g / dm³) was fed until pH 8-9. Then stirring was proceeded for 1 hour. When a precipitant was added to the raffinate, a dark green solution with the precipitate was produced. As the NaOH solution was added, the amount of increased precipitate was formed and the color intensity of the solution increased. The precipitate of Ni-Co concentrate was filtered using a vacuum pump through the two layers of blue tape filter. The mass of the obtained wet Ni-Co concentrate (75.67% of humidity) was 534.23 g.

Then the precipitate was washed with water, filtered and dried in a drying cabinet at a temperature of 105 °C to a constant weight. Dry sediments were ground in a porcelain mortar.

Results and discussion

According to the X-ray analysis data, absorption bands of valence ν (OH) - 3413 cm⁻¹, deformation δ HOH-1647 cm⁻¹ and librational ν_L H₂O - 674 cm⁻¹ of molecular water fluctuations are recorded in the raffinate spectrum (concentrate solution for precipitation) [19]. The group [HSO₄]⁻K - 1196, 1053, 890, 598 cm⁻¹ [20]. The group [SO₄]²⁻K - 1117, 627 cm⁻¹ [18, 20]. The group [NO₃]⁻K - 1386, 1348 cm⁻¹ [19, 22].

The optical density measurements were made at the peak point of the absorption bands describing the fluctuations of ν OH, δ HOH, ν_L H₂O, ν_3 of nitrate-ions, ν_3 (F₂) of sulfate ion, ν_4 (F₂) of sulfate ion, ν_2 (SO₃) of hydrosulfate ion; ν_4 (SO₃) of hydrosulfate ion; ν_1 (S - OH) of hydrosulfate ion; ν_3 , ν_5 (OSO) of hydrosulfate ion.

The ultimate composition of the produced concentrate without washing was determined by X-ray fluorescence analysis, wt. %: Ni - 14.786; Co — 1.844; O - 43.912; Na — 21.917; Al = 0.936; Si - 0.075; S - 12,350; Ti = 0.055; Cr - 1,688; Fe - 0.339; As — 0.014; Mo - 0.096; Re - 0.031; Pb - 0.007.

According to the x-ray phase analysis of a dry concentrate without washing, the following phases are in it: a base - 62.6 wt. % of Na₂SO₄; 37.4 wt. % of Ni₂(NO₃)₂(OH)₂·2H₂O and <2.5 wt. % of Co(OH)₂.

The X-ray analysis has shown the following in the Ni-Co concentrate: Thenardite Na₂SO₄ - 1131, 638, 617 cm⁻¹ [20, 22-25]. The group of [SO₄]²⁻ -1131, 996, 977, 638, 617 cm⁻¹ [19-21]. The group [NO₃]⁻K - 1384, 1040, 833 cm⁻¹ [19, 21]. The band at 996 cm⁻¹ can be attributed to the ν_1 (A₁) fluctuation of iron, cobalt, and nickel sulfates [20, 23]. ALUMINITE Al₂(SO₄)(OH)₄·7H₂O - 977cm⁻¹ [22] may be present. The band at a 406 cm⁻¹ wave number corresponds to the stretching fluctuations of Co-O, Ni-O [24]. CoO is probably present - 406 cm⁻¹ [20, 24]. The spectrum recorded absorption bands of ν (OH) - 3442 cm⁻¹ valence and deformation δ HOH-1635 cm⁻¹ oscillations of water molecules [20]. The infrared spectrum of Ni-Co concentrate is in Figure 2.

The filtrate (solution after Ni-Co concentrate precipitating) is a volume of 680 ml. The filtrate is colorless, bright. According to the chemical analysis, the filtrate contains, g / dm³ Ni - 0.460; Co - 0.100; Re - 0.078; Mo — 0.005; W — 0.0001; Al - N/A; Cr - N/A.

Chemical analysis of the filtrates showed that the metals present in the raffinate, when alkali added are almost completely precipitate.

The infrared spectrum of the filtrate recorded absorption bands of valence ν (OH) - 3422 cm⁻¹, deformation δ HOH-1648 cm⁻¹, and librational ν_L H₂O - 678 cm⁻¹ vibrations of molecular water [19]. The group [SO₄]²⁻K is 1108, 624 cm⁻¹ [19, 21]. The group [NO₃]⁻K is 1397, 1376 cm⁻¹ [19, 21]. In the filtrate, the content of nitrate ion is lower than in the initial solution (raffinate). At the maximum of the absorption band characterizing the vibration of ν_3 (F₂) sulfate ion at a wavenumber of 1108 cm⁻¹, the optical density was 0.515. At the maximum of the absorption band characterizing the vibration of ν_4 (F₂) sulfate ion, at a wavenumber of 629 cm⁻¹, the optical density was 0.479. At the maximum of the absorption band, which characterizes the vibration of ν_1 (A₁) sulfate ion, at a wavenumber of 974 cm⁻¹, the optical density was 0.023.

When comparing the spectra of solutions - of the initial raffinate with the filtrate (Figure 3), a

decrease in the intensity of the ν OH band in the filtrate is observed after deposition (2) compared with the initial raffinate (1), which indicates a decrease in the salt content in the filtrate.

The study of obtained Ni-Co concentrates without washing using thermogravimetry. Thermogravimetric analysis allows establishing the presence of chemical interaction of substances or phasing transformations by the accompanying thermal effects. The application of the method is based on the tendency of solid materials to

chemical and physical transformations, accompanied by thermal effects. All processes occurring during the formation are recorded with a thermogravimogram (Figure 4).

Intense endothermic effects on the DTA Ni-Co concentrate curve are manifested with maximum development at 179.7 °C, 281.2 °C, 366.6 °C. They are developed against the background of weight reduction. The additional endothermic effects can be noted on the dDTA curve, with extremes at, °C: 125.2, 144.4, 155.8, 340.8.

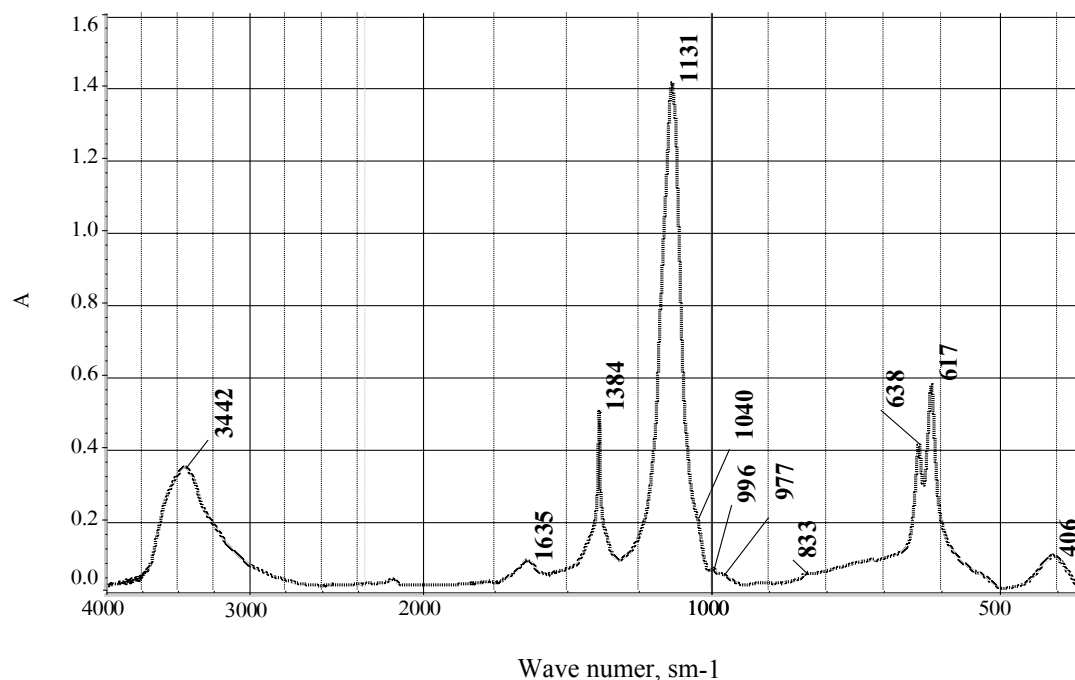


Figure 2 Infrared spectrum of Ni-Co concentrate without washing

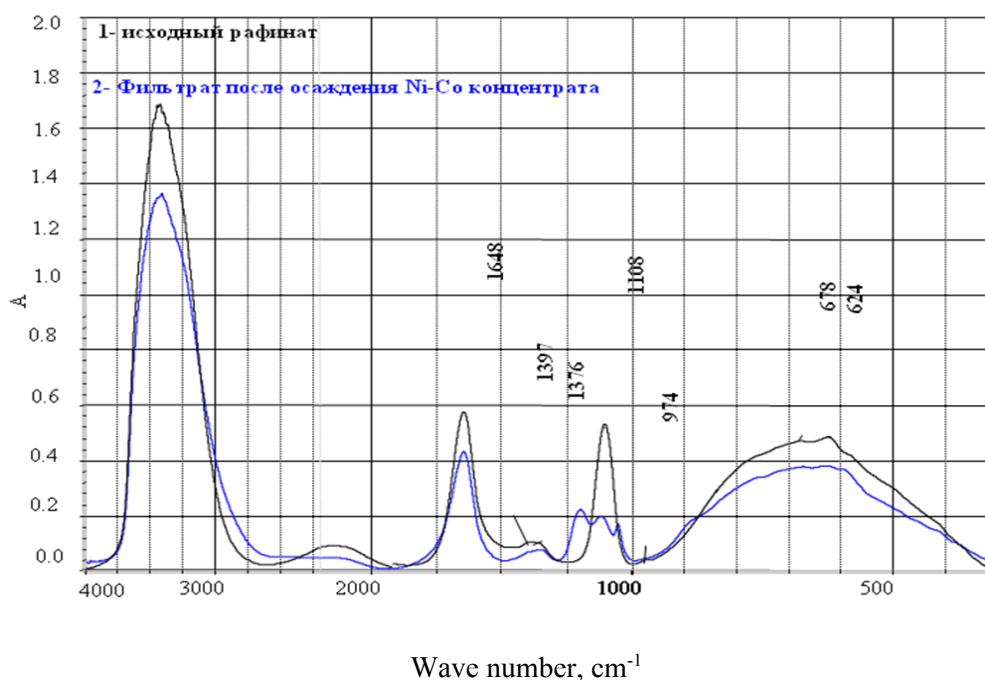


Figure 3 Comparison of the infrared spectra of the filtrate with the raffinate

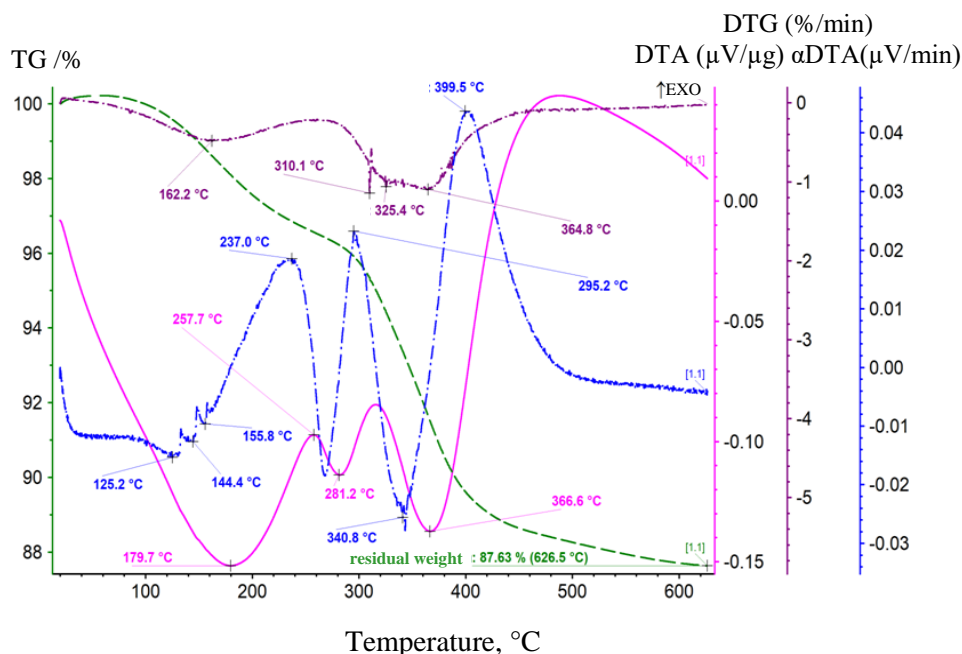


Figure 4 Thermogravigram of Ni-Co concentrate without washing

There are also exothermic effects with peaks at 237 °C, 295.2 °C, 399.5 °C. In this sample, a high content of sodium, therefore, apparently, the effect of polymorphic transformation of sodium sulfate (281.2 °C) is well manifested even in the DTA curve. Also in this sample, elemental sulfur (125.2 °C), ReO_4 (144.4 °C), ReO_3 impurity (155.8 °C) is present. At 366.6 °C, nickel hydroxide is dehydrated and nickel oxide is formed. This effect can also be a manifestation of the de-concentration of co-oxyoids. Effects with extremes at 179.7 °C (DTA) and 399.5 °C (dDTA) can be associated with the manifestation of chromium hydroxide.

The lows at the DTG curve in the temperature range 300–400 °C reflect the dehydration of Fe, Al, Ni, Cr, Co hydroxides. The presence of amorphous and fine hydroxides is also not excluded. Their dehydration probably reflects a stretched low at 162.2 °C on the DTG curve, and the products crystallization reflects exothermic effects with peaks at 237 °C, 295.2 °C, 399.5 °C.

The total weight loss was 12.37%.

Based on the results, it should be concluded that Ni-Co concentrate is necessary to wash with water from sodium, after precipitating it from the raffinate with a NaOH solution.

Washing of Ni-Co concentrate out of sodium.

We washed the Ni-Co concentrate with distilled water at room temperature 25-27 °C, ratio L:S = 10:1. The concentrate was wet, weight - 100g. The moisture content of the concentrate is 76.35%. Dry concentrate weight is 23.65 g.

The concentrate was pre-dispersed in the water (50 ml), then the pulp was moved to a filter and washed with water to pH7 (by test paper). The results of testing of the Ni-Co concentrate washing process are in Table 1.

The chemical composition of the rinse after washing of the Ni-Co concentrate is, g/dm³ Ni - 0.00025; Co - 0.00005; Re 0.0059; Mo - 0.00032; W = 0.00023; Al = 0.00022; Cr - 0.00003. The influence of the washing process on the content of elements in the dry concentrates is provided in Table 2.

Table 1 Washing of nickel-cobalt concentrate with water

Test No	L:S	Service water		Concentrate after washing			Filtration time, min	Drying concentrates, hour
		pH	Volume, ml	Wet weight, g	Humidity, %	Dry weigh, g		
19	10:1	7	975	52,52	81,17	9,89	49	5

Table 2 Effect of the washing process on the elements content in the dry concentrates before and after washing with water

Element	Content, wt. %		Element	Content, wt. %	
	before washing	after washing		before washing	after washing
Ni	15,68	37,55	Hf	0,05	0,13
Co	1,89	4,48	Si	0,31	0,21
Cr	1,77	4,24	S	11,77	3,65
Al	0,88	2,41	O	43,89	43,33
Mo	0,10	0,22	Na	23,19	2,11
Re	0,04	-	Fe	0,33	0,87
W	0,02	0,02	Ti	0,08	0,52

Note - the dry weight of the concentrate without washing - 23.65 g, after washing - 9.89 g.

As provided by Table 1 and 2 the mass of Ni-Co concentrates decreases (~ 2.4 times), the sodium content in the concentrate decreases, the content of nickel and cobalt increases after washing. According to X-ray phase analysis (Figure 5), the dry Ni-Co concentrate have the following phases after washing: 33 wt. % Na_2SO_4 ; the rest is $\text{Ni}_2(\text{NO}_3)_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$; $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$; $\text{NiSO}_4(\text{H}_2\text{O})_7$; $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$; $\text{CoSO}_3 \cdot 3\text{H}_2\text{O}$.

A decrease in the intensity of the Thenardite Na_2SO_4 – 1129, 638, 617 cm^{-1} band is observed in the spectra from 4 to 0.85 when comparing the IR spectra of Ni-Co concentrates without washing and after washing with water, which also indicates a decrease in the Na_2SO_4 content in the washed concentrate.

The thermogravigram of a Ni-Co concentrate after washing with water is provided in Figure 6. The DTA curve demonstrates intense endothermic effects with maximum development at 194 °C, 381.8 °C. They are developed against the background of a sample weight reduction. Additional endothermic effects can be marked with extreme values at 117 °C, 136.9 °C, 148 °C, 180.9 °C, 268.8 °C, 287 °C along the dDTA curve. Exothermic effects are present with peaks at 244.5 °C, 303.5 °C, 415.2 °C as well.

The exothermic effect combination with a peak at 244.5 °C on the dDTA curve and an endothermic effect with an extreme value at 381.8 °C can be interpreted as nickel hydroxide occurrence.

The effect at 381.8 °C reflects the dehydration process of this phase and the formation of nickel oxide. The endothermic effect with an extreme value at 268.8 °C on the dDTA curve can be an occurrence of the polymorphic transformation of sodium sulfate. The combination of the endothermic effect with the

maximum development at 194 °C and the exothermic effect with a peak at 415.2 °C can be interpreted as a chromium hydroxide occurrence. The exothermic effect reflects the conversion of Cr^{+3} into Cr^{+4} with the formation of the α -phase of a variable composition. Since the sample under study may have hydroxides of iron, aluminum, cobalt, so this peak may be an occurrence of the solid solutions formation of spinels.

A number of least values are emphasized on the DTG curve, in the temperature range 300-400 °C, which reflect the hydroxides dehydration Cr, Fe, Al, Ni, Co. In addition, amorphous or finely dispersed Fe, Al, Co. hydroxides may be present in the sample.

As well known the cobalt hydroxides include unstable blue and stable pink hydroxide $\text{Co}(\text{OH})_2$, CoOOH oxyhydroxide, hydrated oxides [26]. Blue hydroxide is finely dispersed, it begins to lose water already at 170°C. Pink is resistant to 300°C.

Dehydration of the aged rhombohedral CoOOH is at ~ 335 °C. That is to say the effect with an extreme value at 381.8 °C may also be an occurrence of CoOOH dehydration. The stretched least value at 192.5 °C on the DTG curve may be an occurrence of the dehydration of amorphous, finely dispersed phases, and the exothermic effects with peaks at 244.5 °C, 303.5 °C, 415.2 °C on the dDTA curve reflecting the crystallization of dehydration products.

The total weight loss was 14.96%. The higher mass loss compared to the concentrate without washing (12.37%) is probably due to a higher nickel content in the form of hydroxide.

To confirm the presence of sodium sulfate, the sample weighing 0.314 g was heated to ~ 860 °C. The endothermic effect with an extreme value at 824.2 °C, which reflects the melting of sodium sulfate was better manifested on this DTA curve.

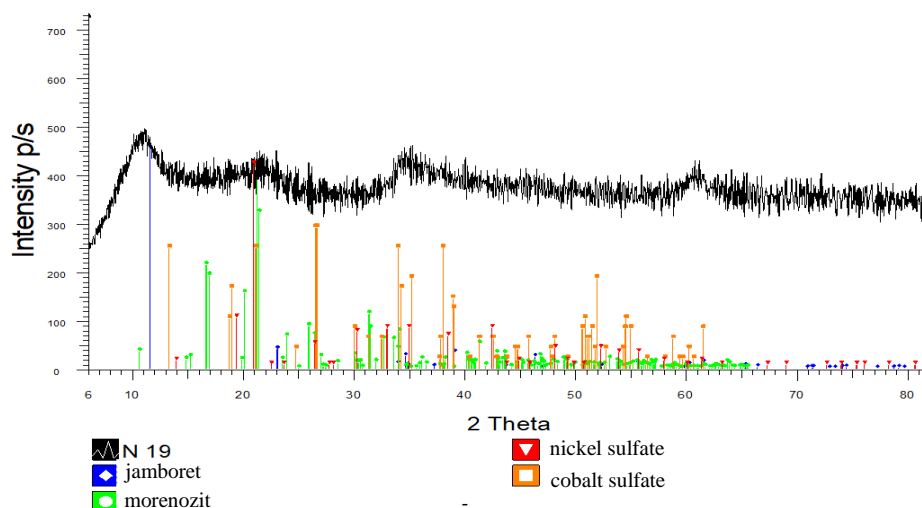


Figure 5 Diffractogram of Ni-Co concentrate after washing

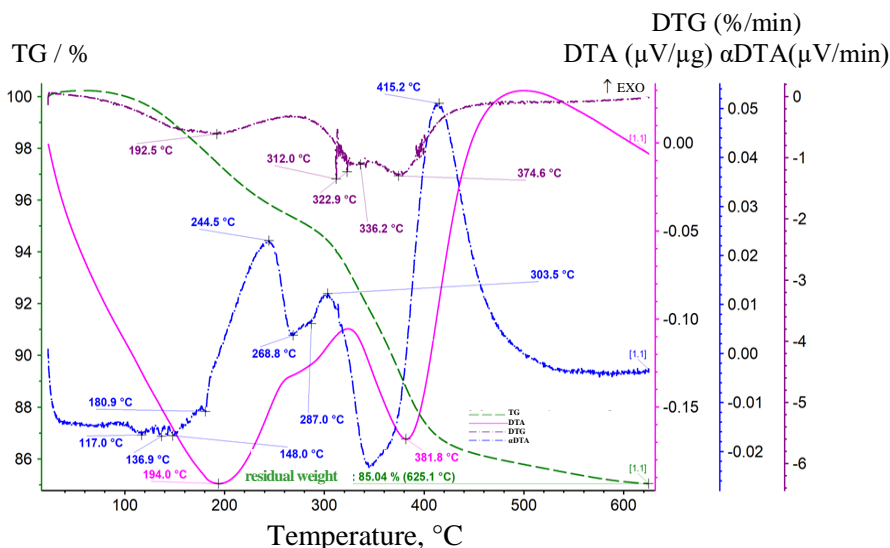


Figure 6 Thermogravitogram of Ni-Co concentrate after washing with water

Thermogravimetric analysis of the concentrates, both without rinsing and after rinsing with water, resulted in that in the temperature range of 300-400 °C occur dehydration of nickel, cobalt, chromium, aluminum, iron hydroxides and their transition into oxide forms.

Annealing of nickel-cobalt concentrates obtained out of the products after the electrochemical break down of the HRNA wastes at a temperature of up to 400 °C will allow to transfer all non-ferrous metal hydroxides to oxides, to reduce the mass of concentrates by 15-20%. Annealed nickel-cobalt concentrates can be used in the smelting of some ferroalloys.

Findings

The studies have shown that nickel and cobalt can be isolated from the waste of rhenium-containing heat-resistant nickel alloys in the form of a concentrate. Start with, the large pieces of waste alloys anode dissolved in sulfuric acid solutions to obtain a rhenium-containing solution and anode slurry. Rhenium, nickel and cobalt are extracted into a solution out of the anodic slurry by chemical dissolution. Solutions from the anodic break down of the wastes and chemical dissolution of the slurries are combined and sent for the extraction of rhenium from them. After extraction of rhenium from the raffinate, nickel and cobalt are precipitated

with a solution of NaOH (500 g / dm³) until the pH value is 8–9 at a temperature of 40 °C, with intensive stirring of the pulp for 1 h. Physical and chemical studies of the obtained concentrate showed that it contains the following phases, wt. %: 62,6 Na₂SO₄; 37,4 Ni₂(NO₃)₂(OH)₂·2H₂O и Co(OH)₂.

Washing the resulting concentrate from sodium with water is proposed at a L:S ratio = 10:1. After the Ni-Co concentrate washing, its mass decreases (~ 2.4 times), the sodium content in the concentrate decreases, the nickel content (from 15.68 to 37.55 wt.%) and cobalt (from 1.89 to 4,48 wt.%). During the annealing of the concentrate in the temperature range of 300-400 °C, the processes of dehydration of nickel and cobalt hydroxides and

their transition into oxide forms occur. In this case, the weight of the concentrate is reduced by 15-20%. The resulting concentrate can be sent for further processing in order to extract non-ferrous metals from it. Also, nickel-cobalt concentrate can be used to produce some ferroalloys.

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Ыстыққа төзімді никельді қорытпаларының қалдықтарынан алынған никель-кобальтты концентраттарын физикалық-химиялық зерттеу

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Түйіндеме. Құрамында ренийі бар ыстыққа төзімді никельді қорытпалар (ЫТНҚ) құрамында 50-75 % Ni, 3-15 % Co. ЫТНҚ қалдықтарын электрохимиялық қайта өңдеу барысында 80-90 % дейін Re, Ni және Co ерітіндіге өтеді, ал олардың аз бөлігі анодтық шламда қалады. Шламдан металлардың қалған бөлігін химиялық ерітумен ертіндіге өткізеді. Қалдықтарды электрохимиялық қайта өңдеуден кейінгі және шламдарды химиялық ерітуден кейінгі ертінділерді біріктіріп, экстракция әдісімен олардан Re-ді шығарады. Re-ді экстракциялаудан кейін рафинаттан (г/дм³: 14,26 Ni; 2,48 Co) NaOH (500 г/дм³) ерітіндісімен (рН-тын мәндері 8-9 шейін орналғанша, 40 °C температурада, 1 сағат бойы араласумен) Ni-Co концентраттын тұндыруы өткізілді. Рентгенфлуоресценттік, рентгенфазалық, термогравиметрлік және ИКС әдістері концентраттын физикалық-химиялық зерттеуі оның құрамында келесі фазалар, мас. %: 62,6 Na₂SO₄; 37,4 Ni₂(NO₃)₂(OH)₂·2H₂O и Co(OH)₂ бар екенін көрсетті. С:Қ = 10:1 қатынасында концентратты натрийден сумен шаюда оның массасын азаяды (~ 2,4 есе), натрий құрамы төмендейді, Ni (15,68-ден 37,55 % дейін) мен Co (1,89-ден 4,48 %дейін) құрамы жоғарлайды. Температура 300 – 400 °C интервалында концентратты қыздыруда Ni және Co гидроксидтерінің дегидратациялау үрдісі болады және олардың оксидтік формаларына көшеді. Алынған концентрат одан әрі қайта өңдеуге жіберілуі мүмкін олардан түсті металдар немесе кейбір ферроқорытпаларын алу мақсатында.
Түйінді сөздер: ЫТНҚ қалдықтары, рафинат, Ni-Co концентраты, тұндыру, шаю, қыздыру.

Физико-химические исследования никель-кобальтовых концентратов, полученных из отходов жаропрочных никелевых сплавов

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Аннотация. Отходы ренийсодержащих жаропрочных никелевых сплавов (ЖНС) содержат 50-75 % Ni, 3-15 % Co. При электрохимической переработке отходов ЖНС в растворы переходит до 80-90 % Re, Ni и Co, а незначительная их часть остается в анодном шламе. Из шлама оставшуюся часть металлов химическим растворением переводят в раствор. Растворы после электрохимической переработки отходов и химического растворения шламов объединяют и методом экстракции извлекают из них Re. Из рафината (г/дм³: 14,26 Ni; 2,48 Co) после экстракции Re раствором NaOH (500 г/дм³) провели осаждение Ni-Co концентрата (до установления значения рН 8-9, при температуре 40 °C, интенсивном перемешивании в течение 1 ч). Физико-химические исследования концентрата рентгенофлуоресцентным, рентгенофазовым, термогравиметрическим и ИКС

методами показали, что в нем содержатся следующие фазы, мас. %: 62,6 Na_2SO_4 ; 37,4 $\text{Ni}_2(\text{NO}_3)_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ и $\text{Co}(\text{OH})_2$. Промывка концентрата от натрия водой при Ж:Т = 10:1 позволила уменьшить его массу (~ в 2,4 раза), снизить содержание натрия, повысить содержание Ni (от 15,68 до 37,55 %) и Co (от 1,89 до 4,48 %). При отжиге концентрата в интервале температур 300 – 400 °С происходят процессы дегидратации гидроксидов Ni и Co и перехода их в оксидные формы. Полученный концентрат может быть направлен на дальнейшую переработку с целью извлечения из него цветных металлов или использован для получения некоторых ферросплавов.

Ключевые слова: отходы ЖНС, рафинат, Ni-Co концентрат, осаждение, промывка, отжиг

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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.

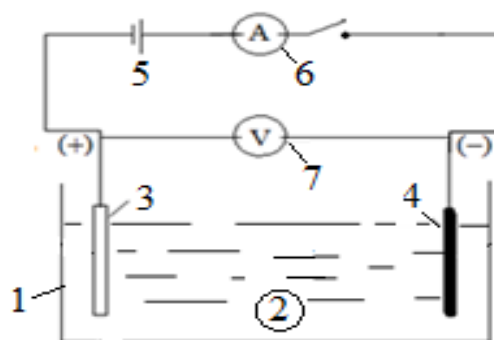
Certain reducing agents that adversely affect the environment or sophisticated equipment are used in selective methods used for selenium removal. As a result, many methods are economically or ecologically inefficient and can not be implemented at the production scale. In this regard, the research and 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).



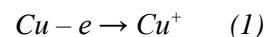
1 - Electrolysis device; 2 - Electrolyte (Se (IV) + HCl + CuCl₂); 3 - copper anode; 4 - titanium cathode; 5 - DC power source; 6 - ammeter; 7 - voltmeter.

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

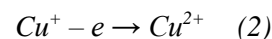
Results

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.

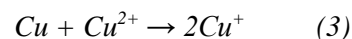
One valence copper ion formed during anode dissolution of a copper electrode and it passes step by step. [10]:



and



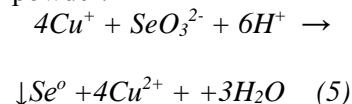
During electrolysis, low-current densities formed by reactions 1, 2, and copper (II) in electrolyte interact with copper anodes, form additional copper (I) ions:



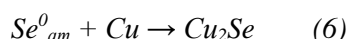
Copper (II) ions contained in the electrolyte are gradually reduced to copper (I) ions on the cathode surface. One valence copper ion is an intermediate product:



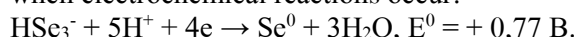
One valence copper ions, formed as a result of the above reactions, react with selenium ions and form selenium powder:



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:

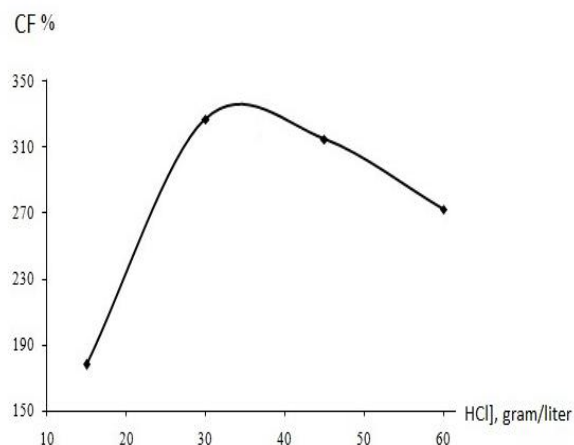


In addition, oxidized copper (II) ions form copper (I) ions by reaction 4 on the cathode surface. This, in turn, suppresses selenium (IV) ions on the surface of the cathode and in this region and forms additional selenium powder.

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, $i = 200 \text{ A/m}^2$,
 $t = 20 \text{ C}^\circ$, $\tau = 0,5 \text{ hour}$

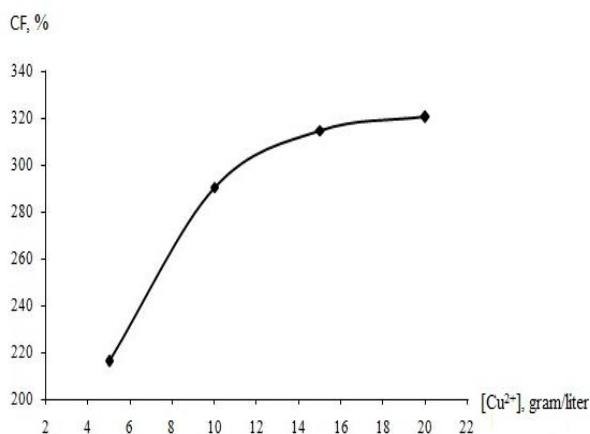
Figure 2 The effect of hydrochloric acid concentration on CF of selenium powder

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.

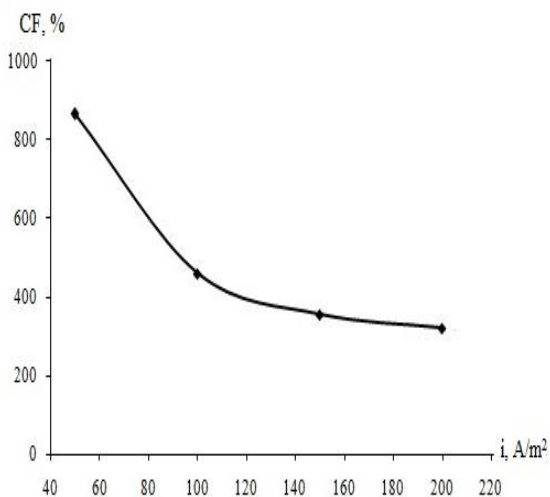
The current density of the electrodes changes the electrode potential in the Tafel equation. The potential of the copper electrode increases the density of the current with a considerable positive value. The shift of the electrode to the positive potential increases the ability of reaction 2 to increase 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, $i = 200 \text{ A/m}^2$,
 $t = 20 \text{ }^\circ\text{C}$, $\tau = 0,5 \text{ hour}$

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, $t = 20 \text{ }^\circ\text{C}$, $\tau = 0,5 \text{ hour}$

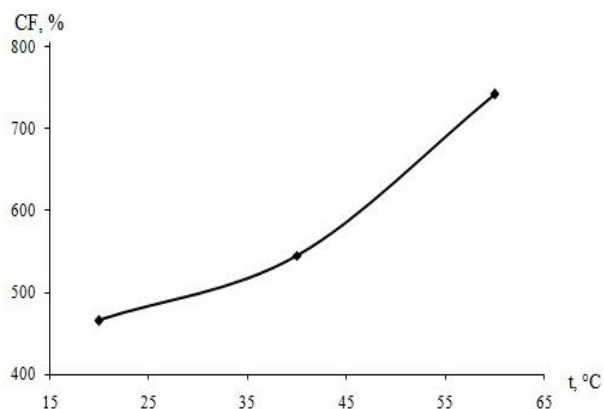
Figure 4 Influence of selenium powder on CF in electrodes density

The effect of temperature on selenium powder formation in CF was investigated. When the temperature increased from $20 \text{ }^\circ\text{C}$ to $60 \text{ }^\circ\text{C}$, 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.

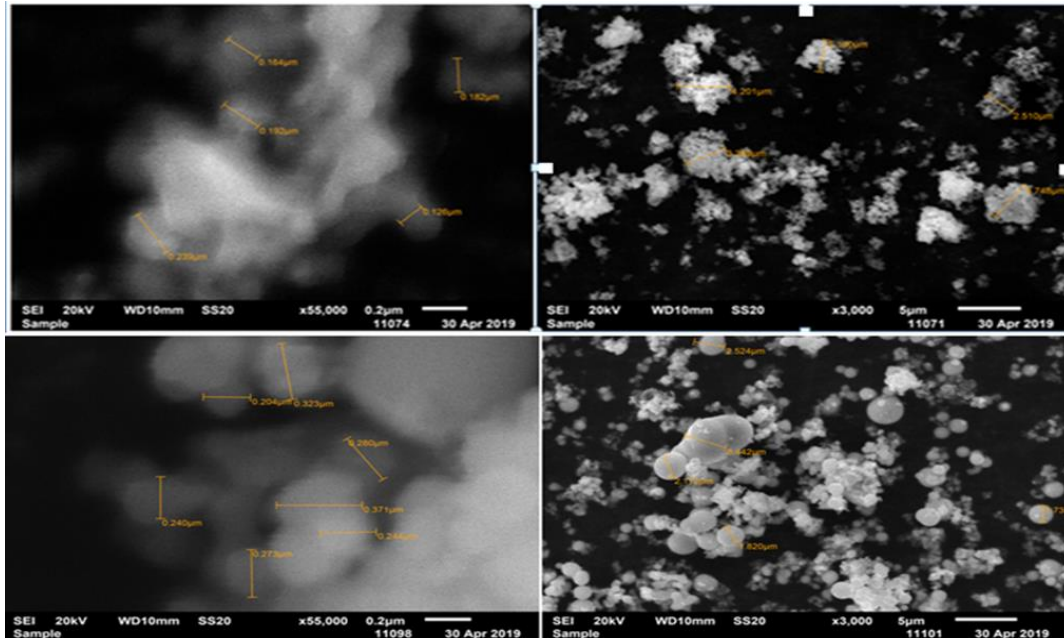


Cu (II) - 20 gram/liter, HCl - 30 gram/liter, Se (IV) - 10 gram/liter, $i = 100 \text{ A/m}^2$, $\tau = 0,5 \text{ hour}$

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	$t, \text{ }^\circ\text{C}$	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.

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

Башов 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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Смарт терезелерге жүргізілген тәжірибелік және теориялық зерттеу жұмыстарына шолу

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Түйіндемe. Смарт терезелер энергияны үнемдеу мақсатында және ғимараттар ішіндегі температуралық жылулық үшін маңызды рөл атқарады. Смарт-терезелер жылу шығынын және кондиционерлеу мен жарықтандыру шығындарын азайтуға мүмкіндік береді. Жалюзи мен перделерге балама қызмет ретінде пайдаланылады. Сұйық кристалды немесе электрохимиялық смарт-терезелер ультракүлгін сәулесін өткізбейді. Өлшенген бөлшекті смарт-терезесі ультракүлгін сәулесін бұғаттау үшін арнайы құрылғыларды пайдалануды талап етеді. Бұл мақалада смарт терезелерге жүргізілген теориялық және тәжірибелік зерттеулерге шолу жасалынған. Кеңістікте және зертханалық сынақтарда әртүрлі өлшеу әдістерінің көмегімен жүргізілген тәжірибелік зерттеу жұмыстарына шолу жүргізілді. Смарт терезелердің шығыс сипаттамалары мен оңтайлы құрылымын талдау мақсатында, теориялық ғылыми зерттеу әдебиеттеріне және теориялық ғылыми зерттеу модельдерге шолу жүргізілді. Орындалған ғылыми зерттеу жұмысы материалтану және құрылыс материалдары ғылым саласында пайдалы ақпарат көздері ретінде қоладнуға зор ықпалын тигізеді.

Түйін сөздер: смарт терезе, энергияны үнемдеу, тәжірибелік өлшеулер, визуалды жайлылық.

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Кіріспе

Энергия тиімділігі үнемдеу және қоршаған ортаны ластаушы заттарды азайту, әлемдік ғылыми зерттеу орталықтарының негізгі мақсаты болып табылады. Қазіргі таңда осы бағытта көптеген ғылыми зерттеу жұмыстары жүргізілуде. Күн сәулесін дұрыс пайдалану - ғимараттарда энергия көзін тұтынуды азайтуға және визуалды жайлылықты арттыруға мүмкіндік береді [1-3]. Аталған талаптарға сай, жаңа технологиялардың бірі болып саналатын смарт терезелер, бөлме ішіндегі жылулық және визуалдылық жағдайларын бақылауда маңызды рөл атқарады [4]. Бұл құрылғының қарапайым шынылардан айырмашылығы, шағын электр өрісін қолдана отырып, оптикалық қасиеттерін өзгертуге мүмкіндік береді. Әдетте, смарт терезелері бес түрлі қабатпен іске асырылады және электр батареясы ретінде де қарастырылуы

мүмкін [5]. Смарт немесе интеллектұлды терезелер – бір қабатты электролиттен (иондық тасымалдағыш қасиеті бар кристалдан), екі металл оксидті қабаттан (катодты және анодты) тұрады және екі мөлдір электр өткізгіштерімен (ITO) қапталады.

Электрохромды (ЭХ) оксидтердің негізгі екі түрі бар: катодты және анодты оксидтер. Қазіргі уақытта ЭХ терезелерінің бірі болып саналатын вольфрам оксиді (WO_3) катодты оксид ретінде смарт терезелер жасау үшін пайдаланады. Көптеген жүргізілген ғылыми зерттеулер жұмыстары, ЭХ-ның жаңа және неғұрлым тиімді материалдарын әзірлеу мақсатында жүргізілсе, ал кейбіреулері бөлмедегі визуалды және жылу жайлылығына, сонымен қатар, олардың ғимараттардағы тұтынатын энергия көзін үнемдеуі және қалай әсер ететінін талдай отырып, смарт терезелерінің негізгі сипаттамаларын анықтады.

Смарт терезелердің беттік ауданы, оның шынылау қасиеттеріне қатты әсер ететіндігіне байланысты болғандықтан, олардың ауқымды шынылауының сипаттамаларын бағалау қажет. Бұл мақалада, сатылымдағы өнімдердің және лабораториялық үлгілердің оптикалық, жылулық және электр тұрғысынан терезелерінің қасиеттерін сипаттайтын негізгі зерттеулер мен талдауларға шолу жүргізілді.

Тәжірибелік ғылыми зерттеулерге шолу

Электрлік, оптикалық және жылулық сипаттамалары тұрғысынан смарт терезелердің сапасын бағалау үшін, кеңістікте және арнайы зертханалық орындарда жүргізілген тәжірибелік ғылыми зерттеу жұмыстарына, шолу жасалынды.

[6] жұмысында, смарт терезе прототиптерінің өнімділігін бағалау үшін кеңселік сынақ стендін пайдалана отырып, тәжірибелік зерттеулер жүргізді. Сынақ стенді жарықтығы реттелетін люминесцентті жарық беру жүйесімен жабдықталған және үш бүйірден тұрды. Стендтің терезесінің ауданы 0,36 м² құрады. Зерттеу стендісінің қалған терезелері (эталондық ретінде пайдаланылған) – көрінетін Күн сәулесінің өткізгіштік мәні, 0,50 (мөлдір) және 0,15 (боялған) тең. Зерттеу нәтижелері келесіні көрсетеді:

1. Жарық деңгейі 89-99% күндізгі жарықпен қамтамасыз етілген;
2. Смарт терезесінің энергия үнемдегіштік қабілетін статикалық терезелермен салыстырғанда 59 % - ға жетуге мүмкін береді.

[7] жұмысының авторлары, смарт шынысын вольфрам оксиді қабаты (WO₃) негізіндегі бекітетін тәжірибелік үлгілеріне (өлшемі 0,40 м * 0,40 м), және вакуумдалған шынылауға зертханалық сынақтар жүргізілді. Зерттеу нәтижелері 0,63 (мөлдір) - тен 0,02-ге дейін (боялған), сондай-ақ ұзақ уақытқа (5000 жұмыс циклынан астам) өзгеріп отыратын процесстің көрінетін Күн сәулесін өткізу мәндерін атап өтті.

[8] - де, смарт шыны құрылысын бөлмедегі климатты салқындату арқылы: жарықтандыруды, смарт шынылардың орналасу бағдарына және ауысу стратегиясына байланысты зерттеулер мен талдаулар жүргізді. Авторлар, ауданы 0,12 м * 0,12 м болатын вольфрам оксиді (WO₃) негізінде смарт шынысының прототипіне тестілеу жүргізді және олардың айтуынша, смарт шынылар Күн радиациясынан қорғау және жылуды басқару үшін пайдалы болуы мүмкін, бірақ дәстүрлі көлеңкелеу жүйелерін қолдануды жоққа шығармайды. Ауысу уақытының ұзақтығының әсерінен күндізгі уақыт флуктуациясын бақылау мүмкін еместігін және көрінетін Күн сәулесінің

өткізгіштік мәндері азайған кезде түс беру индексінің мәні азаятынын анықтады.

[9] - жұмысында, смарт-шынының әр түрі үш түрін салыстыру бойынша негізгі қасиеттерін, артықшылықтары мен кемшіліктерін, сондай-ақ материалдың энергия тиімділігі мен оны тұрмыста пайдалану және жарықтандыруды жақсарту бойынша зерттеу жұмыстары жүргізілді. Смарт-шынының әртүрлі технологияларының келтірілген сипаттамасы негізінде оның артықшылықтары мен кемшіліктері анықталды және олармен байланысты болған қиындықтары келешекте шешілуі тиіс. Нақты мысалдарда мөлдірлігі басқарылатын смарт шыныны қолдану салалары қарастырылған. Авторлар, зерттеу нәтижесінде, смарт-шыны өндірісінің техникасы мен технологиясының дамуымен қатар, өзіндік құнының азайту кезіндегі оптикалық қасиеттері жақсаратынын және осы материалдың қол жетімділігінің артуына алып келетіндігін жазады. Сонымен қатар, өлшенген бөлшектердегі смарт шынылар – автокөліктердің шынысына орнату үшін аса қолайлы, ал электрохромды қабаты бар смарт шынылар – тұрғын үй және кеңсе бөлмелері үшін аса қолайлы екенін айтады, өйткені ол, мөлдірлікті ұстап тұру үшін үздіксіз кернеу беруді қажет етпейді.

[10] - зерттеу жұмысында смарт терезелері мен жұмысшылар арасындағы өзара әсерді зерттеді. Авторлар, батысқа бағытталған конференц-залда автоматты басқарылатын смарт терезесі мен жаңа тиімді қараңғыланған жарықтандыру жүйесін назарға алды. Тәжірибелік зерттеу кезінде, ғимараттың сыртқы және ішкі жарығының деңгейін, жарықтандыруға жұмсалатын электр энергиясын, жұмысшылардың жұмыс уақытын, смарт терезелерінің екі жағындағы беттік температурасын, терезелердің боялған және мөлдір күйде болатын уақыты, сондай-ақ жолаушылардың смарт терезесін қолмен басқару жиілігі зерттелінді. Қарастырылып отырған бөлменің жыл сайынғы жылытуы, желдетуі, ауаны баптау және жарықтандыру үшін пайдаланылатын энергияны зерттеу үшін Energy Plus бағдарламалық кешені қолданылды. Зерттеудің негізгі нәтижелері:

1. Жұмысшылардың 4% смарт терезесін қолмен басқарды.
2. Конференц - залдың жыл сайынғы тұтыну энергиясы 39% - дан 48% - ға дейін үнемделінді.
3. Электр энергиясының ең жоғары сұранысын 22% - дан 35% - ға дейін азайтуға болатынын анықтады.

[11] - ғылыми зерттеу жұмысында, электрохромизмнің теориялық негіздері,

электрохромды құрылғылардың принципті сұлбасы және оларды жасау үшін пайдаланылуы мүмкін материалдар қарастырылған. WO_3 , V_2O_5 , TiO_2 , Cr_3O_8 , NiO , MO_3 сияқты тотықты материалдарға ең көп көңіл бөлінген. Осы материалдардың сипаттамалары және оларды алуудың ықтимал әдістері көрсетілген. Вакуумды пайдаланбай, жабынды жағуға мүмкіндік беретін ерітінділік әдісті қолдана отырып, никель оксидінің жұқа пленкаларын алу бойынша тәжірибелік деректер келтірілген. Алынған және зерттелген электрохромды материал кернеуді қолдану кезінде жарық өткізуін өзгертеді және ұзақ уақыт қараңғылау және түссіздендіру процестерін циклдей алады. Экстракциялық-пиролитикалық әдіспен электрохромды құрылғы дайындалған, онда никель оксидінің пленкасы $NiO(OH)$ қалпына келтірілген күйден $Ni(OH)_2$ тотықтандырылған күйге – қоңыр түстен мөлдір түске ауысып өтеді. NiO біркелкі электрохромды пленкасын алу үшін 2% концентрациясы бар сығынды ерітіндісін пайдаланыңыз. Термогравиметриялық деректерге сәйкес оксидті пленканың пайда болуы 370-450 $^{\circ}C$ кезінде орын алады.

[12] жұмысында, ИТО ($In_2O_3:Sn$) электрлі өлшенген катодты және анодтық мономерді қолдану арқылы ауданы 0,305 м * 0,305 м смарт органикалық терезесі ұсынылды және зерттелінді. Авторлар, жарық контрастының мәнін анықтау мақсатында, тұрақтылықты, оптикалық өткізгіш қасиетін және ауысу уақытын бағалауға бағытталған зертханалық тестілеу көмегімен электрохимиялық және оптикалық қасиеттерді анықтады. Алынған нәтижелерге сүйенсек, жарық контрастының жоғары мәні (580 нм бағалау кезінде 0,62 және 628 нм бағалау кезінде 0,57), зарядтың циклдік өзгеру тұрақтылығы, ауысу уақыты бояу үшін 12 секунд және мөлдір процесі үшін 5 секундты қамтыды.

[13] -де, смарт шыныларын ғимараттардың терезелері ретінде және үлкен масштабты практикада пайдалануға бола алатынын және қолданысқа кепілдік беретін жоғарғы қажетті мәндерін, сонымен қатар, тиімділік көрсеткіштерін анықтады. Зерттеу нәтижелері келесіні көрсетеді:

1. Ауысу тогының кернеуі (≤ 5 В).
2. Ауысу уақыты (≤ 10 сек -5 мин).
3. Оптикалық жады (2-24 сағ).

4. Күн өткізгіштігінің көрінетін коэффициенттері (ашық климат үшін 60-70%, зерттеулер жүргізілген климат үшін (және) энергия үшін 6-7% және визуалдық жайлылық үшін $< 3\%$).

5. Күн факторы (≥ 0.6 ашық климат үшін және ≤ 0.2 бұлдыр климат үшін).

6. Көрінетін Күн сәулесінің шағылысу коэффициенттері (≤ 0.1 ашық климат үшін және ≥ 0.7 бұлдыр климат үшін).

7. Жылу өткізу (≤ 1.2 В/м²К).

8. Түс беру (≥ 80).

9. Жұмыс температурасы (-30 дан 90 $^{\circ}C$ дейін).

10. Қызмет мерзімі (20-30 жыл, бұл 25 000-50 000 жұмыс циклына сәйкес келеді).

Теориялық ғылыми зерттеулерге шолу

Смарт терезелердің жұмысын және пайдалы қасиетін бағалау үшін сандық және теориялық зерттеу жұмыстарына шолу жүргізілді.

[14] - зерттеу жұмысында, екі түрлі интеллектуалды терезелерін оңтайлы басқару стратегиясын анықтау үшін Integrated Energy Use Simulation (IENUS) кеңейтілген модельдеу бағдарламалық кешені пайдаланылды. Жалпы сыртқы күн сәулесіне байланысты оптикалық және жылу сипаттамаларының мәнін өзгертетін смарт терезесінің құрылымы үлгіленді. Ғимараттың жылыту, салқындату және жарықтандыру үшін қажетті тұтынатын энергия тұрғысынан, мыналарды ескере отырып зерттеу жүргізілді: а) екі басқару стратегиясы (қосу/өшіру және желілік басқару), б) смарт терезенің мөлдірлігін зерттеу үшін қолданылатын Күн сәулесінің әр түрлі мәндері, с) Италияның 3 қаласы, д) терезенің негізгі төрт бағыты және е) ішкі жағдайларды басқаруға екі түрлі тәсіл қажет (энергетикалық тәсілі және көзбен шолу тәсілі).

Модельдеудің негізгі нәтижелері:

1. Энергетикалық тәсіл алғашқы энергияны азғана арттырады.

2. Кейбір жағдайларда, энергиялық тәсіл үшін статикалық терезелер ЭХ қарағанда ең жақсы көрсеткіштерді көрсетеді.

3. Көрінетін Күн сәулесін өткізу мәні ЭХ жағдайын басқару үшін қолданылатын тағайындаманың оңтайлы мәніне қатты әсер етеді.

4. Ені тағайындаманың мәніне әсер етеді.

5. Желілік басқару стратегиясы ең жақсы визуалды жайлылыққа кепілдік береді.

[15] - терезенің жаңа түрінің потенциалын түсіну үшін, қарапайым ЭХ тереземен салыстыра отырып, инфрақызыл диапазонына жақын электрохромды пленкасына теориялық зерттеулер жүргізілді. Инфрақызыл диапазонына жақын электрохромды пленкасының қарапайым ЭХ терезеден айырмашылығы, көрінетін Күн сәулесін өзгеріссіз, инфрақызыл диапазонындағы

жарықтың өту қасиетін 0,8 ден 0 ге дейін өзгертеді.

[16] - жұмыста, TRNSYS динамикалық моделдеуді бағдарламасымен әзірленген смарт терезесінің теориялық моделін тексеру үшін, сынақ ұяшығының көмегімен алынған тәжірибелік деректерді пайдаланған. Эксперименттік сынақтар барысында сынақ ұяшықтарының бетінің ішкі және сыртқы температуралары, қоршаған ортаның температурасы, жел жылдамдығы, ішкі ауаның температурасы, диффузиялық және көлденең сәулелену, оңтүстік жазықтықтағы жаһандық сәулелену, ішкі жарықтандыру, сыртқы жаһандық және диффузиялық көлденең жарықтандыру, сондай-ақ шынылаудың ішкі және сыртқы бетінің температурасы алынды. Терезелердің теориялық моделін үлгілеу барысында болжанатын ішкі ауа температурасының өлшенген мәндерін салыстыру арқылы тексерілді. Зерттеудің негізгі нәтижелері сыртқы жағдайларға байланысты ЭХ терезесінің сипаттамаларын басқару ең жақсы стратегия болып табылатынын көрсетті.

[17] авторлары, аз энергия жұмсалынатын, кеңсе ішіндегі жарықтықты белгілі бір мәнде ұстап тұратын, ЭХ терезесінің оңтайлы басқару стратегиясын зерттеді. Жасанды жарықтандыру үшін де, ЭХ терезелері үшін де басқарудың екі стратегиясы қарастырылды: i) қосу / өшіру басқару стратегиясы және ii) желілік басқару стратегиясы. Модельдеу келесілерді есепке ала отырып жүргізілді: 1) ЭХ терезелерінің әртүрлі типтері, 2) көрінетін Күн сәулесін өткізу қасиеті бар, көлеңкеленетін моторланған құрылғылары бар типтік терезелер, 3) әр түрлі 3 қала және 4) терезелердің екі бағдары (оңтүстік және солтүстік).

[18] өз жұмысында, вольфрам оксиді (WO_3) негізінде ЭХ прототипінің (0,12 м x 0,12 м) эксперименталды сипаттамасынан бастады. Сынақ ұяшығының көмегімен ЭХ прототипінің жазғы маусымдағы нақты ауа райында өтетін жарықтың әсерімен, күн факторын және ішкі температураны бақылау қабілеті талданды. Сынақтар оңтүстік және батыс бағыт үшін ЭХ прототипін басқарудың екі стратегиясын (статикалық және динамикалық) ескере отырып жүргізілді. Эксперименттік деректер негізінде сынақ ұяшығының өтпелі жылу тәртібін сипаттай алатын теориялық модель әзірленді және сынақтан өткізілді. Ішкі ауа температурасының эксперименталды мәндерін модельденген үлгімен салыстырған, 3% құрады. Зерттеу нәтижелері, ЭХ терезесі динамикалық стратегияға сәйкес бақыланғанда, жылу жүктемесін шамамен 31% - ға төмендетуге болды

және төмен сәулелену коэффициенті бар екі әйнектелген терезенің көмегімен алуға болатынын көрсетті.

[19] авторлары, ыстық және құрғақ климаттағы күн сәулесінен қызып кетуді бақыланатын сыртқы көлеңкеленудің қарапайым жүйелерімен салыстыру үшін ЭХ терезелерінің тиімділігін зерттеуге арналған Design Builder модельдеу бағдарламалық кешенімен офистік ғимаратты модельдеді. Зерттеу нәтижелер келесіні көрсетті: (1) ЭХ терезелері талданғандар арасында ең жақсы шешім болып табылады және (2) ЭХ терезелері көлеңкеленбеген шыны пакеттермен салыстырғанда күн жылуының өсуін ай сайын 53% - дан 59% - ға дейін төмендетуге мүмкіндік береді.

[20] жұмыстың авторлары, ЭХ терезесінің көмегімен жарықтың үнемделуін бағалау үшін имитациялық зерттеу жүргізді. Зерттеу объектісі ЭХ екі терезесі бар оңтүстік бағдармен жеке кеңсе болды. Модельдеу үшін арналған Radiance бағдарламалық кешенінің көмегімен жарықтық пен жарықтандырудың ішкі мәндері жыл бойы және бір сағат уақыт қадамымен алынды. Модельдеу нәтижелері негізгі жұмыс жазықтығын жарықтандырумен қамтамасыз ету мақсатында ЭХ терезесінің конфигурациясын және жасанды жарықтандыру салымын анықтау үшін оңтайландыру алгоритмі қолданылды. Зерттеу нәтижелері ЭХ терезелері энергия үнемдеу мақсатында оңтүстік бетте пайдалануға тиімді екенін көрсетті және мөлдір әйнекпен салыстырғанда ЭХ терезесі энергия көзін 48% үнемдеуге мүмкіндік берді.

Қорытынды

Смарт терезелер қарапайым статикалық мөлдір тереземен салыстырғанда бірнеше артықшылықтары бар. Эксперименталды және теориялық зерттеулер нәтижесі бойынша смарт терезелерінің тиімді түрі ретінде, энергияны үнемдейтін, визуалды жайлылық пен Күн радиациясын бақылауға арналған автоматты басқарылатын құралдарын пайдалануды ұсынды. Дегенмен, бір жағынан смарт құрылғыларын пайдалану энергия көзін 39% - дан 59% - ға дейінгі диапазонда үнемдеуге мүмкіндік берсе, онда екінші жағынан смарт терезелердің орналасу бағдары, басқару стратегиясы және климаттық жағдайы нақты қолданыста пайдалану үшін қатты әсер етеді. Зерттеу жұмыстарына шолу жасау барысында смарт терезелердің солтүстікте орналасу бағдарына қатысты аз ғана артықшылығы байқалды және қарапайым стандартты мөлдір тереземен салыстырғанда

энергияны үнемдеуі және визуалдық жайлылығы жағынанан артта қалатынын көрсетті. Сонымен қатар, смарт терезелерінің ұзақ ауысу уақыты (7-20 минут) нақты ауа райы жағдайларын бақылауға мүмкіндік бермейді.

Ауданы әртүрлі смарт терезелердің физикалық сипаттамаларын түсінуге және эксплуатациялық шарттарының нақты пайдасын анықтау үшін одан әрі тәжірибелік және теориялық зерттеулер жүргізуді қажет етеді.

Осы мақалаға сілтеме: Аймаганбетов К. П. Смарт терезелерге жүргізілген тәжірибелік және теориялық зерттеу жұмыстарына шолу: *Комплексное Испол'зование Mineral'ного Syr'a (Complex Use of Mineral Resources)* – 2019. – №3 (310). – Б. 34-40. <https://doi.org/10.31643/2019/6445.26>

Review of experimental and theoretical research works of smart windows

Aimaganbetov K. P.

Abstract. Smart windows play an important role in a energy saving and for thermal heat inside buildings. Smart windows allow you to reduce heat consumption and air conditioning and lighting costs. It is used as an alternative to blinds and curtains. Liquid crystal or electrochemical smart windows do not transmit ultraviolet light. The measured-value smartphone requires the use of special devices to block ultraviolet light. This article provides an overview of the theoretical and experimental research in the field of smart windows. A review of experimental studies performed using various methods of measurement in space and in laboratory studies. A review of theoretical research literature and theoretical research models was conducted to analyze the output characteristics and the optimal structure of smart windows. Conducted research have a great influence in the field of materials science and construction materials as a useful source of information.

Key words: smart windows, energy saving, experimental measurements, visual comfort.

Обзор экспериментальных и теоретических исследовательских работ смарт окон

Аймаганбетов К. П.

Аннотация. Смарт окна играют важную роль в энергосбережении и для температурного тепла внутри зданий. В этой статье сделан обзор на теоретические и экспериментальные исследования в области смарт окон. Смарт окна позволяют снизить потребление тепла, а также расходы на кондиционирование и освещение. Используется как альтернатива жалюзи и шторам. Жидкокристаллические или электрохимические смарт окна не пропускают ультрафиолетовый свет. Смарт окна с измеренными значениями требует использования специальных устройств для блокировки ультрафиолетового света. Сделан обзор экспериментальных исследований, выполненных с помощью различных методов измерения в космосе и в лабораторных исследованиях. Обзор теоретической исследовательской литературы и теоретических исследовательских моделей был проведен для анализа выходных характеристик и оптимальной структуры смарт окон. Проведенные научные исследования оказывают большое влияние в области науки материаловедение и конструкционные материалы как полезный источник информации.

Ключевые слова: смарт окна, энергосбережение, экспериментальные измерения, визуальный комфорт.

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X-RAY diffraction and mössbauer studies of fe-57 implantation into the metallic Ta AND Mo

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Abstract. Development of nuclear and thermonuclear energy poses a number of problems for materials scientists related to the creation of structural materials. It should be noted that to date, the material of the fuel rod ducts, which would be able to realize the economical, long-term and safe operation of FNR in full scope, has not been developed. The study of the properties of structural materials for operating and future nuclear plants is still one of the most important scientific and technical challenges. The methods of X-ray diffraction and Mössbauer spectroscopy on ^{57}Fe nucleus were used to study the effect of implanting ^{57}Fe ions of 1 MeV energy and the fluence of $5 \cdot 10^{16} \text{ ion/cm}^2$ on the radiation resistance properties of the structural materials of the nuclear industry of metallic Ta and Mo. Mössbauer studies were of two methods: 1) standard transmission geometry (MS) and 2) conversion electrons registration from the material surface (KEMC). Concentration of the implanted Fe atoms was calculated using STRIM software. Two phases formation was found at the result of implantation into Ta and Mo matrices. The main phase in molybdenum (84%) is a solid solution of Fe replacement into Mo. The main phase in tantalum (78%) corresponds to formation of Fe complexes in the matrix of Ta. The obtained results of the study could be used to solve the issues of NPPs safe operation and to improve the efficiency of their operation, enabling the resource characteristics of core materials to be correctly assessed and to predict their behavior at high damaging radiation doses.

Key words: implantation, conversion and absorption Mössbauer spectroscopy, X-ray diffraction, STRIM software, radiation damage.

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Introduction

The development of nuclear and thermonuclear energy makes the material scientists to create the new structural materials that are resistant to various types of radiation. The study of radiation resistance under reactor irradiation conditions is easy to implement through the implantation of atoms on charged particle accelerators.

The alloying of metals upon irradiation with ions with energy of more than 10 keV has a number of special features that distinguish them from alloys synthesized by the metallurgical method.

To begin with, it leads to the formation of atomic mixtures in the surface area of the material, the composition of which is not limited by the principles of thermodynamics.

Secondly, the concentration profile of embedded atoms along the target depth with increasing ion fluence can vary from the portion of a percent to tens of percent. The limiting impurity content in the doped layer is determined by the sputtering coefficient, to a large extent and sometimes by diffusion processes.

Thirdly, a large number of displaced atoms (structural defects) are generated along with the ion-beam doping, which strongly affect the location of the introduced atoms in the crystal lattice and can cause the movement of atoms both at small and long distances.

Fourthly, since ion implantation is an athermal process, thermally activated phenomena can be independently controlled by the target temperature.

This allows (with a high degree of accounting and reproducing rate) to create alloys with the very

different properties in the near-surface area of the implanted material with a length of 0.01 to 1 μm . By changing the type and dose of ions, the target temperature, or the rate of dose collection, it is possible to obtain equilibrium alloys, supersaturated solid solutions, metastable, intermediate phases or amorphous materials [1].

The M \ddot{u} ssbauer effect makes it possible to measure hyperfine electric and magnetic fields on ^{57}Fe nucleus, which are determined by the local atomic environment. With this in mind, the phases in which iron atoms are localized can be determined in a M \ddot{u} ssbauer experiment.

A large number of monographs and original articles have been devoted to the study of the physical and chemical state of matter using M \ddot{u} ssbauer spectroscopy with all the variety of its methodological approaches [2,3]. In [4], the grain boundaries of polycrystalline molybdenum were studied by M \ddot{u} ssbauer emission spectroscopy on $^{57}\text{Co}(^{57}\text{Fe})$ nucleus. The Co atoms have been demonstrated to diffuse along grain boundaries by the interstitial mechanism. The authors show that the effective diffusion coefficient in the boundary regions of crystallites is significantly higher than the volume diffusion coefficient, but the width of the zone of accelerated diffusion does not exceed several atomic layers. Based on the temperature dependences analysis of the isomeric shift of the spectral lines, the grain boundaries and the boundary regions of crystallites are concluded to be enriched with interstitial impurities. Moreover, the degree of this enrichment is greater, the lower the annealing temperature.

This paper provides the samples of metallic tantalum and molybdenum irradiated with ^{57}Fe ions were studied by X-ray diffraction, M \ddot{u} ssbauer spectroscopy, and electron microscopy. These two materials are structural materials that are used in the nuclear energy. Irradiation with ^{57}Fe ions makes it possible to conduct M \ddot{u} ssbauer studies on the atoms that directly create radiation damage. High doses of radiation were applied in the work, creating damage in the surface layer corresponding to approximately 200 displacements per atom. In similar conditions, iron atoms do not dissolve in metallic Ta [5] and to a limited extent dissolve in metallic Mo [6]. The study was aimed to determine which phases or local structures of Fe atoms form in Mo and Ta as a result of powerful irradiation and subsequent radiation annealing.

The two methods for M \ddot{u} ssbauer studies were used: 1) in standard transmission geometry (MS) and 2) with registration of conversion electrons from the material surface (KEMC). In the first case, the M \ddot{u} ssbauer spectra contained information about all

implanted Fe-57 atoms. As concerns KEMS, only Fe atoms were recorded that were in the surface irradiated layer with a thickness of about 0.1 μm . The thickness was determined by the yield of ^{57}Fe conversion electrons with energies of 7.3 - 13.6 keV.

Testing

The studied samples were Ta and Mo foils with a thickness of 20 μm . The thickness of the studied foils was selected so as to conduct M \ddot{u} ssbauer measurements in transmission mode (MS). Foils were obtained by repeated cold rolling of the original bulk samples. Recrystallization annealing for the foils was carried out in vacuum $5 \cdot 10^{-6}$ mm of mercury for 2 hours at a temperature of 1000 $^{\circ}\text{C}$. The purity of the initial Ta and Mo was no worse than 99.9.

Irradiation with ^{57}Fe ions with an energy of 1 MeV was carried out using a UKP-2-1 heavy-ion accelerator at the Institute of Nuclear Physics (Almaty). A special holder made of aluminum was designed and manufactured to carry out irradiation experiments, an appropriate sample of metallic iron was placed inside enriched up to 95% with ^{57}Fe isotope, for its further ionization in a source of heavy ions and subsequent acceleration. The ion current density was maintained in the range of 50 - 100 nA. The ion flux fluence for all samples was 5410^{16} ion / cm^2 .

X-ray diffraction analysis was carried out using BRUKER D8 ADVANCE diffractometer. The diffraction patterns were measured both from the side of the irradiated surface and from the reverse side in the range of angles $2\theta = (20 \text{ } \varphi 90)$.

M \ddot{u} ssbauer studies were carried out in two modes: 1) in the standard transmission geometry (MS) and 2) with registration of conversion electrons from the irradiated surface of the material (KEMC). The measurements were carried out on an MS-110Em spectrometer at room temperature. A ^{57}Co radioactive source in a chromium matrix served as the M \ddot{u} ssbauer source of gamma rays. The M \ddot{u} ssbauer spectra were analyzed and processed using the least square method using the SpectrRelax program [7].

The SRIM-2008 software [8] was used to assess the degree of influence of the ion beam on the crystal lattice of Mo and Ta. The results are provided in Table 1.

Table 1 SRIM calculation data

Element	Projective mileage R, nm	vacancies number / ion	Total number of displaced atoms	DPA (CHA)
Ta	272	7670	3.8410^{20}	250
Mo	315	6580	3.3410^{20}	165

Note that the average range of Fe ions (projective range, R) is approximately the same for all matrices, $R \approx 300$ nm. The average number of displacements per atom (DPA) for two matrices is approximately 200.

Figure 1a provides the dependence of the concentration of Fe, $n(\text{Fe})$ atoms implanted in a tantalum foil on the x distance to the irradiated surface (curve 1, concentration is expressed in at.%).

The calculations were performed taking into account the diffusion of the matrix atoms. The calculated Ta diffusion coefficient turned out to be small and equal to 3.09 Ta atoms / ion. Accordingly, a fluence of $5 \cdot 10^{16}$ at / cm^2 causes a sputtering of a Ta layer with a thickness of 28 nm, which is

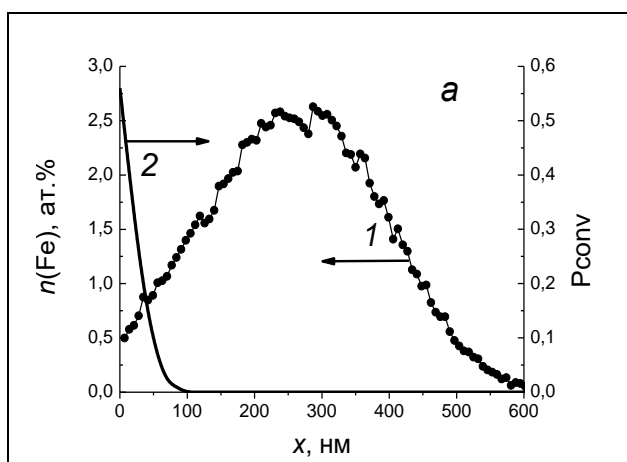


Fig. 1. a Concentration of implanted atoms Fe, $n(\text{Fe})$, in the Ta matrix from the x depth (curve 1); curve 2 – output probability of conversion electrons P_{conv} from x depth (right axis Y)

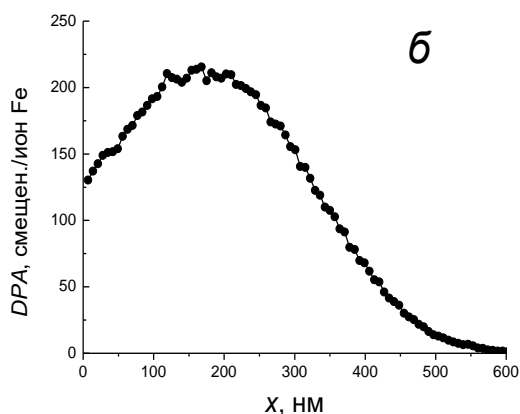


Fig. 1. b DPA parameter - the number of displacements per ion, as a function of x depth

noticeably less than the thickness of the implanted layer. Similar concentration curves were obtained for Mo. The maximum concentration of ^{57}Fe implanted atoms in Ta and Mo is approximately 2.6 at.%.

Figure 1b provides the dependence of the DPA parameter in tantalum on the distance to the irradiated

surface, DPA (x). This parameter, equal to the average number of displaced matrix atoms per ion, represents the degree of matrix destruction upon irradiation. STRIM calculations specify only the initial conditions for the problem of material transformation under radiation exposure. The final phases and structure of the material is determined by radiation annealing, which occurs during irradiation.

Mössbauer spectra of ^{57}Fe in Mo and Ta

Figures 2a and 2b provide the Mössbauer spectra of ^{57}Fe implanted in Ta. Figure 2a provides the conversion electron spectrum (KEMS). The spectrum corresponds to ^{57}Fe atoms located in the surface layer at a depth of ≈ 100 nm. The probability curve for the exit of conversion electrons from Ta is shown in Fig. 1 a, curve 2 [9, 10].

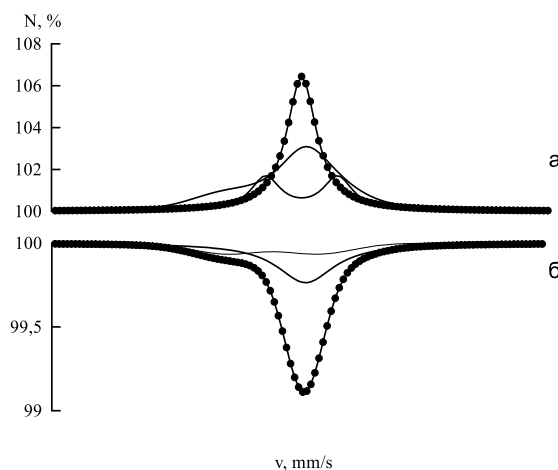


Fig. 2. Mössbauer spectra of ^{57}Fe implanted in the Ta matrix. a - conversion electron spectrum (KEMS); b - transmission spectrum (MS).

The KEMS spectrum consists of a broadened singlet and a strongly broadened doublet; the intensities of the sub-spectra are 70% and 30%, respectively. Presumably, the doublet corresponds to a strong distortion of the crystal lattice, and the singlet to a less distorted phase.

The Mössbauer transmission spectrum in Fig. 2b also consists of a singlet and a doublet. A consistent analysis of the conversion electron spectra (KEMS) and transmission spectra (MS) was carried out in the work. When processing transmission spectra (MS), it was taken into account that they should contain a KEMS spectrum, as well as an additional contribution from deeply located Fe atoms. With this in mind, the transmission spectrum processing model contained a KEMS spectrum in which all parameters except the total intensity were recorded, plus an additional singlet spectrum. The parameters of this singlet within the errors coincided with the KEMS singlet.

Figures 3a and 3b provide the Mössbauer spectra of ^{57}Fe implanted in Mo: the conversion electron spectrum of KEMS is 3a and the transmission spectrum of MS is 3b. The spectra of Mo are similar to those of Ta, and contain singlet and doublet contributions.

The KEMS spectra for both Ta and Mo show that both “doublet” and “single” phases are present near the surface ($x \approx 100$ nm). At large depths, a “singlet” phase is predominantly formed. This phase distribution is especially characteristic of Mo, for

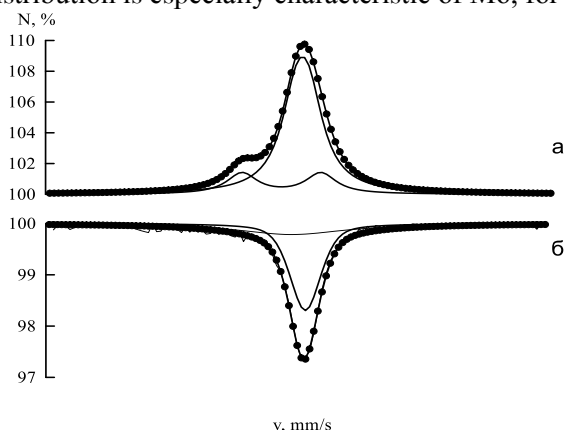


Fig. 3. Mössbauer spectra of ^{57}Fe implanted in a Mo matrix. a - conversion electron spectrum (KEMS); b - transmission spectrum (MS).

which a single line in the transmission spectra dominates and amounts to 93%. This line in the spectrum of Mo has a width of $G_s = 0.27$ mm / s, which only slightly exceeds the natural width of the Mössbauer line for ^{57}Fe [11]. This means that the monopic in Mo corresponds to Fe atoms, which replace Mo atoms in the crystal lattice. In other words, even with strong radiation exposure ($DPA = 200$), a solid solution of substitution of Fe in Mo is mainly formed in the Mo matrix.

The KEMS spectrum of the “singlet” phase Ta is greatly broadened, and in the case of the MS spectrum it is described by a small quadrupole splitting $QS = 0.17$ mm / s. It is known that Fe atoms do not dissolve in Ta at room temperature under equilibrium conditions [12]. With this in mind, we can assume that the “singlet” phase is the formation of Fe + Ta + vacancy complexes in the Ta matrix. These assumptions do not contradict the results of [12], in which the Mössbauer isotope ^{57}Co was introduced into the samples of high purity molybdenum (99.999%) to an average concentration of 0.001 at.%. The diluted MoCo alloy thus obtained was irradiated with protons with an energy of 70 keV to a fluence of $2 \cdot 10^{18}$ cm $^{-2}$ at a temperature of 300 K, and then isochoric annealing was carried out in the temperature range 300–1300 K, followed by measurement of γ -resonance spectra. In addition to

the single line corresponding to the position of Co in the position of substitution, six additional components were found, five of which (2-6) are symmetrical doublets with the initial width, and component 1 is a single broadened line. Component 1 is attributed to the complexes: (intrinsic interstitial atom) - (Co atom). Components 2–4, which appear after annealing in the temperature range 400–500 K, bind to complexes (vacancy) — (Co atom), and components 5 and 6 — with nonequilibrium segregation of Co atoms.

The issue of identifying the “doublet” phases for Ta and Mo remains open. Mössbauer data do not provide clear guidance. We list the possible phases: these are the phases of the Fe-Ta and Fe-Mo diagram, as well as the β -Ta phase. The initiation of cluster formations of Fe + Ta or Mo + vacancies or partial amorphization cannot also be ruled out.

Discussion of the results

The least irradiation effect is observed for metallic Mo. The “singlet” phase in Mo, constituting 84% of the surface layer, is a solid solution of substitution of Fe in Mo, which is confirmed by X-ray diffraction data, which showed a decrease in the lattice parameter from 3.15980 Å for the unirradiated side to 3.14194 Å for the irradiated one. In the case of tantalum, the “singlet” phase with an intensity of 78% apparently corresponds to the formation of complexes (Fe + vacancy) in the Ta matrix. Such complexes can serve as a source of additional stresses.

As for the “doublet” phases found both in tantalum and in molybdenum, the question remains open. X-ray diffraction performed by the Bragg-Brentano method did not detect additional phases. In particular, the β -Ta phase [13, 14] and phases of the Fe-Ta system: Fe-Ta: Fe $_2$ Ta, Fe $_7$ Ta $_6$ and Fe $_2$ Ta $_3$ [15] were not found for the tantalum matrix. For the molybdenum matrix, no traces of the phases of the Fe – Mo system were detected: Fe-Mo: Fe $_2$ Mo, Fe $_7$ Mo $_6$ and Fe $_2$ Mo $_3$ [16]. The diffraction patterns measured from the irradiated and back sides practically coincided. For the Ta matrix, a slight broadening of the lines was observed in the diffractogram of the irradiated side; for the Mo matrix, there was practically no additional line broadening. The broadening of the diffraction lines indicates disturbances in the crystal lattice of the surface layer. The “doublet” phases, apparently, refer to the formation of Fe + Ta complexes or Mo + vacancy in the regions of grain boundaries, or are associated with regions of partial amorphization of materials.

Based on the Mössbauer measurements and the dependence of the n (Fe) concentration on the depth

(Fig. 1a), the localization of phases in Ta and in Mo can be estimated. In the Ta matrix, a “doublet” phase and a “singlet” phase of substitution of Fe in Ta coexist in a 350 nm thick near surface layer; in the layer from 350 to 600 nm, only the “singlet” substitution phase is localized. In the Mo matrix, the “doublet” phase and the “single” monopick of Fe substitution in Mo are localized in the surface layer with a thickness of 250 nm; next is the “singlet” phase of the solid solution of substitution of Fe in Mo.

Conclusions

The effect of the implantation of ^{57}Fe ions with an energy of 1 MeV and a fluence of $5 \cdot 10^{16} \text{ ion/cm}^2$ on the properties of structural materials of the nuclear industry [17], Ta, Mo was studied. Implantation took place in a surface layer with a thickness of about 600 nm and corresponded to approximately 200 displacements of the matrix atoms per ion ^{57}Fe .

For metallic Ta and Mo, Mössbauer spectroscopy also showed the formation of two phases. The main “single” line in the spectrum of molybdenum (84%) is a solid solution of Fe in Mo substitution. The monopik in the tantalum spectrum (78%), taking into account the zero solubility of Fe in Ta, most likely corresponds to the formation of a complex (Fe + vacancy) in the Ta matrix. The nature of the surface “doublet” phases has not been completely established.

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Металл Та мен Мо-де Fe-57 имплантациясын рентгенқұрылымдық және мессбауэрлік зерттеулер

Бедельбекова К. А.

Түйіндеме. Атомдық және термоядролық энергетиканың дамуы материалтанушыларға конструкциялық материалдарды жасаумен байланысты бірқатар мәселелер қойып отыр. Қазіргі таңда ШНП үнемді, ұзақ мерзімді және қауіпсіз жұмысын толықтай жүзеге асыруға мүмкіндік беретін жбэлтері қапшықтарының материалын әзірлеу іске аспағанын атап өткен жөн. Жұмыс істеп тұрған және перспективалық ядролық қондырғыларға арналған конструкциялық материалдардың қасиеттерін зерделеу әлі де маңызды ғылыми-техникалық міндеттердің бірі болып табылады. Рентгендік дифракция және мессбауэрлік спектроскопия әдістерімен ^{57}Fe ядроларында атом өнеркәсібінің металл Та мен Мо конструкциялық материалдарының радиациялық тұрақтылық қасиеттеріне 1 МэВ энергиялы және $5 \cdot 10^{16} \text{ ion/cm}^2$ флюенсті ^{57}Fe иондары имплантациясының әсері зерттелді. STRIM программасының көмегімен ендірілген Fe атомдарының концентрациясы есептелді. Матрицаларға Та және Мо ендіру нәтижесінде екі фазаның түзілуі айқындалды. Молибдендегі (84%) негізгі фаза Мо-де Fe ауыстыратын қатты ерітінді болып табылады. Танталда (78%) негізгі фаза Та матрицасында Fe жиынтықтарының түзілуіне жауап береді. Алынған зерттеулер нәтижелері ядролық қондырғыларды қауіпсіз пайдалану мәселелерін шешуге және олардың жұмысының тиімділігін арттыруға пайдаланылуы мүмкін, бұл активті аймақтың материалдарының ресурстық сипаттамаларын дұрыс бағалауға және жоғары зақымдаушы дозаларда сәулелендіру кезінде олардың әрекетін болжауға мүмкіндік береді.

Түйін сөздер: Имплантация, конверсиялық және абсорбциялық мессбауэрлік спектроскопия, рентгендік дифракция, STRIM программасы, радиациялық зақымдану.

Рентгеноструктурные и мессбауэровские исследования имплантации Fe-57 в металлический Ta и Mo

Бедельбекова К. А.

Аннотация. Развитие атомной и термоядерной энергетики ставит перед материаловедом ряд проблем, связанных с созданием конструкционных материалов. Следует отметить, что на сегодняшний день материала чехлов твэлов, который позволил бы в полной мере реализовать экономичную, длительную и безопасную работу РБН, разработать не удалось. Изучение свойств конструкционных материалов для эксплуатируемых и перспективных ядерных установок по-прежнему остается одной из важнейших научно-технических задач. Методами рентгеновской дифракции и мессбауэровской спектроскопии на ядрах ^{57}Fe исследовано влияние имплантации ионов ^{57}Fe с энергией 1 МэВ и флюенсом $5 \cdot 10^{16} \text{ion/cm}^2$, на свойства радиационной устойчивости конструкционных материалов атомной промышленности металлических Ta и Mo. Мессбауэровские исследования проводились по двум методикам: 1) в стандартной геометрии на пропускание (MC) и 2) с регистрацией электронов конверсии из поверхности материала (КЭМС). С помощью программы SRIM была рассчитана концентрация имплантированных атомов Fe. В результате имплантации в матрицы Ta и Mo обнаружено образование двух фаз. Основная фаза в молибдене (84%) представляет собой твердый раствор замещения Fe в Mo. Основная фаза в тантале (78%) отвечает образованию комплексов Fe в матрице Ta. Полученные результаты исследования могли бы применяться для решения проблем безопасной эксплуатации ядерных установок и повышения эффективности их функционирования, позволив правильно оценивать ресурсные характеристики материалов активной зоны и предсказывать их поведение при высоких повреждающих дозах облучения.

Ключевые слова: Имплантация, конверсионная и абсорбционная мессбауэровская спектроскопия, рентгеновская дифракция, программа STRIM, радиационные повреждения.

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Исследование водородопроницаемости мембран, покрытых различными металлическими пленками (обзор)

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Аннотация. В последнее время поиск эффективного способа получения сверхчистого водорода является одной из наиболее актуальной задачей, который позволяет решить промышленные задачи, где использование водорода чистотой свыше 99,9999% является критическим. Водород составляет 10% массы живых систем на нашей планете, однако основным источником его получения служит углеродное сырье, в частности природный газ, из которого добывают $\geq 90\%$ водорода в мире. Одним из наиболее перспективных способов выделения водорода из газовых смесей, образующихся при паровой конверсии, является одностадийное мембранное разделение с получением сверхчистого водорода. Разработка мембраны для отделения водорода от газовых смесей является одной из важнейших задач водородной энергетики. Нам известно, что молекула водорода двухатомна — H_2 . При нормальных условиях это газ без цвета, запаха и вкуса. Водород хорошо растворим во многих металлах (Ni, Pt, Pd и др.), особенно в палладии (850 объемов H_2 на 1 объем Pd). С растворимостью водорода в металлах связана его способность диффундировать через них.

Ключевые слова: водород, углеродное сырье, мембрана, паровая конверсия, растворимость.

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Введение

Промышленное производство водорода это неотъемлемая часть водородной энергетики, первое звено в жизненном цикле употребления водорода. Водород практически не встречается в природе в чистой форме и должен извлекаться из других соединений с помощью различных химических методов. Разнообразие способов получения водорода является одним из главных преимуществ водородной энергетики, так как повышает энергетическую безопасность и снижает зависимость от отдельных видов сырья. К ним относятся: паровая конверсия метана и природного газа; газификация угля; электролиз воды; пиролиз; частичное окисление; биотехнологии. Использование водородопрони-

цаемых металлических мембран в процессе получения водорода из газовых смесей позволяет получать водород высокой чистоты. Задача получения дешевого высокочистого водорода в промышленном масштабе требует разработки высокопроизводительных мембран, обладающих целым комплексом свойств. Одним из основных подходов к повышению производительности мембранных элементов для извлечения высокочистого водорода из водородосодержащих газовых смесей является разработка сплавов на основе палладия с повышенной водородопроницаемостью толщиной ~ 10 мкм. [1].

Проблема «водород в металлах» привлекает внимание ученых различных специальностей: электрохимиков, металлургов, металловедов и др. Практическая важность

исследований водородопроницаемости (ВП) металлов очевидна: большинство коррозионно-электрохимических процессов в водных растворах сопровождается выделением водорода и неизбежным наводороживанием металла. Металл-водородные системы используются в порошковой металлургии; в качестве замедлителей, отражателей, экранов в ядерных реакторах; в ядерной технологии для разделения изотопов металлов в форме гидридов; при подборе оптимальных режимов работы термоядерных реакторов; в водородной энергетике для хранения и транспортировки водорода-теплоносителя; в качестве электродов для аккумуляторов и топливных элементов и т.д. Системы металл-водород оказались своего рода модельными объектами, удобными для изучения ряда важных физических явлений, например, сверхпроводимости и фазовых переходов второго рода, и «оттачивания» экспериментальных методов исследования, в частности, ядерно-магнитной рентгенографии (ЯМР), нейтронографии, эффекта Мессбауэра и способов измерения коэффициентов диффузии, теоретическая интерпретация которых в данном случае оказывается связанной с необходимостью учета необычного явления зависимости этих коэффициентов от формы образца. Развиваются теоретические представления о диффузионных перемещениях водорода в металлических структурах, которые рассматриваются как с классических позиций (прыжковый надбарьерный механизм), так и с учетом возможностей реализации подбарьерных туннельных переходов и коллективных актов перемещения водорода при парном взаимодействии Н-Н. Диффузионный процесс зависит от состояния электронной подсистемы металла и природы ионного остова, формирующего кристаллическую структуру твердого тела, и может осложняться химическим взаимодействием с формированием гидридных фаз [2-6].

Металлы 5-й группы обладают наивысшей среди других металлов способностью к транспорту водорода сквозь металлическую решетку [7-11]. Соответственно на основе металлов 5-й группы можно изготавливать мембраны для выделения водорода из газовых смесей более эффективные, чем применяемые в настоящее время мембраны из сплавов палладия (себестоимость таких мембран ниже). Проблемой является химическая активность этих металлов. В результате взаимодействия с химически активными газами, а также поверхностной сегрегации кислорода, растворенного в решетке, поверхность металлов 5-й группы покрыта оксидной пленкой, которая чрезвычайно

тормозит необходимую для абсорбции водорода каталитическую диссоциацию молекул H_2 на поверхности [8-12]. Эта пленка, однако, при рабочих температурах ($> 520K$) не защищает металлы от дальнейшего окисления и других химических реакций с компонентами газовой смеси, содержащей водород [12].

Однако для того чтобы использовать мембраны из металлов 5-й группы или их сплавов для выделения обычного молекулярного водорода из типичных газовых смесей, содержащих H_2O , CO , O_2 , C_nH_m и другие химически активные компоненты, поверхность мембраны должна иметь покрытие, обеспечивающее каталитическое разложение молекул H_2 и защиту материала мембраны от коррозии, но не препятствующее при этом транспорту водорода сквозь мембрану. Этим требованиям удовлетворяет покрытие из палладия или его сплавов, если оно не толще нескольких микрон [13].

Основными характеристиками палладиевых мембран для выделения водорода из газовых смесей являются скорость проникновения водорода через мембрану, ее прочность и стойкость при эксплуатации. Использование чистого палладия ограничено существованием при температуре ниже $300^\circ C$ и давлении 2 МПа α и β гидридных фаз, взаимные превращения которых приводят к разрушению мембран после нескольких циклов нагрева и охлаждения в атмосфере водорода [14]. Сплавы палладия с рядом d и f элементов механически прочны при пропускании водорода, сохраняют при этом высокую растворимость и проницаемость [15]. Наиболее хорошо изученными материалами для водородопроницаемой мембраны являются сплавы палладия с серебром, в которых проницаемость водорода изменяется по экстремальному закону и достигает максимума при содержании серебра 15-25% [16-18].

Экспериментальные исследования

В работе [19] представлены результаты исследований влияния толщины слоя вольфрама, нанесенного на поверхность мембран из ниобия и тантала методом магнетронного распыления, на их водородопроницаемость в условиях контакта с аргон-водородной смесью. В ходе проведенных исследований установлено, что нанесение вольфрамовой пленки на поверхность мембраны из тантала способствует увеличению ее водородопроницаемости.

Для исследования зависимости водородопроницаемости от толщины мембраны

в работе [20] была разработана экспериментальная ячейка, позволяющая герметизировать мембраны до 6 мкм без нарушения целостности мембраны. Эксперимент показал, что мембраны толщиной 200, 150, 100, 50 мкм без предварительного отжига перед испытанием обладают водородопроницаемостью — $1-1,2 \text{ нм}^3 \cdot \text{мм} / \text{м}^2 \cdot \text{ч} \cdot \text{Мпа}^{0,5}$ при работе до 450°C . В некоторых мембранах (—50%) толщиной 20, 12, 10 и 6 мкм после предварительного отжига в высоком вакууме $\text{Рост} = 1 \cdot 10^{-5} \text{ мм. рт. ст.}$ при температуре 850°C в течение 30 мин с дальнейшим охлаждением в вакууме наблюдается нарушение целостности, водородопроницаемость герметичных мембран составила $0,02-0,04 \text{ нм}^3 \cdot \text{мм} / \text{м}^2 \cdot \text{ч} \cdot \text{Мпа}^{0,5}$. После двукратного проведения измерений при 500°C величина водородопроницаемости неотожженной мембраны толщиной 66 мкм понизилась от 1,2 до $0,45-0,3 \text{ нм}^3 \cdot \text{мм} / \text{м}^2 \cdot \text{ч} \cdot \text{Мпа}^{0,5}$.

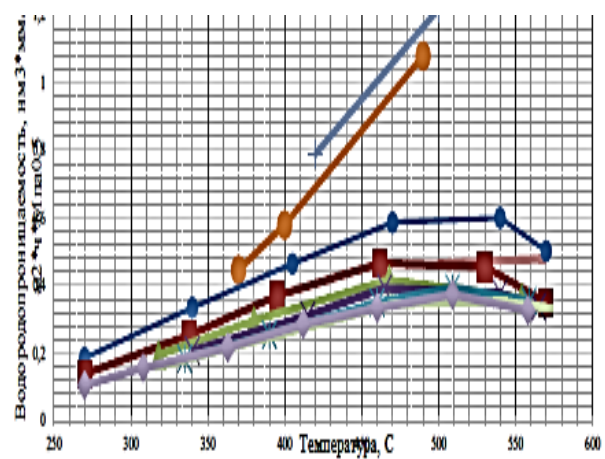


Рисунок 1 Зависимость водородопроницаемости от температуры

В статье [21] предлагается замена Nb элементами VI и Mo подгруппы, которая проводилась для двухфазных сплавов Nb-Ti-Ni. Легирование влияние на характеристики проникновения водорода как функцию концентрации W / Mo было проанализировано на основе описание с учетом химического потенциала водорода. Замена Nb на W или Mo приводит к пониженной растворимости водорода, что способствует повышению устойчивости к водородному охрупчиванию. Эффект W/Mo легирование на подвижность атома H и, следовательно, проницаемость водорода зависит от концентрации W/Mo и рабочая температура. Одновременно улучшается подвижность водорода и механическая стабильность мембраны, особенно при более низкой

температуре $T \leq 523 \text{ K}$, было достигнуто после легирования W / Mo на 5 ат. %.

[22] Представлены результаты измерения водородопроницаемости и дилатации мембран из фольг ниобия и тантала толщиной 40 мкм, с одной стороны покрытых слоем твердого раствора NbMo, NbW и TaMo, TaW соответственно. Измерения проведены при контакте газовой смеси аргона и водорода технической чистоты в соотношении 1/5 при избыточном давлении 500 кПа в условиях циклического колебания температуры с постепенным снижением ее средней величины от $580-585^\circ\text{C}$. Показано, что напыление слоев NbMo, NbW, TaMo толщиной $\sim 1 \text{ мкм}$ позволяет увеличить максимальную водородопроницаемость мембран в сравнении с мембранами из чистых ниобия и тантала. Наиболее существенное влияние на этот параметр оказывает легирование ниобия вольфрамом в количестве 14 мас. %. Этот эффект может быть объяснен как более развитой и чистой от оксидных пленок поверхностью осаждаемых пленками твердых растворов, так и ролью легирующих элементов при диссоциативной абсорбции. Водородопроницаемость мембран после достижения максимального значения снижается. Степень снижения водородопроницаемости ниже у мембран со слоем более высоколегированного твердого раствора, что объясняется их высокой коррозионной стойкостью. Показано, что дилатация и период работы до разрушения мембран со слоем твердого раствора существенно варьируется в отличие от мембран тантала и ниобия, что объясняется высоким влиянием примесей газов в составе используемого при магнетронном распылении аргона. Это объясняется сродством ниобия и тантала с такими газами как кислород и азот, наличие их малых примесей в пленках приводит к снижению величины водородопроницаемости мембраны в целом. На основании проведенных исследований показана принципиальная возможность использования высоколегированных твердых растворов Nb - 30 мас. % W, Nb - 40 мас. % Mo и Ta - 25 мас. % Mo в качестве материалов для осаждения барьерных слоев на поверхность мембран из тантала и ниобия для отделения их от палладиевого каталитического слоя.

В работе [23] впервые предлагается получить методом диффузионного легирования градиентный слой на поверхности водородопроницаемых мембран на основе тантала и ниобия, с целью повышения их коррозионной стойкости и снижения водородной хрупкости. Представлены результаты серии экспериментов

по отработке методики диффузионного легирования фольг из ниобия и тантала, включающих подготовку поверхности фольг, нанесение пленки легирующих элементов и термическую обработку. Для подготовки поверхности фольг к нанесению слоя легирующего элемента сопоставлены методы электролитической полировки, ионно-атомной очистки и их комбинации. Выбраны условия для осаждения покрытий на фольги из ниобия и тантала методом магнетронного распыления, при которых обеспечиваются минимальные напряжения в поверхностных слоях. Описано разработанное оборудование для диффузионного легирования фольг из ниобия и тантала в условиях вакуума при их резистивном нагреве. Представлены данные о коррозии фольг из ниобия и тантала при их отжиге в низком вакууме. Приведены результаты исследования структуры поверхности и состава по сечению градиентных слоев диффузионно-легированных фольг из ниобия и тантала такими элементами как W, Zr, Mo, Al. Показано, что наиболее интенсивно в ниобий и тантал диффундировали молибден и вольфрам. Цирконий и алюминий практически не диффундировали в ниобий. Алюминий удовлетворительно диффундировал в тантал с образованием кристаллов интерметаллического соединения $TaAl_3$ на поверхности фольги. Из полученных данных следует, что, варьируя время и температуру отжига, можно существенно воздействовать на концентрацию легирующих элементов на поверхности ниобиевой и танталовой водородопроницаемых мембран, глубину их распространения с формированием в диффузионном слое твердых растворов переменного состава.

В статье [24] водородопроницаемость мембраны из сплава Pd- 27 мол.% Ag была проанализирована с учетом нового описания водородной проницаемости, основанного на химическом потенциале водорода. Поток водорода постоянно пропорционален фактору P_{CT} , f_{PCT} , который отражает форму соответствующей изотермы состав-давление-давление (кривая P_{CT}), независимо от того,

выражена ли растворимость водорода в формате закона Зиверта или нет. Из двух точек фактора P_{CT} , f_{PCT} и DBTC (концентрация водорода в пластичном хрупком переходе), получена концепция конструирования сплава мембран из сплавов, не основанных на Pd. Например, сплав V-9 мол.% Al предназначен для условий температуры и давления. Для этого условия эта мембрана из сплава обладает превосходной проницаемостью для водорода с сильным сопротивлением водородному охрупчиванию.

Для системы Nb – W – Mo в работе [25] исследовано легирующее влияние молибдена на растворимость водорода, устойчивость к водородному охрупчиванию и водородную проницаемость. Установлено, что растворимость водорода снижается при добавлении молибдена в сплав Nb-W. В результате стойкость к водородному охрупчиванию улучшается за счет снижения концентрации водорода в сплаве. Показано, что сплав Nb-5 мол.% W-5 мол.% Mo обладает превосходной водородной проницаемостью, не проявляя водородного охрупчивания при использовании в соответствующих условиях водородной проницаемости, то есть при температуре и давлении водорода.

Выводы

Таким образом, показано, что к существенным недостаткам мембран относятся сравнительно малый ресурс работы (не выше нескольких тысяч часов) ввиду их недостаточно высокой механической прочности, а также высокая стоимость основного компонента - палладия. Тем не менее последние успехи в разработке сверхтонких композитных мембран на различных носителях свидетельствуют о перспективности внедрения мембранной технологии в водородную энергетику.

Авторы выражают признательность и особую благодарность Министерству образования и науки за оказанную помощь при написании настоящей статьи.

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Металл қабықшалармен қапталған мембраналардың сутегі өткізгіштігін зерттеу (шолу)

Кәрбоз Ж. Ә., Досаева С. К.

Түйіндеме. Соңғы уақытта аса таза күйдегі сутекті өндірудің тиімді әдісін іздеу ең маңызды міндеттердің бірі болып табылады, бұл өнеркәсіптік мәселелерді шешуге мүмкіндік береді, мұнда тазалығы 99,9999% -дан асатын сутегі өте маңызды. Сутек планетамыздағы тірі жүйелер массасының 10% құрайды, бірақ оны өндірудің негізгі көзі - көміртегі шикізаты, атап айтқанда табиғи газ, оның ішінде әлемдегі сутектің 90% -ы өндіріледі. Бұды қайта құру нәтижесінде пайда болатын газ қоспаларынан сутекті бөліп алу ең перспективті әдістерінің бірі – аса таза күйдегі сутекті алу үшін мембраналардың бір сатылы бөлінуі. Сутекін газ қоспаларынан бөлетін мембрана жасау сутегі өндірісінің маңызды міндеттерінің бірі болып табылады. Сутек молекуласы биатомды - H_2 болатынын білеміз. Қалыпты жағдайда бұл түссіз, иіссіз немесе дәмсіз газ. Сутегі көптеген металдарда тез ериді (Ni, Pt, Pd және т.б.), әсіресе палладийде (1 көлем Pd үшін H_2 850 көлем). Сутектің металдардағы ерігіштігі оның олар арқылы таралу қабілетімен байланысты.

Түйін сөздер: сутегі, көміртегі шикізаты, мембрана, бу конверсиясы, ерігіштік.

Study of hydrogen permeability of membranes coated with various metal films (review)

Karboz Zh. A., Dossayeva S. K.

Abstract. Recently, the search for an effective method for producing ultrapure hydrogen has been one of the most urgent tasks, which allows us to solve industrial problems where the use of hydrogen with a purity of more than 99.9999% is critical. Hydrogen makes up 10% of the mass of living systems on our planet, but the main source of its production is carbon raw materials, in particular natural gas, from which $\geq 90\%$ of the world's hydrogen is produced. One of the most promising methods for the evolution of hydrogen from gas mixtures resulting from steam reforming is single-stage membrane separation to produce ultrapure hydrogen. The development of a membrane for separating hydrogen from gas mixtures is one of the most important tasks of hydrogen energy. We know that the hydrogen molecule is diatomic - H_2 . Under normal conditions, it is a gas without color, odor or taste. Hydrogen is readily soluble in many metals (Ni, Pt, Pd, etc.), especially in palladium (850 volumes of H_2 per 1 volume of Pd). The solubility of hydrogen in metals is associated with its ability to diffuse through them.

Key words: hydrogen, carbon raw materials, membrane, steam conversion, solubility.

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Silver, gold and palladium leaching from pre-prepared electronic scrap using bromine-bromide solution

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Abstract. The leaching of silver, gold, and palladium from printed circuit boards in the bromine - bromide system after preliminary removal of the associated metals and copper has been investigated. It was established experimentally that the dissolution of gold with a turnover of leaching solution from a previously prepared PCB concentrate in comparison with the leaching of the original electronic scrap proceeds at a higher rate and much more completely, so the average degree of gold extraction rose from 87.2 to 89.39%. The consumption of bromine decreased from 20-32 to 12 kg Br₂ per ton of scrap. So by seven leaching stages, it was possible to obtain a productive solution with the content, g · dm⁻³: 0.0652 Au, 0.015 Pb, 0.00052 Cu. Pretreatment PCB concentrate also increases the rate and completeness of silver and palladium leaching. At the same time, preliminary removal of the main part of copper allows reducing its content in the productive solution by almost 10 times. Under the conditions of collective leaching of silver, gold and palladium with a slightly acidic (pH = 1.98) bromine-bromide solution, with a content of 100.8 g · dm⁻³ of bromide ions, it is possible to convert 98.64% Au, 97.23% Ag and 98.33% Pd to the solution. The kinetics of precipitation of gold, silver and palladium from productive solutions using zinc dust, copper powder and hydrazine solution has been studied. As a results it was to precipitate gold on zinc dust in the form of cement powder with a purity of 99.4% and collective (Ag-Pd) and (Au-Ag-Pd) products using a 10% solution of hydrazine with content, mass. %: 1.18 Cu, 90.6 Ag, 7.2Pd and 1.2 Cu, 83.31Ag, 7.15 Pd, 7.95 Au, respectively.

Key words: hydrometallurgy of gold, silver, gold and palladium leaching in the bromine-bromide system, cementation of noble metals from bromide solutions.

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Introduction

Previously [1], we have studied in detail the thermodynamics and kinetics of leaching silver, gold, palladium and platinum from the initial electronic scrap represented by printed circuit boards in the bromine-bromide system in the presence of a phosphate buffer solution. The effect of pH noble metals, concentration of active bromine, content of bromide ions and concentration of buffer solution on the speed and entirety of leaching was studied. It was found that gold dissolves in the studied system practically in an alkaline environment quite selectively, fully and with a high speed. However, silver and palladium can be converted into a solution

only using a slightly acid bromine - bromide solution, which causes the dissolution of the accompanying metals, especially copper and leads to an increased consumption of bromine. In this regard, it was of interest to study the behavior of silver, gold, and palladium in the process of their bromine-bromide leaching from PCB concentrate after preliminary removal of accompanying metals and copper from it. As the initial sample, a PCB ordinary concentrate (Printed Circuit Boards) was used obtained as a result of physical and mechanical processing of dismantled electronic equipment by means of an industrial application of the Israeli company All Recycling Ltd (www.AllRecycling.co.il), of

composition, wt. %: 26.15 Cu, 4.7 Al, 3.6 Sn, 2.92 Pb, 2.1 Fe, 1.8 Zn, 1.32 Ni, 0.65 Cr, 0.163 Ag, 0.0150 Au, 0.0136 Pd, 0.007 Pt. This concentrate is characterized by a complex composition, and, along with copper, both ferrous (Fe, Cr) and non-ferrous (Al, Sn, Pb, Zn, Ni) metals with different chemical resistance are present as accompanying metals. Speaking by their position in a number of electrochemical tension of metals: $Al < Zn < Fe < Ni < Sn < Pb < H_2 < Cu < Ag < Pd < Au$, most of the present metals can be removed chemically under non-oxidizing conditions [2-5]. Speaking by the literature and our data, copper can be selectively separated by treating the concentrate with a solution of sulfuric acid in the presence of hydrogen peroxide as an oxidizing agent [6-11]. In this regard, the study of the optimal conditions for the leaching of gold, silver and palladium from a partially unmetallized PCB concentrate in the bromine - bromide system and the subsequent isolation of noble metals from the bromide solution is of theoretical and practical interest.

Thus, the present paper is devoted to:

- the study of the conditions of selective leaching of related metals and copper from the provided PCB concentrate;
- the study of the kinetics of leaching of silver, gold and palladium from pre-processed concentrate of printed circuit boards in the bromine-bromide system depending on pH, the concentration of active bromine, the concentration of bromide ions and the content of phosphate buffer solution;
- the study of the kinetics of the deposition of precious metals from bromide productive solution using cement dust, copper powder and a solution of hydrazine.

Testing. Devices and reagents

A series of experiments was prepared using the PCB concentrate sample presented above, previously grinded using a Retch GmbH laboratory hammer mill to a particle size of 0.5-2 mm. As reagents used: $MgCl_2$ (Fluka Israel), HCl (Fluka Israel), HNO_3 (Fluka Israel), $10.6 \text{ mol} \cdot \text{dm}^{-3}$ hydrogen peroxide solution (Negev Peroxide, Israel), NaBr (Fluka Israel), HBr (Fluka Israel), NaH_2PO_4 (Fluka Israel) and concentrated ($434 \text{ g} \cdot \text{dm}^{-3} Br_2$) solution of elemental bromine (Bromine Compound Israel). Reagent solutions were prepared using bidistilled water. Preliminary leaching of the accompanying metals was carried out at 368 K, the ratio of the contacting phases S:L = 1:3 with a hydrochloric acid

solution containing additional magnesium chloride in a liter flask with a mechanical stirrer ($300 \text{ rpm} \cdot \text{min} \cdot \text{g} \cdot \text{dm}^{-3}$) and reflux condenser which was placed in a thermostat, which allowed to control the temperature of the liquid coolant within $\gamma 0.5-1,0^0 \text{ C}$. Copper was leached at 348 K. For this purpose, 0.5 dm^3 of sulfate leach solution of the desired composition was poured into a liter flask installed with nozzles installed under a tin electrode for monitoring the redox potential (Eh), a mechanical stirrer ($600 \text{ rpm} \cdot \text{min} \cdot \text{g} \cdot \text{dm}^{-3}$), for supplying an oxidizing agent (H_2O_2 solution), loading solid material and sampling the solution. Bromine-bromide leaching was carried out at 298.5 K, the ratio of the contacting phases S:L = 1:5 and the speed of rotation of the stirrer $300 \text{ rpm} \cdot \text{g} \cdot \text{dm}^{-3}$. The required amount of leaching solution containing $20 \text{ g} \cdot \text{dm}^{-3} NaBr$ and $70 \text{ g} \cdot \text{dm}^{-3} NaH_2PO_4 \cdot H_2O$ was poured into a reaction vessel equipped with a mechanical stirrer and electrodes for measuring pH and redox potential (Eh), after which the required amount was poured chopped scrap, then the vessel was placed in a Huber GmbH Unistat thermostat and the temperature in the reactor was adjusted to the desired value, after which the stirrer, measuring instruments were turned on and the pre-calculated amount of concentrated elemental bromine solution ($434 \text{ g} \cdot \text{dm}^{-3}$) was supplied reading recorded original redox - potential, hereinafter in the course of the reaction, if necessary adjusting the pH injected $20 \text{ g} \cdot \text{dm}^{-3} NaOH$ solution. The metal content in the solution was analyzed on an ISP-OES set up. Each leach residue was washed, dried, weighed, and the whole sample was decomposed sequentially: first with $6 \text{ mol} \cdot \text{dm}^{-3}$ with HNO_3 solution and then in aqua regia solution at 303.5 K, the resulting solution was analyzed by ISP-OES. Thus, the degree of extraction of associated metals, copper, silver, gold and palladium was determined by the material balance.

Results and discussion

Leaching of associated metals

Non-oxidative leaching of the accompanying metals was carried out with a solution of $2.5 \text{ mol} \cdot \text{dm}^{-3} HCl$ in the presence of $2.6 \text{ mol} \cdot \text{dm}^{-3} MgCl_2$. The leaching results are shown in Fig. 1. As can be seen from the presented results, after 200 min of processing the concentrate, it was possible to transfer the main part of the initial aluminum, zinc and tin to the solution, %: 94.4 Al, 92.3 Sn, 89.2 Zn. Along the way, a substantial part of iron, nickel and lead is extracted into the solution, %: 75.8 Fe, 72.4 Ni, 44.8 Pb, with the degree of dissolution of copper 1.2%, and silver 0.56%. Gold and palladium pretreatment are not affected.

The resulting hydrochloric acid solution contained $11.6 \text{ g} \cdot \text{dm}^{-3}$ Sn. Due to the increased demand for tin in the modern electronic industry and a reduction in the raw materials of this metal, its value on the London Metal Exchange has noticeably increased. The conditions for the extraction of tin from chloride productive solutions were examined in detail by us earlier [12].

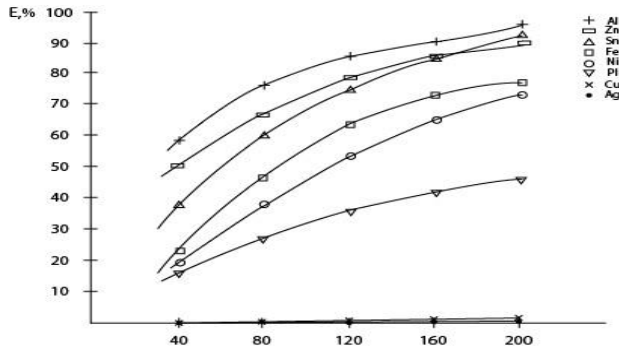


Figure 1 Results of preliminary leaching of the accompanying metals with hydrochloric acid solution: 368 K is temperature, the ratio of the contacting phases is S:L = 1:3, the rotation speed of the stirrer is 300 rpm

Copper leaching

The PCB concentrate (chemical concentrate 1) thus prepared was washed, dried to constant weight, and was used to study the kinetics of oxidative leaching of copper with a dilute solution of sulfuric acid in the presence of hydrogen peroxide as an oxidizing agent with scrap particle sizes ranging from 10-20 to 0.5-1 mm. As shown in the experiments, the fineness of the grinding of the material plays an important role, since electronic circuits containing copper and copper alloys are located inside the organic polymer material of the printed circuit board and are often additionally insulated with a protective varnish coating. Grinding scrap, especially in a ball mill, allows solvent to access the surface of the copper parts of the circuit. The experimental results are given in Table 1.

Table 1 The results of copper leaching with $1 \text{ mol} \cdot \text{dm}^{-3}$ sulfuric acid solution at a controlled redox potential of 520-680 mV, depending on the size of the scrap particles. The conditions of the experiments: temperature 348 K, the ratio of the contacting phases L:S = 3 and the rotation speed of the mechanical stirrer $600 \text{ rpm} \cdot \text{min}^{-1}$.

Time, min	Cu extraction into solution, %		
	10-20 mm	2-10 mm	0.5-1 mm
40	26.45	32.16	38.35
120	34.52	42.32	49.34
180	48.93	56.74	67.32
240	58.72	68.92	78.68
300	67.56	78.83	92.67

As a result of oxidative leaching, the results of which are presented in Table 1, it is possible to finely grind scrap to selectively transfer into solution up to 92.67% of the initial copper. At the same time, the remainder of the iron and nickel pass into the solution. Due to the reduction of material as a result of preliminary leaching, the concentration of precious metals increased by almost 1.4 times.

The resulting sulfate solution with a content of $68.5 \text{ g} \cdot \text{dm}^{-3}$ of copper can be electrochemically processed to obtain cathode copper suitable for subsequent refining.

Bromine-bromide leaching of precious metals

Chemical concentrate (2) obtained after sulfuric acid leaching, which contained, mass. %: 4.08 Cu, 0.55 Sn, 0.34 Al, 0.125 Fe, 0.136 Zn, 0.43 Pb, 0.324 Ag, 0.0297Au, 0.027 Pd and 0.0012 Pt were used for further experiments on the kinetics of gold leaching in the bromine-bromide system at pH 6 and subsequent leaching of silver and palladium from the residue at pH 1.98. The experimental results are provided in Tables 2 and 3. In the first case, experiments with the circulation of the productive solution were carried out on chemical concentrate 2.

Table 2 The results of the gold leaching in the bromine - bromide system at an initial pH of 6.1, the ratio of phases S:L = 3:1 with a revolution of the productive solution

Stage	[Br ₂] initial	[Br ₂] terminal	Br, ml	NaOH, ml	Buffer solution, ml	Eh, mV	pH	[Au], Ppm	[Au], Ppm terminal	E _{Au} , %
I	34.26	26.5	-	-	-	923	5.1	97	198	98.34
II	23.84	28.7	1.6	1.0	9.2	932	5.2	176	266	96.56
III	26.8	22.5	1.8	1.2	12.4	919	5.3	257	346	92.30
IV	20.4	18.6	1.8	1.2	18.6	917	5.2	342	428	90.65
V	17.6	14.3	1.8	1.2	28.9	908	5.1	389	472	86.58
VI	13.2	10.6	1.8	1.2	28.6	900	5.4	478	568	82.67
VII	9.6	6.8	1.8	1.2	28.6	882	5.3	572	652	78.63

Gold leaching with the circulation of the productive solution from the previously prepared scrap proceeds more fully, the average degree of gold recovery rose from 87.2 to 89.39%. Moreover, as a result of reducing the consumption of active bromine, it was possible to increase the number of stages to 7. The consumption of bromine per ton of scrap was reduced, thanks to these factors, from 20-32 to 12 kg

of Br_2 per ton of scrap. As a result of leaching, a productive solution (1) was obtained with a content of $0.0652 \text{ g} \cdot \text{dm}^{-3} \text{ Au}$, 0.0015 Pb , 0.00052 Cu .

Table 3 The results of the leaching of palladium and silver from the residue from the leaching of gold in the bromine - bromide system at an initial pH of 1.98, a bromine solution volume of 16 ml, a phase ratio of S:L = 1:5 and a concentration of bromide ions of $100.5 \text{ g} \cdot \text{dm}^{-3}$

Time, min	$[\text{Br}_2]$, $\text{g} \cdot \text{dm}^{-3}$	Eh, mV	pH	$[\text{Ag}]$, ppm	E_{Ag} , %	$[\text{Pd}]$, ppm	E_{Pd} , %
0	29.86	922	1.98				
60	24.10	918	1.50	300	46.34	15.46	28.63
240	21.54	908	1.40	404	62.34	24.64	45.26
300	20.43	912	1.50	567	87.45	37.86	68.82
360	19.78	900	1.30	612	94.32	48.64	89.15
420	19.13	899	1.50	625	96.20	53.08	97.20

The experimental results provided in Table 3 show that as a result of preliminary treatment of scrap, the speed and completeness of leaching of palladium increases. It should be noted that, probably, due to the easier conversion of the passivating AgBr film to the well-soluble AgBr_2^- anion complex, silver dissolves much faster than palladium. The resulting productive solution (2) contained, $\text{g} \cdot \text{dm}^{-3}$: 0.0053 Pd , 0.0625 Ag , 1.4 Cu , 0.00032 Fe , 0.0067 Pb . Thus, as a result of preliminary dissolution of the bulk of the initial copper, its content in the productive solution decreased by almost 10 times.

Table 4 presents the results of experiments on the kinetics of co-leaching of gold, palladium and silver at pH 1.98.

Table 4 The results of gold leaching, palladium and silver in a bromine - bromide system at a controlled pH of 1.98 and a redox potential of 920-908 mV, a bromine solution volume of 20 ml, a phase ratio of S:L = 1:5 and $100.5 \text{ g} \cdot \text{dm}^{-3} \text{ Br}^-$

Time, min	$[\text{Br}_2]$, $\text{g} \cdot \text{dm}^{-3}$	$[\text{Au}]$, ppm	E_{Au} , %	$[\text{Ag}]$, ppm	E_{Ag} , %	$[\text{Pd}]$, ppm	E_{Pd} , %
0	29.86						
60	23.72	34.95	58.84	321	49.62	15.30	28.32
240	20.18	57.51	96.82	430	66.34	25.10	46.48
300	19.64	58.41	98.34	599	92.40	39.10	72.34
360	19.18	58.43	98.45	626	96.62	47.88	88.67
420	18.44	58.56	98.64	628	97.23	53.10	94.33

The results of collective leaching of precious metals are presented in table. 4 show that under the presented conditions, silver and gold leach at close rates and after 6 hours of contact of the phases pass into the solution almost completely. Palladium also exhibits a high degree of recovery, however, as a result of passivation of the reaction surface, it dissolves relatively more slowly. The resulting solution (3) obtained by co-leaching contained, $\text{g} \cdot \text{dm}^{-3}$: 0.0059 Au , 0.0053 Pd , 0.0628 Ag , 1.8 Cu , 0.00032 Fe , 0.0067 Pb , 16.23 Br_2 and 110 Br^- .

Next, the conditions for the separation of gold, palladium and silver from productive solutions (1), (2) and (3) were studied.

Isolation of precious metals from bromine-bromide solutions by cementation

The separation of precious metals from productive solutions by cementation is complicated by the presence in the final solutions of a residual concentration of active bromine. In order to reduce the Br_2 content and its regeneration, the final solutions were evacuated before cementation. In this case, the outgoing gaseous bromine was passed through a solution with $100 \text{ g} \cdot \text{dm}^{-3} \text{ NaBr}$, which absorbed up to 80% bromine, the rest was hydrolyzed in an alkaline solution trap.

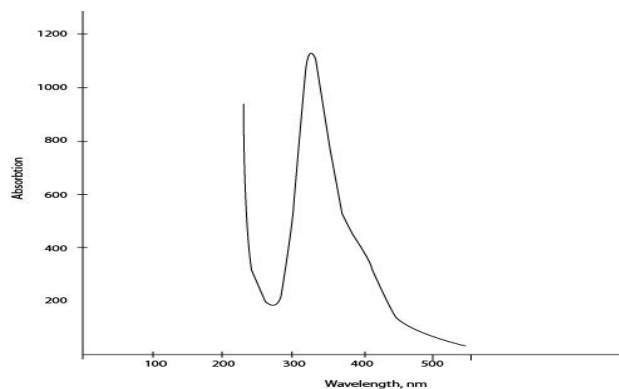


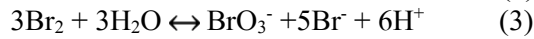
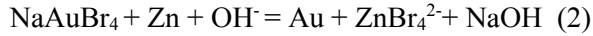
Figure 2 UV spectrum of a gold-containing bromine-bromide solution

Regenerated bromine-bromide solution can be used in the leaching stage.

In order to determine the composition of gold anionic bromide complexes present in the productive solution, the solution was analyzed using a UV spectrophotometer. The resulting spectrum shown in Fig. 2, it is characterized by a pronounced peak at 379 nm, which is usually associated with the presence of the most stable tetrabromaurate (III) AuBr_4^- in the solution under the studied conditions.

Figure 3 and table 5 show the results of studying the kinetics of gold deposition on zinc dust from solution (1) after its preliminary evacuation and adjustment of the corresponding pH value.

Cementation of gold on zinc dust in an alkaline medium can be described by reaction (2):



In this case, hydrolysis of active bromine by reaction (3) with the release of an H^+ -ion neutralizes the formation of sodium hydroxide, which stabilizes the pH of the medium.

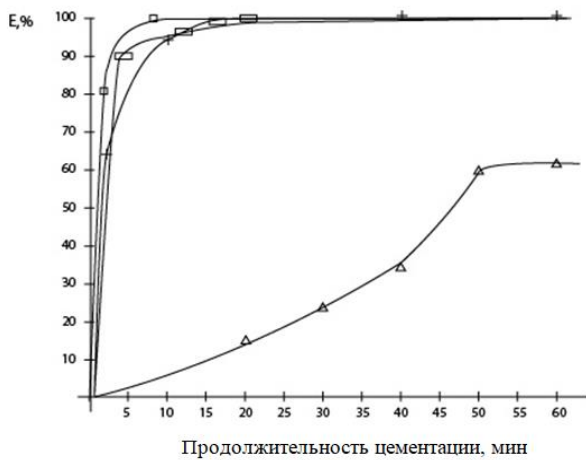


Figure 3 The results of the cementation of gold on zinc dust, depending on the initial pH of the productive solution

As can be seen from the data presented (Figure 3 and Table 5), gold cementation at zinc dust from

Table 5 Gold cementation results using zinc dust (-230 mesh) from bromine-bromide solution at pH 6 and a temperature of 290 K

Time, min	[Br ₂], g · dm ⁻³	pH	Eh	[Au], ppm	E _{Au} , %	Solution color
0	1.20	4.30	701	572	0	Brilliant orange
Start	0.86	8.11	697	567	0	Brilliant orange
2	0.82	8.19	650	121	78.66	Brilliant orange
15	0.80	8.40	465	30.3	94.66	Light-yellow
20	0.76	8.23	305	28.4	94.99	colorless
30	0.72	8.21	286	23.3	95.89	colorless
60	0.65	8.50	272	1.2	99.79	colorless

a pre-evacuated bromide solution in a relatively alkaline medium at pH 8, proceeds slowly and practically does not end, since the hydrolysis of dissolved zinc complicates the formation of cement gold. In slightly alkaline solutions, gold cementation occurs quickly and the bulk of the metal precipitates during the first 15 minutes.

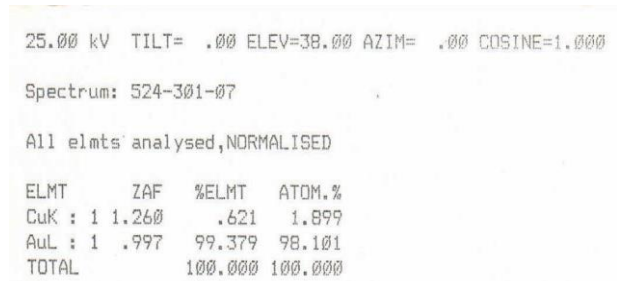


Figure 4 Results of SEM analysis of cement gold extracted from bromine-bromide solution on zinc dust

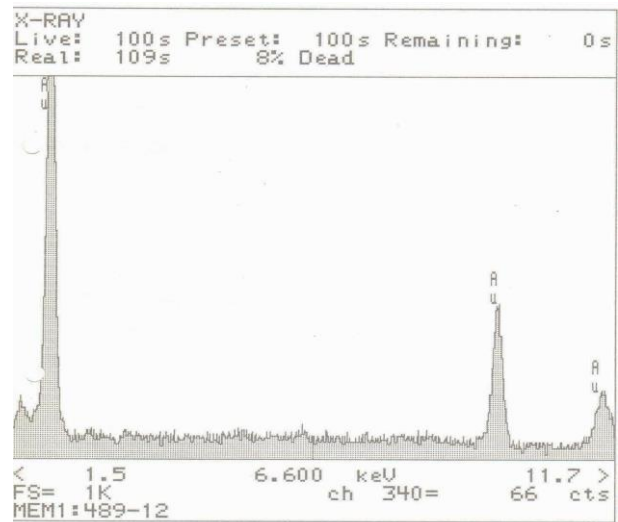


Figure 5 X-ray of cement gold isolated from bromine bromide on zinc dust

The cement slurry obtained from the bromine - bromide solution was analyzed using an X-ray phase analyzer (see Fig. 4) and an electron microscope (see Table 6). As can be seen from the results of the analysis, by zinc cementation, gold can be isolated in the form of a metal powder with a purity of 99.4%. The main impurity (0.6%) is copper.

Tables 6 and 7 show the kinetics of the deposition of precious metals from solutions (2) and (3) after their preliminary evacuation. Given the high content of copper ions in these solutions, preliminary experiments were carried out on the cementation of gold, palladium and silver on a copper powder, but no positive results were obtained because active bromine passivated the reaction surface of the copper powder.

Table 6 The results of the recovery of palladium and silver from a bromide solution (2) 1 ml of 10% solution of $N_2H_4 \cdot H_2O$ at pH 6, temperature is 278 K

Time, min	[Br ₂], g · dm ⁻³	pH	Eh	[Ag], ppm	E _{Ag} , %	[Pd], ppm	EPd, %
0	6.32	1.9	734	625	0	53.0	0
Start	5.86	8.10	697	574	0	50.5	0
2	3.23	8.23	650	141	77.4	8.9	82.3
15	1.86	8.40	465	43.3	93.1	2.7	94.6
20	1.23	8.67	305	32.4	94.8	1.9	96.2
30	1.20	8.72	286	28.3	95.5	0.7	98.6
60	1.18	8.78	272	8.2	98.7	0.6	98.8

Table 7 The results of the recovery of gold, palladium and silver from solution (3) 1.3 ml of 10 solution of hydrazine at pH 6 and temperature

Time, min	[Br ₂], g · dm ⁻³	Eh	[Ag], ppm	E _{Ag} , %	[Pd], ppm	EPd, %	[Au], ppm	E _{Au} , %
0	16.23	908	628.0	0	53.0	0	59.0	0
Start	7.23	762	616.0	0	52.0	0	57.8	0
2	6.12	332	197.7	67.8	9.0	82.6	11.4	80.3
15	4.34	282	69.6	88.7	2.5	95.2	4.3	92.6
20	3.56	223	47.2	92.4	2.1	96.0	2.2	96.2
30	3.18	234	22.3	96.4	0.8	98.5	0.75	98.7
60	2.76	216	7.4	98.8	0.4	99.2	0.81	98.6

For precipitation of noble metals from a bromide solution containing copper, a hydrazine solution was chosen as a reducing agent. The data on the separation of gold, palladium and silver from the productive solutions (2) and (3), presented in tables 7 and 8, showed that noble metals can be extracted by reduction with a 10% solution of $N_2H_4 \cdot H_2O$ with high speed and almost completely. It was found that the copper present in the solution is also reduced with the successive formation of oxides Cu_2O , CuO and metallic copper. The resulting precipitates were purified from copper by treating them at a temperature of 313 K with a dilute sulfuric acid solution containing $2.5 \text{ mol} \cdot \text{dm}^{-3} H_2SO_4$ and $0.9 \text{ mol} \cdot \text{dm}^{-3} H_2O_2$. Chemical analysis of the obtained collective products found that the final collective products isolated from solutions (2) and (3) contained, mass. %: 1.18 Cu, 90.6 Ag, 7.2 Pd, the rest is moisture, lead; 1.20 Cu, 83.31 Ag, 7.15 Pd, 7.95 Au, the rest is moisture, lead.

Collective products obtained may be sent to a refinery. Considering that from each ton of PCB concentrate, usually sent to the refinery, using bromine - bromide technology it is possible to obtain only 10-15 kg of the collective product, the advantages of hydrometallurgical processing associated only with lowering the cost of refining and reducing technological losses are obvious.

Findings

Within 180 minutes of treating the initial PCB concentrate with a hydrochloric acid solution containing $2.5 \text{ mol} \cdot \text{dm}^{-3} HCl$ in the presence of $2.6 \text{ mol} \cdot \text{dm}^{-3} MgCl_2$, it is possible to transfer to the solution, %: 94.4 Al, 92.3 Sn, 89.2 Zn, 75.8 Fe, 72.4 Ni, 44.8 Pb, while the degree of dissolution of copper is 1.2%, and silver 0.56%. Gold and palladium pretreatment are not affected.

As a result of oxidative leaching of the residue from hydrochloric acid treatment, it is possible to finely grind scrap of 0.5-1 mm scrap into the solution to 92.67% of the initial copper.

The dissolution of gold with the circulation of the leaching solution from a pre-prepared concentrate of printed circuit boards in comparison with the leaching of the initial electronic scrap proceeds with a higher speed and much more complete, as the average degree of gold recovery increased from 87.2 to 89.39%. Bromine consumption decreased from 20-32 to 12 kg of Br_2 per tonne of scrap. Moreover, for 7 stages of leaching, it was possible to obtain a productive solution with a content of, $g \cdot \text{dm}^{-3}$: 0.0652 Au, 0.015 Pb, 0.00052 Cu.

Pretreatment of scrap also increases the speed and completeness of leaching of silver and palladium.

Under conditions of collective leaching of silver, gold and palladium with a weakly acid (pH = 1.98) bromine-bromide solution containing $100.8 \text{ g} \cdot \text{dm}^{-3}$ bromide ions can be converted into a solution of 98.64% Au, 97.23% Ag and 98.33% Pd.

Gold cementation on zinc dust from a pre-evacuated bromide solution proceeds quickly and the bulk of the gold precipitates at pH 6 during the first 15 minutes. In this case, gold is released in the form of a metal powder with a purity of 99.4%. The main impurity (0.6%) is copper.

The deposition of gold, palladium and silver from collective productive solutions by reducing precious metals with a 10% solution of $N_2H_4 \cdot H_2O$ proceeds with high speed and almost completely. In this case, the copper present in the solution is also reduced with the successive formation of oxides Cu_2O , CuO and metallic copper. The resulting precipitates can be purified from copper by treating them at a temperature of 313 K with a dilute sulfuric

acid solution containing $2.5 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{SO}_4$ and $0.9 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{O}_2$. Final collective products contain, mass. %:
- 1.18 Cu, 90.6 Ag, 7.2 Pd, the rest is moisture, lead;
- 1.20 Cu, 83.31 Ag, 7.15 Pd, 7.95 Au, the rest is moisture, lead and suitable for refining.

The obtained experimental results made it possible to recommend the proposed technological methods for the design of a pilot plant for semi-

industrial optimization of bromine-bromide technology.

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Бром-бромид ерітіндісін пайдалана отырып алдын ала дайындалған электрондық жиындыдан (скраптан) күмісті, алтынды және палладийді ерітінділеу

Коган В. С., Беркович И. В.

Түйіндеме. Бұл жұмыста ілеспе металдар мен мысты алдын ала алып тастағаннан кейін бром-бромид жүйесіндегі баспа платаларынан күмісті, алтынды және палладийді ерітінділеу зерттелді. Бастапқы электрондық жиындыны ерітінділеумен салыстырғанда алдын ала дайындалған баспа платаларының концентратынан ерітінділеу ерітіндісінің қайтарымымен алтынды еріту жоғары жылдамдықпен және айтарлықтай толық өтеді, сондықтан алтынды бөліп алудың орташа дәрежесі 87.2-ден 89.39% - ға дейін көтерілді. 1 тонна жиындыдағы бромның Br_2 шығыны 20-32 кг-нан 12 кг-ға дейін қысқарды. Сонымен қатар ерітінділеудің 7 кезеңінде құрамында $\text{г} \cdot \text{дм}^{-3}$: 0.0652 Au, 0.015 Pb, 0.00052 Cu бар өнімді ерітінді алынды. Жиындыны алдын ала өңдеу күміс пен палладийді ерітінділеудің жылдамдығы мен толық жүруін арттырады. Бұл ретте мыстың негізгі бөлігін алдын ала алып тастағанда оның өнімді ерітіндідегі құрамын 10 есеге төмендетуге мүмкіндік береді. Күміс, алтын және палладийді құрамында $100.8 \text{ г} \cdot \text{дм}^{-3}$ бромид ионы бар әлсіз қышқыл бром-бромид ерітіндісімен ($\text{pH}=1.98$) біріктіріп ерітінділегенде ерітіндіге 98.64% Au, 97.23% Ag және 98.33% Pd бөлуге болады. Мырыш шаңын, мыс ұнтағын және гидразин ерітіндісін пайдалана отырып, өнімді ерітінділерден алтынды, күмісті және палладийді тұндыру зерттелді. Нәтижесінде цемент ұнтағы түріндегі мырыш шаңында тазалығы 99.4% болатын алтын және 10% гидразин ерітіндісін пайдаланып құрамында массалық %: 1.18 Cu, 90.6 Ag, 7.2 Pd және 1.2 Cu, 83.31 Ag, 7.15 Pd, 7.95 Au болатын ұжымдық (Ag-Pd) және (Au-Ag-Pd) өнімдері алынды.

Түйін сөздер: алтын гидрометаллургиясы, бром-бромид жүйесіндегі күмісті, алтынды және палладийді ерітінділеу, бромид ерітінділерінен жасалған асыл металдарды цементациялау.

Выщелачивание серебра, золота и палладия из предварительно подготовленного электронного скрапа с использованием бром-бромидного раствора

Коган В.С., Беркович И.В.

Реферат. Изучено выщелачивание серебра, золота и палладия из печатных плат в бром-бромидной системе после предварительного удаления сопутствующих металлов и меди. Экспериментально установлено, что растворение золота с оборотом выщелачивающего раствора из предварительно подготовленного концентрата печатных плат в сравнении с выщелачиванием исходного электронного скрапа протекает с более высокой скоростью и существенно полнее, так средняя степень извлечения золота поднялась с 87.2 до 89.39%. Расход брома сократился с 20-32 до 12 кг Br_2 на тонну скрапа. Причем за 7 стадий выщелачивания удалось получить продуктивный раствор с содержанием, $\text{г} \cdot \text{дм}^{-3}$: 0.0652 Au, 0.015 Pb, 0.00052 Cu. Предварительная обработка скрапа увеличивает также скорость и полноту выщелачивания серебра и палладия. При этом, предварительное удаление основной части меди, позволяет снизить её содержание в продуктивном растворе практически в 10 раз. В условиях коллективного выщелачивания серебра, золота и палладия слабокислым ($\text{pH}=1.98$) бром-бромидным раствором, с содержанием $100.8 \text{ г} \cdot \text{дм}^{-3}$ бромид-ионов удается перевести в раствор 98.64% Au, 97.23% Ag и 98.33% Pd. Изучено осаждение золота, серебра и палладия из продуктивных растворов с использованием цинковой пыли,

медного порошка и раствора гидразина. В результате удалось выделить золото на цинковой пыли в форме цементного порошка чистотой 99.4% и коллективные (Ag-Pd) и (Au-Ag-Pd) продукты с использованием 10% раствора гидразина с содержанием, масс. %: 1.18 Cu, 90.6 Ag, 7.2 Pd и 1.2 Cu, 83.31Ag, 7.15 Pd, 7.95 Au соответственно.

Ключевые слова: гидрометаллургия золота, выщелачивание серебра, золота и палладия в бром-бромидной системе, цементация благородных металлов из бромидных растворов.

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Innovative technologies providing enhancement of non-ferrous, precious, rare and rare earth metals extraction

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Abstract. The article provides the technologies of enrichment and metallurgy processing of mineral and man-made raw materials. New technical solutions are proposed to increase the end-to-end copper extraction, industrial products processing of copper production to obtain high purity selenium; extraction of gold from resistant mineral raw materials with the use of new reagents and equipment, processing of ferrous bauxite and alumina production waste, extraction of rare and rare earth metals from industrial products and wastes of chrome, phosphorus and uranium production, obtaining rhenium and Nickel-cobalt concentrate from the wastes of heat-resistant Nickel alloys. Innovative Bayer-hydrogenative technology of ferruginous bauxite processing was developed and tested using pilot facility. The technologies and equipment to produce a composite hydrogen permeable membrane based on niobium and obtaining castings of implants by casting method of titanium alloys with application of additive technologies were developed.

Keywords: mineral raw materials, processing, technologies, copper, selenium, gold, rare metals, rare earth metals, new materials.

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Introduction

Involvement of resistant, complex mineral and man-made raw materials into processing is challenging issue for the metallurgy industry over the world. Commercial exploitation of these raw materials is confined owing to lack of effective and profitable technologies.

The aim of enhancing end-to-end extraction of metals from ores, man-made wastes and secondary raw materials is crucial for the leading industry – non-ferrous metallurgy.

Thus, the processing of converter slag is one of the major production problems in the technology of copper sulfide concentrates processing. There are various methods of processing converter slag, both in liquid and solid form [1]. However, the available technologies do not allow for high recovery of precious metals [2]. The proposed technical solution is characterized by the fact that due to the use of a

complex reducing agent, the copper content in the slag is reduced to 0.7% compared to the existing indicator of 1.0% [3].

The technologies used of the selenium extraction from middlings of copper production provide roasting of selenium-containing materials and producing crude selenium (90% of the main component). The defective moment of the process is the formation of process gases that complicate the selenium purification [4, 5]. We have developed a reagent-free vacuum distillation technology for producing branded selenium (99.5% of the main component) [6].

90 % of selenium is obtained from copper-electrolyte slag, 10 % - from man-made products of the chemical and pulp and paper industry in the world [7]. There is no a technology for selenium production from the slags of sulfuric acid of copper plants, so they are sent to lead factories, or in the dumps. We

have developed a technology for processing slag from washing solutions to obtain ammonium perrenate and release selenium-containing slag into an independent man-made product [8].

When flotation of mineral raw materials compositions of collectors (flotation reagents), the mechanism of their interaction with the surface of minerals is determined by the activity of each component of the collector and the peculiar features of the surface of minerals [9]. The paper [10] shows the technological and economic efficiency of using a mixture of hexyl and butyl xanthogenates.

Performed flotation of gold-containing raw materials using a composite reagent allowed us to significantly reduce the consumption of reagents (an average of 20 %) to increase gold recovery by 2.0-2.2 %.

Pre-oxidation (roasting, autoclave process, bioleaching) are used for processing of resistant, mineral-complex ores, which is associated with additional operating costs, which can be compensated by higher extraction of gold from ores [11, 12].

We offer ore beneficiation technologies with the use of new modern technological devices and the use of pre-oxidation of the raw materials before cyanidation.

To ensure the profitability of alumina production in the processing of low-quality bauxite a waste disposal to obtain commercial products is required [13].

The studies provided has shown the principal possibility of creating an effective technology for processing waste products of alumina production to obtain iron oxide pigments, cast iron, titanium concentrate and construction materials [14]. The problem of efficient chromium-containing wastes disposal in the world has not been solved so far. In this regard, the studies of the complex processing of stale slags of ferrochrome production with the extraction of rare and rare earth metals are of great practical importance.

The technologies of rare earths elements extraction from the wet-process phosphoric acid by sorption are well-known [15, 16]. The weakness is the low degree of REM sorption (at least 25 %) due to the presence of iron, aluminum and thorium impurities. The technology developed by us for obtaining REM concentrate with the use of new sorbents will provide an increase in REM extraction, while reducing the negative impact of impurities.

Currently, the man-made raw materials are involved increasingly as a raw material source of the rare earth elements into industrial processing. Basically, it is red slime alumina production, ash and slag wastes from coal combustion, waste processing of phosphate ores [13, 17].

SARECO LLP produces a REE concentrate from the man-made mineral formations after the processing of phosphate uranium ores. The applied technology has a number of lacks: losses of rare earth elements with cake when refining productive solutions from impurities, a large consumption of reagents when a concentrate depositing. We propose an improved technology for the extraction of REE in the form of a concentrate from this type of raw material [18].

The wastes of heat-resistant nickel superalloys (HRNS) contain up to 9% of rhenium, 60% of nickel and 10% of cobalt and that is why their complex processing is required. There are known methods of processing wastes by electrolysis methods. In the patent [19], the electrochemical processing of HRNS wastes is carried out in a solution of hydrochloric acid, out of which nickel and cobalt are extracted as a concentrate. During the processing of HRNS wastes by the method of anodic dissolution in a nitric acid solution the nickel transferred to the solution is released at the cathode in the form of Ni-concentrate [20]. The lacks of the methods are the use of solutions of hydrochloric and nitric acids for opening wastes. In the process of electrolysis in the hydrochloric acid at high current densities, chlorine gas can be released, and special corrosion-resistant equipment is required for nitric acid solutions.

We have developed an electrochemical technology for processing HRNS wastes. Ni and Co can be extracted from the obtained solutions after rhenium extraction as a concentrate [21].

Thus, currently, the most important problem of the metallurgy industry is the development and implementation of innovative technologies that allow with the maximum completeness to extract non-ferrous, rare and rare earth metals contained in ores, industrial wastes and secondary raw materials.

In this paper, the issues of increasing the extraction of non-ferrous, noble, rare and rare earth metals in the complex processing of mineral, man-made and secondary raw materials are considered and new technical solutions are proposed.

General part

The technology of depletion of copper slag dump of the Vanyukov furnace (VF)

of the Balkhash copper-smelting plant of "Kazakhmys Smelting" was developed.

An appropriate composition of waste slags as to the main components (30-31% of silicon dioxide, no more than 5% of magnetite and no more than 5% of zinc in the slag, the moisture content in the feed stock – no more than 6.5%) has been developed. Dependences of copper content in a slag on magnetite content in it are obtained, which indicate negative

influence of magnetite (more than 8 %) on copper content in a slag (Figure 1).

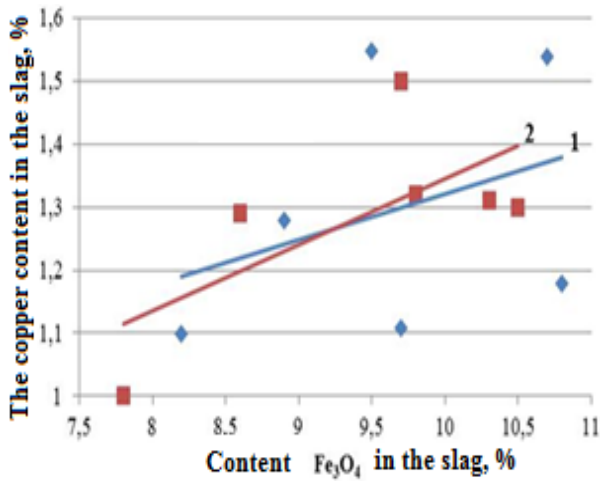
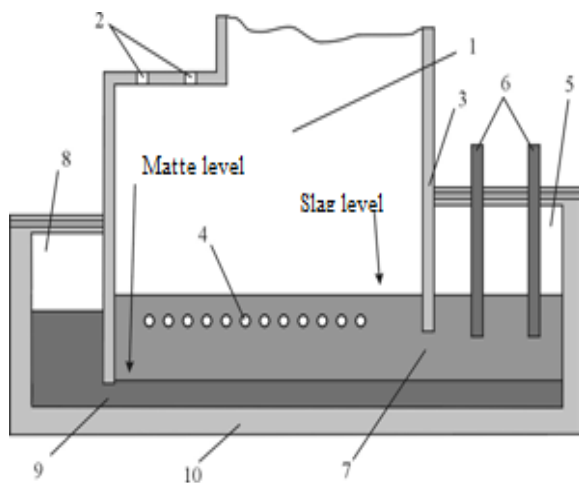


Figure 1 Dependence of copper content in the VF-1 slags (1) and VF -2 (2) on magnetite content

The use of additional electric heating is proposed to enhance the process of slag separation and matte in the slag siphon; the effective mode of the electric mixer of the Vanyukov furnace operation is developed (Figure 2). The introduction of technological and structural changes in the work of the VF complex allowed to increase the extraction of copper into the matte and to obtain a slag with a copper content of 0.5-0.7 %. In comparison with the existing analogues, the developed technology provides copper reduction in the waste slags from 1.0 to 0.7 % [22].



1 - uptake; 2 – for the feed stock; 3 - slag baffle; 4 - tuyere; 5 - slag siphon; 6 - electrodes; 7 - slag - matte siphon; 9 - matte; 10 –furnace bottom

Figure 2 Vanyukov Furnace

In the process of producing copper, the slurries of copper electrolyte and sulfuric acid production containing selenium are made. We have developed technology to extract elementary selenium from these middlings with further refining it into a vacuum distillation.

A method of separating selenium from a solution slurry after washing metallurgical gases of copper production is developed, installed material composition of selenium contained in the sludge. Appropriate conditions of sludge separation from the washing solution by centrifugation were determined [23].

As a result of vacuum distillation of rough selenium in the conditions of separation of the condensation surface by temperature zones in the middle zone, selenium containing 99.928% of the main component was obtained (Table 3). The proposed method allows to obtain refined selenium (up to 90% corresponding CT1 model and to 10% corresponding CT0 model) [24] in one stage [25].

Now, a production site for the processing of rough selenium according to the technology developed by us is arranged at the Kazakhmys Smelting LLP.

The technology of flotation enrichment of resistant, complex by mineral composition of gold-containing ores with the use of water-air microemulsion generator, improving the floatability of sludge particles, and composite flotation reagents is proposed (Table 1).

During flotation enrichment of Bestobe ores using microflotation and composite aerofloat, gold recovery increased by 4-5 %, while the reagent consumption decreased by 20% compared to the baseline [26].

When the gravitational enrichment of disseminated gold-bearing mineral raw materials a centrifugal separator was used to capture the free fine gold, which increased its recovery by 3-4 %. Enrichment of the gold-containing ore of the Sekisovskiy Deposit on the centrifugal apparatus in the appropriate mode showed the possibility of obtaining a heavy fraction with a mass fraction of 58.9 g/t at the extraction of 21.57 % (Table 2) [27].

Table 1 Flotation parameters comparing by using the developed air-water microemulsion generator

Parameters	General mode	With generator
Bubble size	300 - 550 μm	20 - 50 μm
Time of flotation	15 - 24 min	11 - 17 min
Valuable components loss	20 - 25 %	15-20 %

Table 2 The results of gold ore enrichment using centrifugal separator

Products	Output, %	Gold content, g/t	Gold extraction, %
Concentrate 1 of Knelson recleaning	2.03	58.9	21.57
Middling 1 of recleaning	13.0	8.68	20.23
Knelson tails	84.97	3.8	58.2
Base ore	100.0	5.55	100.0

The technology of gold extraction from refractory gold-containing ores with the use of pre-oxidation has been developed. The appropriate parameters of leaching refractory ores of JSC "Altyntau-Kokshetau" with the use of the reagents- activators of Na_2O_2 oxidation and $\text{Ca}(\text{ClO})_2$ (1 g/t), at this the degree of gold extraction at S:L = 1 : 3 for 24 h amounted to 73.1 %, which is higher than production performances (60-65 %) Table 4) [28].

A waste-free resource and energy-saving Bayer-hydrogarnet technology for processing ferruginous bauxite has been developed. A pilot

Table 3 The results of x-ray fluorescence analysis of powdered selenium

Element	Se*	Te	Sb	Ca	Mg	Si	Al	Fe	Ni	Pb	Cu	As	S
mass %	99.928	0.054	0.01	0.001	0.01	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001

*N/D: Hg, Ag, Cd, Na, K, Bi, Ti, Cl

Table 4 The results of the gold extraction out of ore using oxidizing reagents

No. of sample	1	2	3	4
Sample weight, g	100.0	100.0	100.0	100.0
pH	11.6	11.3	12.0	11.6
Liquid phase, l	0.3	0.3	0.3	0.3
The concentration of cyanide, %	0.1	0.1	0.1	0.1
The gold content in a cake, g	0.45	0.43	0.63	0.65
The gold content in the base ore, g	1.6	1.6	1.6	1.6
Gold extraction, %	71.9	73.1	60.6	59.4

plant has been created and Bayer-hydrogarnet technology has been tested with the production of pilot batches of products: production alumina, micronized aluminum hydroxide, hydrogarnet sludge, samples of building bricks made of slag and hydrogarnet sludge.

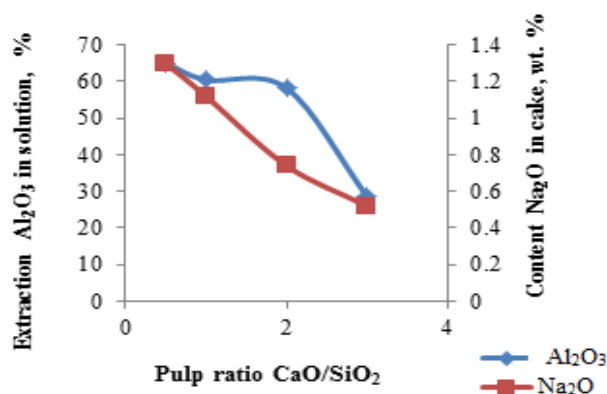
A technological regulation have been prepared and a feasibility study has been carried out for the construction of an alumina refinery with a capacity of 1 million tons per year in the Kostanay oblast of the Republic of Kazakhstan. The industrial implementation of the new technology will provide higher performance compared to the Bayer sintering process: it will provide a 35% reduction in energy costs; saving soda ash by 90%, reducing environmentally harmful emissions by 2–3 times and reducing capital costs for the construction of an

alumina plant with a capacity of 1.0 million tons by 25% [29, 30].

A technological scheme has been developed for the non-waste processing of red slurry (waste after alumina production) to produce iron oxide pigments, cast iron, titanium dioxide concentrate and construction materials [31].

The parameters of the hydrochemical processing of ferruginous sand with the release of iron-containing cake to obtain iron oxide pigments and cast iron are determined. In a high-modulus alkaline solution with the addition of CaO , the maximum extraction of Al_2O_3 (58.2%) in the

solution was achieved by leaching of ferrous sands after firing at a temperature of 600 °C at a molar ratio in the CaO pulp: $\text{SiO}_2 = 2$ (Figure 3).

**Figure 3** Impact of the $\text{CaO} / \text{SiO}_2$ ratio on the extraction of Al_2O_3

Sodium-ferrite clinker with a sodium ferrite content of 62.4% was synthesized from the man-made raw materials - red slurry, iron oxide, soda ash sodium ferrite clinker and lime. The color of the pigment is determined by the iron compounds contained in it: $\alpha\text{-Fe}_2\text{O}_3$ oxide, iron oxide — substituted by $\text{Fe}_{2-x}\text{M}_x\text{O}_3$. [32].

A technology has been developed for the processing of ferruginous sand of alumina production, including the operation of calcining ferruginous sand at 600 °C, hydrochemical hydrogarnet processing in a high-modulus alkaline solution at a temperature of 240-260 °C with the addition of CaO to produce an aluminate solution and a hydrogarnet cake leaching, magnetic separation of the cake with fine separation fractions to obtain pigments, reductive melting of the magnetic fraction to produce cast iron and slag. The obtained fine fraction was analyzed by Mossbauer spectroscopy. It was found that the red-brown color of the fraction is determined by $\alpha\text{-Fe}_2\text{O}_3$ oxide and substituted iron oxide $\text{Fe}_{2-x}\text{M}_x\text{O}_3$. Paramagnetic Fe^{3+} phases are a mixture of hydroxides $\beta\text{-FeOOH}$ - acaganeite and $\gamma\text{-FeOOH}$ - lepidocrocite (Figure 4) [33].

The studies for the deep processing of chromite-containing dusts from ferrochrome production to obtain chromite concentrate, gallium, vanadium pentoxide and rare-earth metal concentrate were carried out (Table 5).

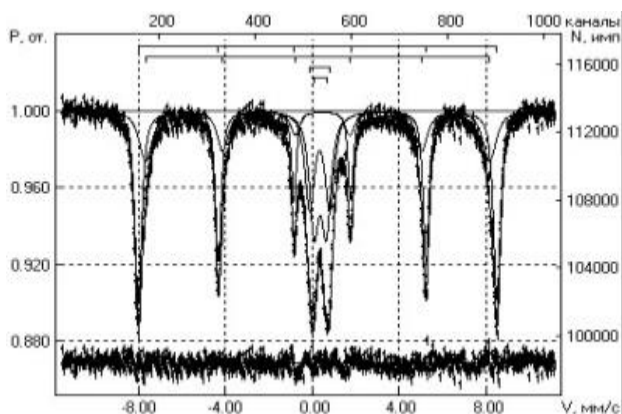


Figure 4 Mossbauer spectrum of a finely divided fraction of iron-containing leach cake of calcined ferrous sands

Table 5 Rare metals concentration in the base products

Chemical compound	Cyclone filter dust	Bag filter dust	Enrichment sludge	Wet scrubbing slurry
	Content, %			
TiO ₂	0,153	0,122	0,0136	0,15
V ₂ O ₅	0,062	0,033	0,0053	0,045
Ga ₂ O ₃	0,008	0,027	0,005	0,033
Rb ₂ O	0,00104	0,012	0,003	0,001
∑P3Э	0,01624	0,04581	0,04711	0,06467

and limestone. Red-brown iron oxide pigment with a particle size of 0.17 microns was obtained by the autoclave leaching of a mixture of red slurry,

The conditions for the extraction of REE out of the dust of cyclone and bag filters of JSC TNC Kazchrome are determined. The recovery of REE during leaching in NH_4HSO_4 solutions with a concentration of 3-30% ranged from 69.42 to 96.1%. A solution containing 10% of NH_4HSO_4 is considered appropriate for the REE isolation, while Cr_2O_3 , SiO_2 and Fe_2O_3 extraction does not occur in the solution, and the REE extraction is 73.83% (Figure 5)

The methods of preliminary chemical activation and sulfuric acid leaching of chromite-containing raw materials, as well as of regeneration of ammonium hydrosulfate have been developed [34].

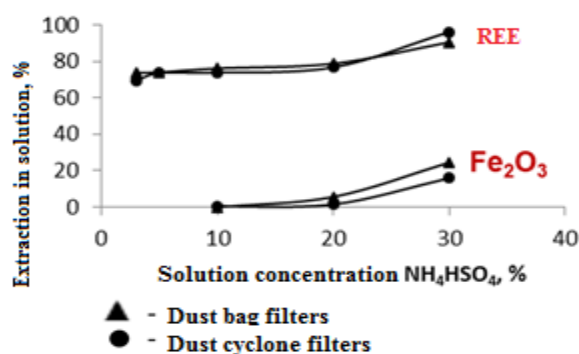


Figure 5 Dependence of the REE extraction and Fe_2O_3 into solution after NH_4HSO_4 concentration

A method has been developed to obtain REM concentrate from the extraction phosphoric acid of Mineral Fertilizers Plant LLP of Kazphosphate LLP using new sorbents. The sorption of rare-earth metals from solutions of extraction phosphoric acid by various ion exchangers was studied. It was found that sorption of rare-earth metals from extraction phosphoric acid most efficiently takes place on Purosorb 140 cation exchange resin (Figure 6). The equilibrium parameters of sorption of rare-earth metals from EPA were determined: 100 min. duration, 25-30 °C, ratio L:S = 50:1. Purosorb 140 ionite is recommended for the extraction of rare-earth metals out of extraction phosphoric acid [35].

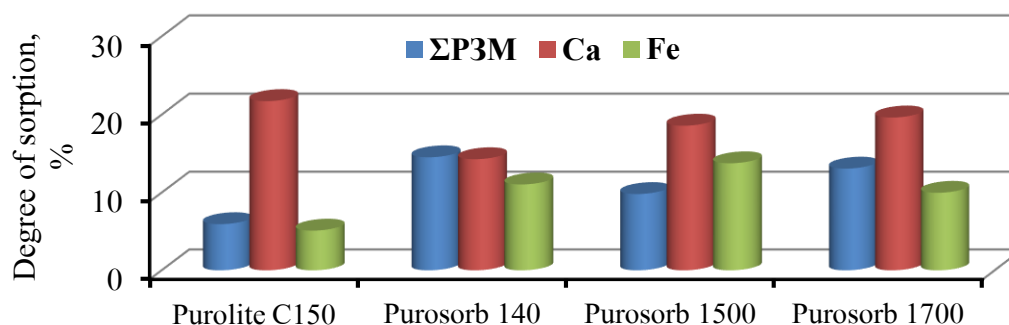


Figure 6 The degree of sorption of the rare-earth metals sum, calcium and iron from EPA on various cation exchangers

In order to improve the existing technology for processing man-made wastes from the processing of phosphate uranium ores, in particular, to reduce the consumption of sulfuric acid during their leaching, we have proposed a method involving preliminary calcination of the feedstock at a temperature of 400-500 °C in the presence of ammonium sulfate. It has been established that at this temperature sulfate ammonium is transformed into bisulfate and in the process of leaching of raw materials, forming an acid-salt mixture with sulfuric acid, helps to reduce the consumption of sulfur acid 4–5 times (Figure 7) [36, 37].

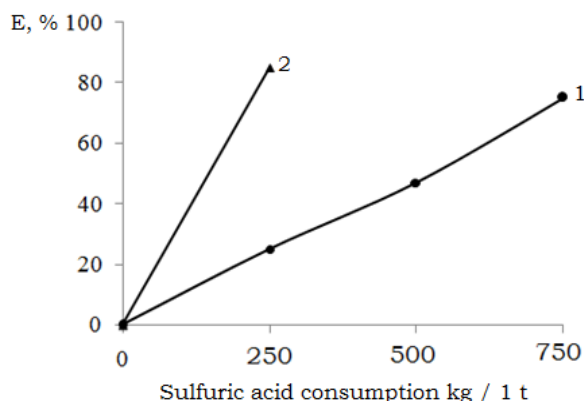


Figure 7 Dependence of sulfuric acid consumption on the degree of REE extraction

1 - existing technology, 2 - proposed technology

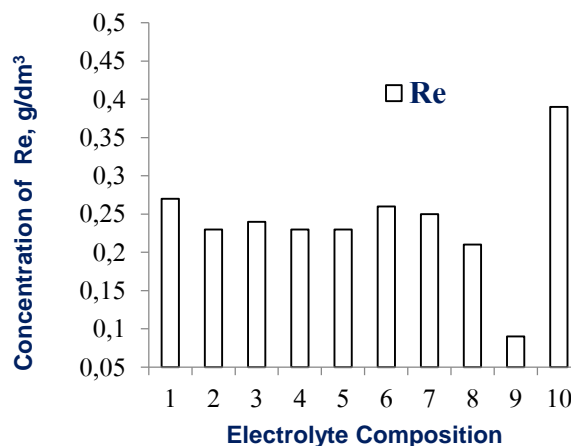
We have developed an electrochemical technology for processing secondary raw materials – wastes of heat-resistant nickel superalloys, which is currently being introduced at the RSE Zhezkazganredmet. The technology consists in combining anodic dissolution of waste in a sulfuric acid solution with the transfer of rhenium, nickel and cobalt into the solution and the precipitation of nickel-cobalt concentrate after extraction of rhenium from it.

When leaching in a sulfuric acid solution with nitric acid additives, Ni and Co almost completely go into solution, Re - by 75% (Figure 7). With a ratio of

S:L = 1:20; at a temperature of 50 °C, the degree of transition to a solution of nickel and cobalt reaches 80-95%, rhenium - 75-85%. Received Nickel-cobalt concentrate with a content, wt. %: 13.24-14.98 Ni and 0.96-1.08 Co [38].

Composite hydrogen-permeable membranes based on niobium and tantalum were obtained by developing separation layers that ensure the stability of the properties of catalytic protective coatings based on palladium and a scheme for attaching the membrane to a flat substrate, which promotes uniform distribution of stresses in the membrane (Figure 8) [39]. The research results are recommended

to be used to arrange innovative production of modules for producing ultra-pure hydrogen from hydrogen-containing gas mixtures.



Electrolyte composition, g/dm³: 1 - 100 H₂SO₄; 2 - 10 H₂SO₄; 70 (NH₄)₂SO₄; 125,2 Na₂SO₄·10H₂O; 3 - 20 H₂SO₄; 40 (NH₄)₂SO₄; 90,7 Na₂SO₄·10H₂O; 4 - 20 H₂SO₄; 40 (NH₄)₂SO₄; 90,7 Na₂SO₄·10H₂O; 20 NaCl; 5 - 20 H₂SO₄; 40 (NH₄)₂SO₄; 90,7 Na₂SO₄·10H₂O; 20 HCl; 6 - 150 H₂SO₄; 7 - 200 H₂SO₄; 8 - 150 H₂SO₄; 20 NaCl; 9 - 200 H₂SO₄; 30 NaCl; 10 - 100 H₂SO₄; 20 HNO₃

Figure 7 Impact of the initial electrolyte composition on the concentration of rhenium in the solution after anodic dissolution of alloy wastes



Figure 8 Upgraded chamber of the magnetron sputtering installation and the surface of the membrane of tantalum and niobium foil

A technology has been developed for the production of implants with improved osseointegration by casting of titanium alloys using a lost-wax 3D model and subsequent processing with application of biocompatible coatings (Figure 9).

Molding materials based on yttrium oxide and a method for their molding on the surface of investment models are proposed, which provides titanium castings with a developed surface using additive technology [40].

The analysis of the feedstock and the obtained products was performed using the following methods: mineralogical, X-ray phase, X-ray fluorescence, thermal analysis methods, electron scanning microscopy, IR spectroscopy, Mossbauer spectroscopy.

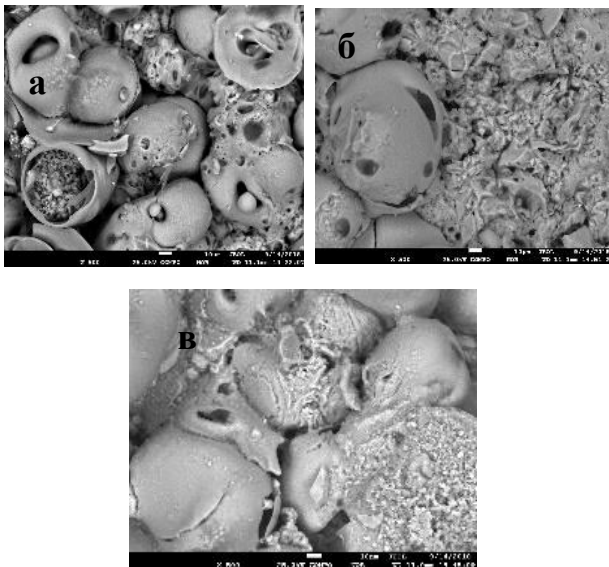


Figure 9 SEM image of a calcium phosphate coating obtained at different pH of electrolytes: a - pH 1; pH 2; pH 3

Elemental analysis was carried out using X-ray fluorescence spectroscopy on an energy dispersive microanalysis system INCA Energy 450 mounted on a scanning electron microscope JSM 6610 LV, JEOL.

X-ray phase analysis. The shooting was carried out on a D8Advance (Bruker) apparatus, α -Cu. Processing of the obtained results and calculation of interplanar distances was carried out using the EVA software. The phase decoding was performed using the PDF-2 diffractometric database.

Mossbauer spectroscopy was used to determine the forms of iron in the feedstock and processing products. The source was Co-57 in a chromium matrix with an activity of 100 mCi. The spectra were processed on a PC using the "least squares" method. The values of isomeric shifts (IS) are given relative to α -Fe. The temperature of the spectra was 293 K. The MS 1104Em spectrometer.

Images of objects using scanning electron microscopy were performed at zooming from 40 to 4000 times.

Findings

As a result of the researches, the technologies have been created that are focused on the needs of industrial enterprises: processing dump and converter slags with additional copper recovery, separating selenium from washing solutions of copper production and obtaining refined selenium (Kazakhmys Smelting LLP); processing of ferruginous bauxite and industrial products and waste from alumina production (JSC Aluminum of Kazakhstan); processing of refractory gold-containing ores (MSC Altyn MM LLP, Altyntau-Kokshetau JSC); extraction of rare and rare-earth metals from wastes and middlings of chromium, phosphorus and uranium production (JSC TNK Kazkhrom, LLP Kazphosphate, JSC NAC Kazatomprom); for producing nickel-cobalt concentrate from heat-resistant nickel superalloys wastes (RGP Zhezkazganredmet), synthesis of composite hydrogen-permeable membranes based on niobium and tantalum and implants with improved osseointegration.

The technologies for the processing of low-quality mineral and industrial raw materials may be of interest to countries with similar raw materials.

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Түсті, асыл, сирек және сирек жер металдардың бөлінуін арттыруды қамтамасыз ететін инновациялық технологиялар

Кенжалиев Б. К.

Түйіндеме. Мақалада байыту және минералдық, техногендік шикізатты металлургиялық қайта өңдеу, функционалдық материалдар алу технологиялары келтірілген. Мысты тікелей бөліп алуды арттыру, таза селен алынатын мыс өндірісінің өнеркәсіптік өнімдерін қайта өңдеу, жаңа реагенттер мен жабдықтарды пайдаланып қиын өңделетін минералдық шикізаттан алтынды бөліп алу, темірлі бокситтерді және сазтопырақ өндірісінің қалдықтарын қайта өңдеу, хром, фосфор және уран өндірісінің өнеркәсіптік өнімдері мен қалдықтарынан сирек және сирек жер металдарын бөліп алу, отқа төзімді никель қорытпаларының қалдықтарынан рений және никель-кобальтты концентраттарды алу бойынша жаңа технологиялық шешімдер ұсынылды. Темірлі бокситтерді өңдеудің инновациялық Байер-гидрогранаттық технологиясы жасалды және құрылған пилоттық қондырғыда оның сынағы өткізілді. Ниобий негізінде сутегі өткізетін композициялық мембраналарды және аддитивті технологияларды пайдаланып титан қорытпаларын құю әдісімен эндопротездердің құймаларын алу үшін технологиялар және қондырғылар әзірленді.

Түйін сөздер: минералдық шикізат, өңдеу, технология, мыс, селен, алтын, сирек металдар, сирек жер металдары, жаңа материалдар.

Инновационные технологии, обеспечивающие повышение извлечения цветных, благородных, редких и редкоземельных металлов

Кенжалиев Б.К.

Реферат. В статье представлены разработанные в АО «Институт металлургии и обогащения» (г. Алматы, Казахстан) технологии обогащения и металлургической переработки минерального и техногенного сырья, получения функциональных материалов. Предложены новые технические решения по увеличению сквозного извлечения меди, переработке промпродуктов медного производства с получением селена высокой чистоты; извлечению золота из упорного минерального сырья с применением новых реагентов и оборудования, переработке железистых бокситов и отходов глиноземного производства, извлечению редких и редкоземельных металлов из промпродуктов и отходов хромового, фосфорного и уранового производств, получению рения и никель-кобальтового концентрата из отходов жаропрочных никелевых сплавов. Разработана инновационная Байер-гидрогранатовая технология переработки железистых бокситов и проведены ее испытания на созданной пилотной установке. Разработаны технологии и оборудование для получения композиционных водородопроницаемых мембран на основе ниобия и получения отливок эндопротезов методом литья титановых сплавов с применением аддитивных технологий.

Ключевые слова: минеральное сырье, переработка, технологии, медь, селен, золото, редкие металлы, редкоземельные металлы, новые материалы.

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Investigation of the leaching process of rare-earth metals from the black shale ores of greater karatau

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Abstract. The purpose of this investigation was studying the process of an acid leaching of vanadium and other valuable components from black shales of Big Karatau of the Republic of Kazakhstan. The maintenance of principal components in ore of 0,8% V_2O_5 , 67,7% of SiO_2 , 3,1% of Al_2O_3 , 0,3% of Mo, 0,2% of U_3O_8 and 0,05% of rare-earth metals. To provide this process was used low-temperature sintering and leaching of this type of raw material for the subsequent extraction of vanadium, uranium, molybdenum and rare earth metal concentrates. Moreover, it was established that with increasing concentration of sulfuric acid to 40 g/l, the degree of leaching of uranium, vanadium, molybdenum and rare earth metals (REM) increases noticeably. The degree of extraction of vanadium includes 81.7 %; uranium – 93,3%; molybdenum – 82.2 % and REM – 78.3%. Besides, it was determined the optimal leaching time, which takes 2 hours long, and the chemical composition of the cakes after leaching.

Keywords: black shale, rare and rare earth metals, leaching, low-temperature sintering.

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Introduction

Black shales, also called a carbonaceous stone, are one of the larger natural sources of vanadium, molybdenum and rare-earth metals (REM). The useful components such as vanadium in form of V_2O_5 amounts 0,8-1,2%, molybdenum - 0,3%, uranium - 0,2-0,5% and REM - 0,05-0,15% [1-3]. The basis of a breed of black shales content short-grained quartz, sulfides and micas, there are organic matters and carbonates [4]. Persistence of ores is caused by two factors: low solubility of minerals concentrators of the useful components and extremely shallow

amount of their selections (ultradispersion) therefore mechanical methods (gravitation, flotation) did not possible to receive the enriched concentrates [5]. Attempts of development of theoretical bases and development of a way of complex extraction of vanadium, uranium, molybdenum and REM from the black shale ores were repeatedly made. Some of the developments are listed below.

Researches [6-9] on the pyro-hydrometallurgical way of processing of vanadium-bearing fields the black shale ores confirmed the possibility of extraction of vanadium from the black shale ores with a method of oxidizing roasting with

sodium additives with the subsequent water or acid lixiviation of residue, in finally hydrolytic deposition of vanadium. In work [6] is studied the process of roasting of ore with additive mix $\text{Na}_2\text{CO}_3\text{-CuSO}_4$.

Various technologies for the processing of black shale are known in world practice. They are aimed to extract metals such as vanadium, uranium, molybdenum and concentrates of rare earth metals (REM). However, due to the structural features of polymetallic carbon-silica ores, the proposed technologies are not effective. To maximize the extraction of valuable components from such complex raw material, new methods of black shale processing are necessary. They contribute to the phase rearrangement of silica and carbon [10-11]

The investigation of the physical properties, chemical composition and structural characteristics of complex carbon - silica ores of the Greater Karatau allowed to determine glassy appearance, conchoidal fracture, the abundance of cracks and voids, isotropic and X-ray amorphism, hygroscopicity, high out of the water, free and chemically bound silica, the lack of correlation of the content of the rare, rare earth and radioactive metals with silica or carbon.

Experiments and results and discussion

As a starting material for carrying out experiments used test of black shale of Big Karatau. Test of black shales represented the homogeneous black dry powder fineness $\sim 53,2\%$ - $0,063$ mm with the content of vanadium V_2O_5 - $0,8\%$; C $\sim 18\%$, SiO_2 - $67,7\%$. Chemical of the investigated ore is shown in table 1. Further, the distribution of sizes of black shales is presented in table 2. To provide sintering of black shale with ammonium hydrosulfate to remove mobile carbon and convert rare earth metals into a water-soluble form was used low-temperature thermal made ($150 - 200$ °C). The content of rare metals in the samples was controlled by chemical methods (bichromatometry, titrimetric optical emission). The phase and elemental composition of the ore of black shale and of samples after sintering and leaching were determined using X-ray phase and X-ray spectral analysis methods.

Table 1 Chemical content of black shales

Composition, %							
V_2O_5	U_3O_8	MoO_3	REM	SiO_2	Al_2O_3	C	Fe-total
0,8	0,2	0,3	0,05	67,6	3,1	18,0	1,91
CaO	P_2O_5	K	S	Na	MgO	BaO	
2,8	0,71	0,47	1,4	0,09	2,2	0,86	

Table 2 Distribution of sizes of black shales

Size, mm	Total, %
+0,2	4,8
-0,2+0,1	34
0,10+0,063	8
-0,063	53,2
	100

X-ray spectral microanalysis was performed on the JXA-8230 microanalyzer with an application of scanning electron microscopy in backscattered and in secondary electrons mode.

Elemental composition of minerals and microinclusions, as well as photography in different types of radiation, were analyzed with the application of an energy dispersion spectrometer "Inca Energy" (PLC "Oxford Instruments"). It was installed on the electron probe microanalyzer "Superprobe -733" at an accelerating voltage of 25 kV and a probe current of 25 nA.

The leaching of the cake was carried out with sulfuric acid solution at different concentrations of sulfuric acid (10-60 g/l): temperature - 80 °C, relation S:L = 1:3, leaching time - 2 hours.

Results and discussion. The investigations of the physical properties with application of X-ray diffraction and electron probe microprobe allowed to establish that rock-forming minerals consist of anorthite, muscovite, quartz, dolomite, paramelaconite and ore minerals of rutile, patronite, monazite, xenotime, uraninite, molybdenite and tungstenite and many other minerals.

In the polished section, the grains from different plots were selected. In the rare and rare earth metals are concentrated. Data of grain composition are presented in table 3.

Table 3 Content of elements in the studied raw materials

Investigated product	Content of elements in the sample segment, %																						
	C	As	Al	Si	P	Cu	Mo	Ti	Fe	W	V	U	Y	La	Ce	Dy	Pr	Yb	Sm	Nd	Gd		
Rutile	2,52			0,47				46,75	0,33		14,69												
Monazite	17,44		0,31	23,96	9,17	0,03			0,46				20,4	9,8	13,6		1,22		3,61	13,7	1,99		
Xenotim	29,32			1,4	11,27								24,68			2,89		1,07					1,64
Nas-turan	13,92	4,74		3,89	4,89	4,03						39,75											
Tungstenite	44,42		0,47	8,74			0,89	0,25	0,36	21,50													
Molybdenite	24,91			11,78			44,60																

Based on the obtained data, rare and rare earth elements in carbon-silica ore are found in various minerals in the form of inclusions in the silicon-carbon matrix. In this regard, during sulfurization of the initial ore – a method currently used for its processing. At the same time, rare-earth elements do not fully pass into solution. The results of the investigation are presented in table 4.

Table 4 Results of the investigation

Sulphuric acid concentration, g/l	Content, g/dm ³			
	V	U	Mo	REM
10	0,81	0,0030	0,012	0,014
20	1,01	0,0037	0,020	0,021
30	1,17	0,0036	0,024	0,032
40	2,19	0,0172	0,047	0,039
60	2,21	0,0173	0,047	0,040

Also, it was found that with an increase in the concentration of sulfuric acid to 40 g/l, the leaching degree of uranium, vanadium, molybdenum and rare earth metals increases noticeably. The degree of extraction of vanadium is 81,7 %; uranium – 93,3%; molybdenum – 82.2 % and REM – 78.3%.

In addition, it was conducted investigations of leaching cake with different durations of contact time of the cake with a solution. The process was carried out at a temperature of 80 °C, relation S:L = 1: 3 and a concentration of sulfuric acid of 40 g/l. The results of the investigation are presented in Figure 1.

As shown in figure 1, the optimal leaching time is 2 hours. The chemical composition of the cakes is presented in table 5.

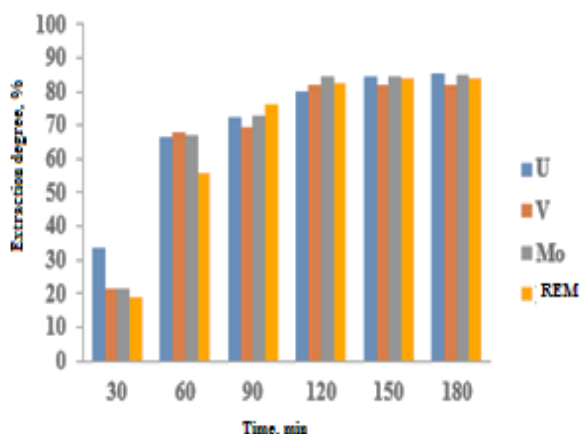


Figure 1 Leaching of rare earth metals from sinter at different durations Leaching of rare earth metals from sinter at different durations

Table 5 The chemical composition of the cake after leaching

Name	Content, %								
	V	U	Mo	REM	Fe	Al	Si	C	CO ₂
Cake	0,04	0,001	0,003	0,007	0,21	0,05	43,7	13,75	0,00

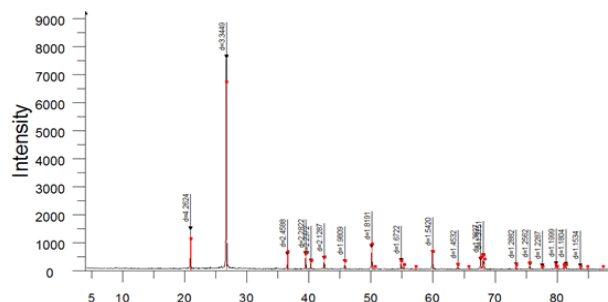


Figure 2 X-ray phase analysis of cake

Further, the cake obtained after leaching in the optimal mode of black color was submitted to X-spectroscopic and X-ray phase analysis. The results of the analyses are presented in figure 2.

From the X-ray phase analysis, it follows that the cakes after decomposition of the ore with ammonium hydrosulfate and subsequent leaching, consist of quartz and elemental carbon.

Further, the cakes were washed with a sulfuric acid solution to remove impurity elements and were sent to carbon enrichment. The enriched product was sent to a batch to obtain ferrosilicon.

Conclusion

It was determined that the sintering process of black shale ore with ammonium sulfate (decomposition products of ammonium hydrosulfate) is accompanied by the release of constitutional water, mobile carbon and hydrogen nitride (NH₃). Herewith the formation of ammonium carbamate and the transition of amorphous silica into a stable crystalline α-modification with an ordered structure occurs. Further after leaching valuable elements from black shale ores such as uranium, vanadium, molybdenum and rare earth elements go into the aqueous phase. The degree of extraction of vanadium, uranium, molybdenum and REM is about 80 % or higher that makes it possible to find the commercial application of this process.

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Үлкен қаратау қара тақтатас кендерінен сирек жер металдарын алу процесін зерттеу

Байгенженов О.С., Юлусов О.Б., Хабиев А.Т., Сыдыканов М.М., Акбаров М.С.

Түйіндеме. Бұл зерттеудің мақсаты ванадийді қышқылмен ерітінділеу процесін және Қазақстан Республикасының Үлкен Қаратау қара тақтатастарынан жасалған басқа да құнды компоненттерді зерттеу болып табылады. Кендегі негізгі компоненттердің құрамы 0,8% V_2O_5 , 67,7% SiO_2 , 3,1% Al_2O_3 , 0,3% Mo , 0,2% U_3O_8 және 0,05% сирек кездесетін металдар. Осы процесті жүргізу үшін шикізаттың осы түрін төмен температуралы күйеженектеу және ары қарай ванадий, уран, молибден және сирек жер металдарының концентраттарын алу үшін ерітінділеу қолданылды. Бұдан басқа, күкірт қышқылы концентрациясы 40 г/л-ге дейін ұлғайса, уран, ванадий, молибден және сирек жер металдарының (СЖМ) ерітінділеу дәрежесі айтарлықтай артады. Ванадийдің бөліну дәрежесі 81,7 %; уранның-93,3%; молибденнің – 82,2% және СЖМ – 78,3% құрайды. Сондай-ақ, ерітінділеудің оңтайлы уақыты анықталды. Ол 2 сағатқа созылады. Ерітінділеуден кейін кектердің химиялық құрамы анықталды.

Түйін сөздер: қара тақтатас, сирек және сирек жер металдары, ерітінділеу, төмен температуралы күйеженектеу.

Исследование процесса выщелачивания редких и редкоземельных металлов из черносланцевых руд большого каратау

Байгенженов О.С., Юлусов О.Б., Хабиев А.Т., Сыдыканов М.М., Акбаров М.С.

Аннотация. Целью настоящего исследования явилось изучение процесса кислотного выщелачивания ванадия и других ценных компонентов из черных сланцев Большого Каратау Республики Казахстан. Содержание основных компонентов в руде 0,8% V_2O_5 , 67,7% SiO_2 , 3,1% Al_2O_3 , 0,3% Mo , 0,2% U_3O_8 и 0,05% редкоземельных металлов. Для проведения данного процесса было использовано низкотемпературное спекание и выщелачивание данного вида сырья для последующего извлечения ванадия, урана, молибдена и концентратов редкоземельных металлов. Кроме того было установлено, что с увеличением содержания концентрации серной кислоты до 40 г/л, степень выщелачивания урана, ванадия, молибдена и редкоземельных металлов (РЗМ) заметно увеличивается. Степень извлечения ванадия составляет 81,7 %; урана-93,3%; молибдена – 82,2% и РЗМ – 78,3%. Также было определено оптимальное время выщелачивания, которое составляет 2 часа и химический состав кеков после выщелачивания.

Ключевые слова: черный сланец, редкие и редкоземельные металлы, выщелачивание, низкотемпературное спекание.

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