In the article the results of studying the process of extracting cobalt out of Dashkesan high-siliceous cobalt ores are cited. The composition of cobalt ore was studied. It was shown that due to the presence of hard soluble minerals and silica compounds of cobalt in the composition of ore leaching of Co with solutions of hydrochloric acid (7 and 20%) and sulfuric acid (up to 2 N) is insufficiently effective. The method of processing ore that provides for its sulfatizing roasting with further leaching with water is suggested. It was observed that extraction of cobalt by sulfatization at 700°C made up 85.52%.

Keywords: Cobalt, ore, sulphatizing roasting, leaching, sintering, extraction.

Introduction

Cobalt and its compounds are widely used in various industries: metallurgical, chemical, radio-electronic. Alloying steel with cobalt increases its heat resistance and improves mechanical properties. From cobalt-containing alloys different tools – drill bits, cutters, etc are produced. To produce permanent magnets cobalt is used as high-performance positive electrode for the production of lithium batteries. Radioactive cobalt (Co₆₀) is used in gammatranslation and in medicine. Cobalt is one of the vital microelements for organism. The daily human need for cobalt is 0.007–0.015 mg. On 28 January 2016 the price of cobalt on the world market, according to the data, Info.geo.ru, was about 22 $/kg.

Basically, minerals of cobalt are sulfides, arsenides and silicates. It often forms a compound with an impurity of iron, copper, manganese, lead and some other metals [1].

Ores from which cobalt is extracted, are very diverse in their chemical and mineralogical composition, the cobalt content in them varies widely – from tenths of a percent to a few percentages. But unoxidized ores (sulfides or arsenic ores), especially complex ones have industrial uses even at the concentration of cobalt 0.15% and less than it, as they enter to the enrichment process [2–7].

Dashkesan is the most important mining district in Azerbaijan. Dashkesan district is not only abundant with its iron ores but also with its cobalt and alunite ores. Azerbaijani scientists G.Kh.Efendiev [7] and M.A.Kashkai [8] have installed characteristics of cobalt sulphoarsenic minerals for all Dashkesan metallogenic region. Basically, they are cobaltite (CoAsS), safflorite (Co,Fe,Ni)As₂, glaucochot (Co,Fe)AsS, skutterudite CoAs₃.

Cobaltite is the main ore mineral of sulphoarsenic complex and the main cobalt mineral of deposit of Dashkesan ore district [9]. Currently processing Dashkesan cobalt ores is not carried out in Azerbaijan.

For the processing of high-silica aluminum ores containing cobalt, appropriate to use acid methods, as these methods allow to selectively allocate silica contained ores already at the acid processing stage, which is a kind of chemical enrichment process of cobalt.

In the acidic methods of processing low-quality aluminum ores they usually use sulfuric and hydrochloric acids, which permit relatively easy to carry out a selective separation of silica and alumina already on the stage of acidic ore processing.

The aim of current work is maximum extraction of cobalt from high-silica-containing Dashkesan deposit ore by using acid methods (hydrochloric and sulfuric acid), also by sintering-acidic methods.

Experimental part

Research objects. The studied cobalt ore of Dashkesan deposit is polyminerall ore. According to the results of X-ray and mineralogical analysis methods this ore contains the following minerals: cobaltite, erythrite, clino-
chlore, andradite, α-quartz, hematite, aluminum phosphide.

Under the microscope, the major rock-forming minerals – aluminosilicates (clinochlore, andradite) are observed in the form of large and small grains of irregular shape.

Cobaltite in polished sections is characterized by its weak anisotropy effects, it is of a pinkish-brown color. Depending on its location it can be found in the cracks among garnet skarns, sometimes it is intergrown with safflorite accompanied with pyrite.

From the results of mineralogical analysis it follows that investigated cobalt ore is also high siliceous aluminum raw material which contains: clinochlore – 44.2%, andradite – 23.3%, α-quartz – 11.2%, aluminum phosphide – 2.2%.

Despite the low aluminum content (4.5–7.6%) the presence of other valuable components such as Mg, K, Ti, Mn, Cr has been revealed. Complexity of this type ore processing, whose enrichment process is difficult, is associated with presence of both sulfoarsenic and oxidized minerals and their intergermination and also presence of other metals-impurities. Dashkesan cobalt ore has the following average of chemical composition (in count of oxides), mas.%: Na₂O – 1.48, MgO – 5.65, Al₂O₃ – 14.29, SiO₂ – 44.64, SO₃ – 0.85, K₂O – 1.32, CaO – 7.19, As₂O₅ – 5.20, Fe₂O₃ – 12.93, MnO – 0.43, TiO₂ – 0.54. Established that the CoO content in the ore is in the 3.58–5.48% range.

**Research methods.** While conducting research ore was pre-milled to a particle size 0.074 mm (200 mesh). Obtained material is close to monodisperse. A weighed sample of the ore or calcine (5–10 g) was placed in a flask in which water or acid leaching was held and stirred under heating with a magnetic stirrer. Leaching was carried out at temperatures of 293–363 K, in different concentrations of acid for 60–300 minutes. The sediment after processing reagent was filtered, washed with water and washing water was combined with the primary filtrate. The influence of parameters on the leaching extraction of components of the ore or calcine in the solution was determined by analyzing samples of the liquid and solid phases of the slurry. Determination of metals (Al, Mg, Cu, Fe, Mn, Co, As) in solution was conducted with the X-ray fluorescence spectrometer "Bruker S2 PICOFOX" (Germany). Thermogravimetric analyses of initial ore and product of its sulfation are carried out on derivatograph Jupiter STA 449 F3 (Germany) in the range of 20–1000°C in an argon flow at speed temperature of rise at 10°C/min. Mineralogical analysis of cobalt ore was performed using the Oxford EDS microscope. X-ray phase analyses of cobalt ore and products was made at AXS diffractometer of company "Bruker".

**Results and Discussion**

In the present work a study in has been made of the decomposition process of cobalt ore from Dashkesan deposit with solutions of sulfuric and hydrochloric acids, and sintering-acidic methods to selectively extract the raw components of raw material and finding the optimal conditions for its decomposition to ensure maximum extraction of valuable components in a solution depending on the different physical and chemical factors.

Preliminary experiments showed that while processing studied ore with water transition of cobalt to solution does not occur. It shows that, basically, cobalt in the ore is in hard uncovered form. pH magnitude of liquid phase does not change too, hydrolysis of compounds, within the ore does not occur. For comparative assessment of the interaction of ore creating elements with various liquid environment their solubility in various concentration of hydrochloric and sulfuric acids was studied.

Figure 1 shows data which describe the effects of initial concentration of sulfuric acid solution at the extraction degree of cobalt from ore. Constant factors are: processing temperature – 20°C, leaching duration – 60 minutes, and S:L=1:5. As is seen from the figure, the processing of raw materials with sulfuric acid, with the increasing acid concentration from 0.5 to 2 N extraction degree of cobalt increased from 7.3 to 35.17%. In conjunction with cobalt to the liquid phase there also move iron sulfates, potassium, calcium, manganese, zinc. Transition copper and aluminum is only 2 and 4% respectively.

Results of experiments (Table 1) show that while the leaching with the solution of 2 N H₂SO₄ concentration of cobalt in solution in-
creases with the increasing duration of the leach. However, with this the content of iron and arsenic impurities in solution significantly increases.

![Fig.1. The dependence of the cobalt content in the solution, from initial concentration of sulfuric acid at a temperature of 20°C, at the ratio S:L=1:5.](image)

Table 1. Dynamic content of elements in solution, depending on the concentration of H$_2$SO$_4$ acid (temperature – 20°C, the ratio S:L=1:5, duration of leaching – 1 hour)

<table>
<thead>
<tr>
<th>No of test</th>
<th>Concentration of H$_2$SO$_4$, N</th>
<th>Content of elements, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>6.8</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>9.1</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>42.1</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>44.6</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>47.2</td>
</tr>
</tbody>
</table>

Increasing the ratio of S:L reduces extraction of Co(II, III) in solution. This may be due to the fact that an increase in water flow reduces the acidity of the solution and, consequently, degrades the leaching of cobalt compounds.

The nature of the curve (Figure 1) leads to the conclusion that increasing the initial concentration of 1N H$_2$SO$_4$ to 2 N exerts no substantial effect on the speed of dissolving of cobalt, which diminishes with time.

The dynamics of dissolving of cobalt, depending on the duration of leaching H$_2$SO$_4$–1N concentration, in a S:L=1:5 ratio, at 20°C temperature has shown in Figure 2.

As is seen from Figure 2, the process is characterized with a high rate of cobalt leaching in the first hours, but after its deceleration was observed.

![Fig.2. Depending extraction rates of Co and Fe while the duration of leaching ore with sulfuric acid (C$_{H_2SO_4}$=1N, at 20°C temperature, in S:L=1:5 ratio).](image)

To determine the optimum temperature mode cobalt leaching from ore experiments to study the influence of the test temperature on the extraction of cobalt in solution were carried out. The data shows that increasing the temperature of the process from 20 to 80°C promotes increasing extraction of cobalt to solution from 31.52 to 76.7%. One can draw a conclusion that the sulfuric acid leaching does not provide a sufficiently high extraction of cobalt to the liquid phase. For looking more effective ways to opening cobalt ores we have also studied the possibility of extracting cobalt with hydrochloric acid solutions.

Effect of hydrochloric acid concentration on the process of the initial ore decomposition was studied at two concentration 7 and 20 %, and established optimal conditions: the process temperature – 90°C, dosage of acid – 120% of the stoichiometry for chlorination of ore components, the duration of the process of acid digestion – 1 hour (Table 2). As is seen from Table 2, increasing the concentration of hydrochloric acid leads to increasing the concentration of cobalt associated elements such as Mg, Al, As, Fe, Ca, K, which dissolving significantly complicate the following purification steps of cobalt from other metals. Reducing acidity of the solutions leads to decrease in extraction degree of cobalt. X-ray phase analysis of filter cake, obtained after leaching, showed that the most minerals in raw material also remain in a filter cake leaching.
The result of sulfuric acid leaching cobalt from studied ores also indicate that it is not possible to achieve sufficiently high extraction into solution: the extraction degree of cobalt does not exceed 66.07–72.92% (Table 2). Thus, studies have shown that the processing of cobalt ores with solutions of sulfuric and hydrochloric acids do not provide sufficient full transition of cobalt in solution. In order to achieve high extraction of cobalt we have tested sulfatized ore roasting and leaching of pre sulfatized calcine.

One of the efficient methods of opening sulfo-arsenic material is its sulfatization of sulfuric acid concentration. Sample ore (10 g) was stirred with concentrated sulfuric acid (1.84 g/sm³) and sintered at 300°C. Weight of sample as a result of sulfatization on average increased by 1.5 times. Decisive impact on sulfatization completeness is provided by amount of acid and temperature. The obtained at various temperatures (T=400–700°C) sulfatized ore mass leached with water at 80°C, during 1 hour. Ratio S:L=1:5. Indices of sulfatization process of cobalt material with concentrated sulfuric acid has shown in Table 3. Sulfatization of cobalt in calcine with sulfuric acid intensively proceeds at 400°C (extraction degree of Co is 73.68%), extraction degree of solution is maximum at 700°C temperature (output 85.52%) after which extraction of cobalt increases with increasing temperature. At higher than 700°C the formation of cobalt ferrite starts. Maximum sulfatization of iron was obtained at 400–500°C. With increasing temperature up to starts 500°C iron sulfatization decreases, while 700°C concentration of iron in solution is 0.245 g/l.

For the opening of mechanism of the sulfatate formation process there were used a thermal and X-ray analysis techniques. In Figures 3 and 4 the thermogram of the original heating and sulfated cobalt raw materials are presented.

**Table 2.** The results of the initial sulfuric acid leaching cobalt ore. Conditions of experiments: temperature – 90°C, leaching time – 1 hour, weighted ore –10 g, ratio S:L=1:5

<table>
<thead>
<tr>
<th>Expenditure of HCl, %</th>
<th>Content, g/l</th>
<th>Extraction degree, %</th>
<th>Content of cake, %</th>
<th>Weight of cake, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Fe</td>
<td>As</td>
<td>Co</td>
</tr>
<tr>
<td>7</td>
<td>3.04</td>
<td>9.6</td>
<td>3.8</td>
<td>66.07</td>
</tr>
<tr>
<td>20</td>
<td>3.32</td>
<td>10.6</td>
<td>4.01</td>
<td>72.92</td>
</tr>
</tbody>
</table>

On the curve of DTA thermogram heating a raw material shown in Figure 3 is registered in the range of endothermic effect at temperatures 151–206°C and exothermal effect at 692–760°C.

This effect at temperatures up to 206°C corresponds to a process of evaporation of crystallization water of minerals. The temperature range 692–760°C occurs oxidation process of minerals included into ore content, mainly aluminosilicate components.

For comparison, in Figure 4 cited is the thermogram of obtained sulfatized cobalt ores with 450°C, which shows that unlike the cobalt raw material were clearly expressed two endoeffects were at the temperature 137–250 and 641–783°C. The second endoeffect corresponds to the process of thermal decomposition of sulfates, which proves the diffraction pattern of the initial and sulfatized material.
Fig. 3. The thermogram of the initial heating of cobalt ore.

Fig. 4. The thermogram of heating sulfatized cobalt ore.
Figure 5 presents the diffractograms of the original ore (a), and the sulfatization products at 400 (b), 600 (c) and 700°C (d). In the diffraction pattern of initial ore there are clearly expressed lines of minerals: α-quartz, feldspar, clinochlore, andradite, cobaltite.

The diffractogram of the sample taken at 400°C (Figure 5) shows the presence in its composition of a divalent sulfate, ferric(III) and α-quartz. Sufficiently clear expressed cobaltite reflexes that testifies to that at this temperature sulfuric acid does not degrade the crystalline structure of this mineral. In the diffractogram of the sample taken at 700°C, presented are mainly reflexes of α-quartz, hematite, iron ferrite, cobalt sulfate and undecomposed iron sulfate. An interesting fact is that the reflexes of andradite in all samples of sulfated material obtained at different temperatures (Figure 5 b–d), does not disappear. Comparison of the results shows that concentrated sulfuric acid mainly decomposes minerals of cobaltite and clinochlore.

Fig.5. Original diffractogram cobalt ore (a) and sulfatizated products produced at 400 (b), 600 (c), 700°C (d). Conditional meanings: 1 – andradite, 2 – hematite, Fe₂O₃, 3 – silica, SiO₂, 4 – cobalt sulfate, 5 – clinochlore (ferruginous), 6 – cobaltite, 7 – iron sulfate(III).
Based on the data obtained by X-ray and thermogravimetric analysis methods, it was established that in spite of incomplete decomposition of ore minerals, extraction of cobalt in solution at temperature ranging 650–700°C makes up 85.92%, that corresponds to the formation of cobalt sulfate.

The obtained experimental data permit to conclude that the investigated sulfatization cobalt ore with concentrated sulfuric acid under optimum conditions, enables to transfer water-soluble form of cobalt (~85.52%) with simultaneous minimal sulfatization iron (1.5%).

As follows from Table 3, in this method of the concentration of extraction degree of valuable components exceeds the previous (Table 1) and makes up for a Co – 85.52%, for Fe – 1.5%, for As – 55.2%.

**Conclusion**

It is established that while leaching the initial ore by water extraction of cobalt to the solution is not observed. It is expedient to use a sulfuric acid solution, which allows to selectively isolate the silica from the ore. However, the use of sulfuric acid to 2 N concentration does not permit completely to extract cobalt to solution. Processing method of ore with its sulfated calcine with next leaching calcine with water is offered. It is was found that extraction of cobalt from sulfatized ore at 700°C is 85.52%.

Studies have showed that at the processing cobalt ores the use of sulfatization ore roasting and subsequent water leaching of calcine is expedient.

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**YÜKSƏKSİLİKATLI KOBALTLI FİLİZLƏRDİN KOBALTIN MINƏRAL TURŞULARLA YUYULMASI ŞORAIİTİNIŅ TƏDQİQİ**

А.А.Гейдаров, Н.В.Юсифова

Daşkəsan yaşayışının kəbəltli filizinin minerololoji tərkibi 逵ranılmışdır. Kəbəltli filizin xlorid və sulfat turşusu ilə yuyulması tədqiq edilmişdir. Göstərilir ki, filizin tərkibində çox 逵ali olan kəbəltin minerallarının və silikatlı birləşmələrinin olması, kəbəltin xlorid turşusu ilə (2 N-qədar) yuyulması təşkil edir. Kəbəltin xlorid turşusu ilə çaxarlanması 77.4 %, sulfat turşusu ilə isə 76.7 % təsəkil edir. Filizin emali üçün sulfatlaşdırıcı birma prosesi və daha sonra su ilə yuma təsəkil edilmişdir. Aşkar olunmuşdur ki, Co çoxarlanması maksimum temperaturda 700°C-də 85.52% təsəkil edir.

**Açar sözlər:** kobalt, filiz, sulfatlaşdırıcı birma, yuyulma, bitişmə, çaxarla.

**ИССЛЕДОВАНИЕ УСЛОВИЙ ВЫЩЕЛАЧИВАНИЯ КОБАЛЬТА ИЗ ВЫСОКОКРЕМНИСТЫХ КОБАЛЬТОВЫХ РУД МИНЕРАЛЬНЫМИ КИСЛОТАМИ**

А.А.Гейдаров, Н.В.Юсифова

Приведены результаты исследования процесса извлечения кобальта из высококремнистых кобальтовых руд Дашкасанскоего месторождения. Изучен вещественный состав исследуемой руды. Установлено, что присутствие в составе руды труднорастворимых минералов кобальта и силкатных соединений является причиной недостаточно эффективного выщелачивания кобальта растворами серной (до 2 н) и соляной (7−20%) кислот. Предложен способ переработки руды, предусматривающий ее сульфатизирующий обжиг с дальнейшим выщелачиванием огарка водой. Найдено, что извлечение кобальта из просульфатизированной при 700°C руды составляет 85.52%.

**Ключевые слова:** кобальт, руда, сульфатизирующий обжиг, выщелачивание, спекание, извлечение.