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EXTRACTION OF THE VALUABLE COMPONENTS FROM NON-FERROUS METALS-CONTAINING POOR ORE AND TAILINGS

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In the article the results of processing oxidized copper polymetal ore and iron ore tailings by heap leaching irrigation and sorption methods have been analyzed. A study was made of conditions for concentrating some non-ferrous metals (Cu, Zn, Ag, Au, Co, Mn) by hydrolytic precipitation and sorption methods. As well, it is reported on the results, were obtained, on utilization of arsenic from technological solutions to the demand level of concentration.

Keywords: ore, tailing, irrigation, thickener, hydrolytic, precipitation, sorption, copper, zinc, gold, silver, cobalt, manganese.

Introduction

As a result of exploitation of fields during a long time by the traditional physical and chemical methods the balanced ore have been considerably exhausted and quantitative composition has been reduced. That’s why around the mining enterprise were collected a large amount of pollution. The mineral tailings accumulated for years around the enterprises can be used as a source raw material for producing some nonferrous metals. Also poor ores and its tailings can be spontaneously irrigate with the affect of atmosphere factors which can pollute environment with metals Cu, Zn, Pb, Mo, Co, As.

As a result of processing ore deposits in Gedebey and Dashkesan districts of the republic million tons of tailings around the enterprise which contain enormous valuable metals.

The main aim of this work is obtaining the effective parameters and regimes of extracting valuable metals and also making harmless arsenic in received processing products to required level from ore and its tailings in Gedebey district around area of "Azerbaijan International Mining enterprise" and Dashkesan Ore Purification factory.

Research methods and materials

One of the economically profitable processing method is underground irrigation one based on selective solution of non-ferrous, rare and noble metals from poor ore and its tailings with chemical reagents. Experiments were carried out in laboratory device-spiral tube and percolation colon which makes similar underground irrigation. The amount of embedded tailing were changed from 500 grams to 5 kilograms. Oxidized copper ore was irrigated with 0.8% NaClO solution, processing tailing of iron ore was irrigated with 1N H2SO4 (pH=0.95). Hypochloride solution received from processing of alynite with NaCl and H2SO4 after electrolysis of Na2SO4 and H2SO4 solutions. Mineralogical analysis of materials were done with Bruker D8 diffractometer, concentration of rare metals with Varian and Perkin Elmer atomic adsorption device, complex element analysis with Bruker S2 Picofox roentgen fluorescent device.

As the samples were taken from different areas research was carried out on different tailing compounds and ore samples. It was determined that 90% of copper polymetallic ore contain pyrite mineral. The rest of polymetallic ore consists of chalcopyrite, sphalerite and barit minerals, Dashkesan iron ore tailings consists of hematit, quartz, pyrite, calcite, dolomite, kaolinite, clinchochlor, andrinite and steatite minerals. During the experiments we observed the affected factors to irrigation of metals to solution (time, initial concentration of acid, L:S phases ratio, pH).

Experimental part

 Extraction of Cu, Ag, and Au from oxidized rocks from Gedabay ore basin

The mass percentage of metals in taken ores was as following, %: Al – 3.63, Fe – 18.57, K – 0.19, Si – 19.99, Cu – 0.15, Zn – 0.06, S – 0.63 and g/t: Au – 1.7–17, Ag – 26–133.1. So-
Dium hypochlorit solution was obtained from electrolysis of natrium chloride solution with 30 g/t concentration. Concentration of observed HClO solution was 0.8%, oxidation-reduction potential was eH=760 mV, and pH=8. By adding HCl to this solution eH reached to 1250 and pH reduced to 4. Experiments were carried out with 0–0.8 and 0–25 mm particles in size.

In Figures 1 and 2 are shown irrigation dynamics of Cu, Au and Ag depended on time. Results show that in early hours in irrigative solution there was observed maximum concentration of the noble metals. If while irrigation fraction of rocks is smaller than 0.8 mm and duration is 80 hours 81.6% of Au, 29.2% Ag, 41.2% Cu extract to solution. In 25 mm rock particle sizes yield percentage of metals as following, %: 58.7 Au, 11.6 Ag and 20.5 Cu. In first solution pH reaches to 5.18 and 9.94 in second solution.

As it can be seen from the rock samples that after 40 hours irrigation of Au with HClO was stopped. This is due to reduced oxidation potential of solution. As HCl solution is very aggressive, from initial hours it was used for irrigation of Cu, Zn, Fe, Ca, Cd and Pb. The composition of solution after irrigation was as following (mg/l): Fe – 56.1, Zn – 55, Cu – 51.5, Ca – 70.5, Cd – 0.41, Pb – 0.74, Mn – 1.57, Ag – 0.54, Au – 2.9. Since the experiments were provided in closed conditions there was not observed atmospheric pollution. Sorption of noble metals from solutions was done with amberlit D360 sorbent which is selective for Au. Complex elementary analysis of sorbent after adsorption showed that it contains 3.06% Au and 10.6% Ag.

For the sorption of Zn and Cu ions from chloric acid and hypochlorite solutions high acidic cationite KY-2 (H-form) and high base anionite AB-17 (Cl-form) were used. Experiments were performed in a wide range of acid (1–10^6–5) N and at different pH. The most important factor affected to the sorption ions is the acidity of solutions and the concentration of metal ions. Therefore, affect of acidity on copper and zinc sorption was studied on (0.1–4) N chloride and sodium chloride, solution as a model and were tested in technological solutions. The results showed that sorption of zinc with cationite from chloride solution decreases, when pH decreases and when concentration of HCl increases to 1N or more it stopped. The sorption of Zn as anionite starts at pH=2. The sorption of Zn with AB-17 anionite increases as increases the concentration of chloric acid and at 1–4 N gets maximum degree. Above 4 N sorption of Zn decreases while sorption of Cu increases. It can be explained by the fact that Zn forms a negative complex ions up to 0.15 N concentration but Cu at 4 N or higher concentrations moves to complex anion forms. At pH=1.3 with the offered anionite form technological solutions Cu does not collapse but 97.1% of Zn sorbed as it is in anionite form. Copper and Zn sorbed with KY-2 cationite desorbed with 100 g/l NaCl solution.
Extraction of metals from enriched Dashkesan iron ore tailings

In Dashkesan district there were calculated at least 20 million tones of tailings around Dashkesan Ore Purification Factory’s area. The samples were taken from different parts of this area were bought to the laboratory and studied their chemical and mineralogical composition. It was determined that the tailings probably consist, %: 40.3 androdit, 12.2 caolinit, 9.3 clinichlor, 14.8 calcite, 3 dolomite, 13.3 quartzs and 5.6 hematite. The chemical analysis of samples taken from different areas showed that the major components of tailings are: Fe, Al, Ca, Mg and Si. There are little amount of valuable components, g/t: Co (27–60), Cu (432–517), MnO (0.24–071), Zn (155), Pb (82), Y (27), Zr (28), As (121). These elements are contented in tailings as an isomorphic mixture. The presented rocks and tailings are different from the ore, due to their minor element content, while their main components are differ by mineralogical composition. The results of six stage irrigation with the sulfuric acid solution showed that the pH was increased from 0.95 to 7.44 after first irrigation. This is explained by the fact that in the first stage of irrigation sulfuric acid neutralizes calcium containing minerals (calcite and dolomite) (pH rises) and the next irrigation stage sulfuric acid used for the forming sulphate contained salts of metals. The subsequent decrease in acidity occurs as a result of the hydrolysis of sulphate salts. The next series of experiments were carried out with 1N H₂SO₄ solution which was kept in percolator column within 24 hours. As it can be seen when irrigation states increases also increases concentration of metals in solution but decreases pH (Figure 3). At last stage concentration of metals in received solutions were as follows, g/l: Al – 3.23, Fe – 13.63, Mn – 1.89, and mg/l: Cu – 635, Co – 58.9, Zn – 81.2. The next series of experiments was not provided with solution, but by circulation of received solution after irrigation to percolation colons (Figure 4). The first three irrigation periods gradually increased extraction of metals to solution and 4th irrigation concentration of metals (Mn, Co, Cu, Zn, Al) gradually decreased. It can be explained by gradually increasing equilibrium pH of solution from 3 to 6.5. In pH>6.5 leads to decreasing concentration of some metals such was as Co, Cu, Zn, Fe. At the lower part of percolator brown colored iron hydroxide sediment was observed. At pH=6.5 all iron ion in solution precipitates as Fe(OH)₃. In the higher part of percolator solved metal ions (Cu²⁺, Zn²⁺, Co²⁺, Al³⁺) in tailings sorbed on Fe(OH)₃ which precipitated in the lower part of percolator.

Provided experiments are based on the fact, that for obtained more amount of the valuable components in productive solutions pH value should be adjusted. This is done by reducing S:L ration from 5:1 to 1:1. The numerous experiments show that it is not suitable to increasing pH of solution up to 3.5–4 while irrigation of non-ferrous metal contained raw material.

![Fig. 2. Yield percentage of extracted of Cu, Au, Ag while irrigation.](image-url)
For the aim to extract and thicken valuable (Cu, Zn, Co, Mn, Al) metals from technological solutions and to reduce toxicity in irrigative solutions ion-exchange sorption and hydrolytic precipitation were used. For the sorption of metals from sulphate contained solutions high acidic KY-2x8 cationite were used, but the desorption of metals were done by NaCl solution. To obtain metals as a selective concentrates from the solutions was used four stage neutralization method.

Rendering harmless arsenic to the required level from Dashkesan cobalt ore and its tailings

Our republic has enormous natural resources. The majority of ore minerals contain arsenic. After extracting the main components (Cu, Zn, Co, Pb, Au, Ag) from ores rendering harmless arsenic from waste and tailings around enterprise is the main issue for nowadays. This is considered to be one of the topical problems both in terms of ecological and complex pro-
cessing of ore materials. It is also known that the maximum permissible concentration of arsenic in waste water should be no more than 0.05 mg/l and 0.003 mg/m³ in the air. The samples of ores and their processing tailing (solid and liquid) around Dashkesan Ore Purification enterprise were brought to the laboratory and their chemical and mineralogical compound were investigated. It was identified that Dashkesan Co ore contains 2.4% arsenic, in the iron ore samples taken from different areas 0.006–0.023%, tailing samples 121–140 g/t, processing solutions of technological tailings 4.7–234.4 mg/l. One of the perspective methods to extract arsenic from technological solutions is to precipitate it as hard ly soluble calcium arsenate and iron(III) arsenate salts. A certain part of arsenic is in the three valent state in technological solutions and wastewater. Three valent arsenic is 60 times more toxic than five valent arsenic. Purification of arsenic from sulphate solutions was carried out in laboratory mixer at 40–90°C temperature range, on the electric slab in glass bottles with n=600⁻¹ rotating frequency. Hydrolytic precipitation duration took 0.5 hours and solution was filtered after 24 hours. Initial experiments were carried out precipitating with CaCO₃ and Ca(OH)₂ with the known concentration of As⁵⁺. It was revealed that arsenic precipitates at three stages. At pH= 0.1–2 interval arsenic precipitates intensively, at 3–4.5 for a minimum concentration, at pH=5–7.5 a certain part of precipitation solves. Also it was revealed that reducing acidity of environment increases the formation of Ca₃(AsO₄)₂ precipitation. At pH= 290°C temperature during 30–35 minutes 91% of arsenic precipitates from solution as calcium arsenate. Precipitation contains 12–15% of arsenic. At pH=1.5–2.1 precipitates gypsum which contains 0.25–0.5% arsenic. Subsequent experiments continued by the learning precipitation conditions of arsenic as a less soluble compounds from model solutions. The results were investigated in Fe₂(SO₄)₃–Na₃AsO₄–ZnSO₄–CuSO₄–CoSO₄ system.

At the same value of pH the less soluble arsenate is iron(III) arsenate (scorodite ore) from Fe, Zn, Cu and Co arsenates. As it can be seen from Figure 5 in comparison with other metal arsenates iron(III) arsenate precipitates completely at low pH.

Independently precipitation process in Na₃AsO₄ and Fe₂(SO₄)₃ solutions was tested in model solutions. Were investigated concentration of iron in Fe(III):As=1:1; 2:1; 3.5:1 ratio, how precipitation duration and temperature changes affect on access of arsenic from solution to solid state (Table 1). Change of concentration iron(III) does not affect to precipitation of degree of As. Increasing temperature and prolonging precipitation duration provides 99.9% precipitation of As. Individuality of Fe(III) arsenate was approved with DTA and DTG analysis and IR spectroscopy. If precipitation occurred done at room temperature it, will be received of pale green color X-Ray amorphous scorodite mineral.

![Fig. 5. Precipitation of arsenic from Fe, Cu, Zn, Co sulphate solutions.](attachment:image.png)
Table 1. The results of precipitation of Arsenic depended on temperature and duration of experiments

<table>
<thead>
<tr>
<th>№</th>
<th>Duration, minutes</th>
<th>20°C Concentration of As, g/l</th>
<th>Precipitation degree of As, %</th>
<th>40°C Concentration of As, g/l</th>
<th>Precipitation degree of As, %</th>
<th>60°C Concentration of As g/l</th>
<th>Precipitation degree of As, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>50</td>
<td>0.0</td>
<td>50</td>
<td>1.16</td>
<td>0.0</td>
<td>97.68</td>
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<td>2</td>
<td>5</td>
<td>253</td>
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<td>3</td>
<td>10</td>
<td>1.765</td>
<td>96.47</td>
<td>0.98</td>
<td>98.54</td>
<td>0.39</td>
<td>99.5</td>
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<tr>
<td>4</td>
<td>15</td>
<td>0.712</td>
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<td>0.4</td>
<td>99.21</td>
<td>0.16</td>
<td>99.76</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>0.232</td>
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<td>0.13</td>
<td>99.74</td>
<td>0.05</td>
<td>99.9</td>
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<td>6</td>
<td>30</td>
<td>0.189</td>
<td>99.62</td>
<td>0.11</td>
<td>99.79</td>
<td>0.04</td>
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<tr>
<td>7</td>
<td>60</td>
<td>0.158</td>
<td>99.68</td>
<td>0.09</td>
<td>99.82</td>
<td>0.04</td>
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Table 2. The results of precipitation of Fe and As from solution

<table>
<thead>
<tr>
<th>Usage of CaCO₃, g/l</th>
<th>pH</th>
<th>Concentration of components in solution, g/l</th>
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<tr>
<td></td>
<td></td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>0</td>
<td>1.0</td>
<td>31.2</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>24.5</td>
</tr>
<tr>
<td>45</td>
<td>2.8</td>
<td>8.2</td>
</tr>
<tr>
<td>60</td>
<td>3.2</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 3. Chemical compound of cake after neutralization at pH=2.8

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al</th>
<th>S</th>
<th>Fe</th>
<th>As</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>№1</td>
<td>4.63</td>
<td>7.03</td>
<td>8.61</td>
<td>1.12</td>
<td>0.28</td>
</tr>
<tr>
<td>№2</td>
<td>2.81</td>
<td>4.85</td>
<td>31.38</td>
<td>4.66</td>
<td>0.046</td>
</tr>
</tbody>
</table>

Above 90°C temperature they obtain low soluble crystalline FeAsO₄·2H₂O. In technogenetical solution at pH=4 FeAsO₄·2Fe(OH)₃ precipitates mostly. In 3000–3600 cm⁻¹ absorption range of IR spectra of received amorphous samples matches wide absorption range with 3377.25 and 3362.49 cm⁻¹ maxima. It is suitable for valent dances of OH group of molecular water. In IR spectra adsorption strips of spectrum AsO₃³⁻ (10.9 cm⁻¹–1.830 cm⁻¹ 479 cm⁻¹) nm and Fe–OH (620 cm⁻¹, 580 cm⁻¹) accurately reflected. It indicates that the precipitated phase is scorodite. Firstly, as the concentration of Fe in solution is 7.5–13.6 g/l and 0.1–0.23 g/l for arsenic. It is easy to precipitate As as FeAsO₄·2H₂O and SO₄²⁻ as a gypsum without adding Fe²⁺ to solution. After neutralization of sulphate contained solution with lime and oxidation of Fe²⁺ and As³⁺ with the reagents (air, H₂O₂, KMnO₄) precipitates a lot of amorphous hydroxides of metals, scorodite and gypsum. Individuality of this precipitation has been confirmed with IR spectroscopy and RFA analysis methods. Content of technological solution after precipitated Fe and As was given in Table 2 and chemical compound of cake in Table 3.

Table 3 content of precipitation after neutralization when usage of lime is 45g/l. As it can be seen in Table 3 at pH=2.8 the amount of arsenic in the first sample is 1.12 and 4.66% in the second sample. Zn²⁺, Cu²⁺, Co²⁺, Mn²⁺, Mg²⁺ ions remain in solution.

After removing precipitations in Table 3 pH of solution increases to 4 with adding lime. At this pH precipitates Al³⁺, As⁵⁺, Fe³⁺ which were not precipitated at pH=2.8. The higher pH value (4.5) leads to precipitation of Cu, Zn,Co.

**Results**

Gedebey copper containing polymetallic ore was irrigated with chlorite and hydrochloride. There have been determined optimal conditions of extracting Ag, Au and Zn with the ion exchange sorbents from irrigated solutions, effective parameters and modes of extracting precious metals from tailing at of Dashkesan Ore Purification company. As a result of provided experiments for the first time in Azerbaijan has been production technology based on processing of ore tailings developed which is the more harmless for the nature. In the laboratory there was prepared test stand which models underground leaching.

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ƏLVAN METAL TƏRKİBLİ KASİB FİLİZ VƏ TULLANTILARDAN QİYMƏTLİ
KOMPONENTLƏRİN ÇIXARILMASI
A.Ə.Heydərov, A.A.Quliyeva, A.B.Mehdiyev, A.N.Ağayev
Oksidlaşmış kolçadan filizinin və damir filizinin emal tullanlılarının topa hallolma üsulu ilə yuyulmasının nəticələri
analiz edilmişdir. Yuyulmuş məhullərdan bir sıra qiymətlü metallərin (Cu, Zn, Ag, Au, Co, Mn) hidrolitik çökək və
sorbsiya üsulları ilə qatılmalıdırması şəraitə araşdırılmış, rejimləri müəyyənəşdirilmişdir. Texnoloji məhullərdan arsen-
in tələbata uyğun hadda qdar vəsaitləşdirilmişdir. Yeyin məhullərindən arsendin tələbə uyğun hadda qdar vəsaitləşdirilmişdir. 

Açar sözlər: filiz, tullanlı, yuma, qatılaşma, hidrolitik çökək, sorbsiya, mis, sink, qızıl, gümüş, kobalt, manqan.

ВЫДЕЛЕНИЕ ЦЕННЫХ КОМПОНЕНТОВ ИЗ БЕДНЫХ РУД ЦВЕТНЫХ
МЕТАЛЛОВ И ОТХОДОВ
A.A.Гейдаров, А.А.Гулиева, А.Б.Мурадова, А.Н.Агаев
Приводятся результаты по кучному выщелачиванию окисленных медных колчеданных руд и хвостов железных
руд. Изучены условия концентрирования некоторых ценных металлов (Cu, Zn, Ag, Au, Co, Mn) из растворов
методами гидролитического осаждения и сорбции. Сообщается о полученных нами результатах утилизации
мышьяка из технологических растворов до предельно допустимой концентрации.

Ключевые слова: руда, отходы, промывание, концентрирование, гидролитическое осаждение, сорбция, медь,
цинк, золото, серебро, кобалт, марганец.