INTRODUCTION

Asgat silver-polymetallic deposit is one of the strategic mineral deposits of Mongolia. It locates in Nogoonnuur, Bayan-Ulgii province, north western part of Mongolia. No operation has been started since 1976’s due to its location in high mountain region and lack of technical feasibility for mining. Silver, copper, antimony and bismuth are the valuable metals of this deposit ore and its main minerals are tetrahedrite and chalcopyrite [1].

Complex polymetal minerals containing in ore and its concentrate has been treated by conventional pyrometallurgical methods. However, these routes are troubled by their higher operating costs and excessive environmental pollutions. This hinders and limits the ability of established smelting or roasting technologies to fill the needs of new sources of polysulfide concentrate. An alternative is to treat polymetals containing concentrate by hydro metallurgical techniques. A hydrometallurgical method is expected to be promising in order to overcome such problems.

In recent years, there has been a heightened interest in the possible application of various reagents in the hydrometallurgical processing of polymetallic ore and concentrate- especially tetrahedrite concentrate. Most of the references on tetrahedrite concentrate leaching refers to the use of alkaline leaching with Na₂S + NaOH [2-5]. Balaz et al. [4] used alkaline leaching to remove selectively antimony, mercury and arsenic from a concentrate containing 41% tetrahedrite.

The process involved a mechano-chemical treatment of the concentrate, where the solid concentrate was ground in an attritor with a solution of Na₂S+NaOH and antimony, arsenic and mercury were leached out. The leaching of Sb and Hg, and the thiourea leaching of silver from a mechanically activated tetrahedrite is also reported by Balaz et al. [5].

According to Correia et al. [6] have studied the leaching of tetrahedrite with ferric chloride, sodium chloride and hydrochloric acid solutions. It involves the breakdown of the tetrahedrite crystal structure with simultaneous liberation of all of its components. The leaching of tetrahedrite can be described by the shrinking core model and the leaching rate is controlled by a surface reaction.

Correia et al. [7] also studied the autoclave leaching of two tetrahedrite concentrates with solutions of cupric and ammonium chloride, cupric and sodium chloride, or ferric and sodium chloride. They summarized that leaching with ammonium chloride was very efficient. It describes almost completely dissolution the tetrahedrite after 3h of leaching at 130°C and 3atm of oxygen partial pressure.

The dichromate ion (Cr₂O₇²⁻) have been used to dissolve chalcopyrite in acidic medium [8] and copper removal from molybdenite concentrate related with their higher oxidation potential [9]. The reduction of dichromate ion in acidic solutions is given by Jackson as [10]:

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad \varepsilon^o = 1.33\text{V}
\]

This potential value (1.33V) is adequate to oxidise almost all metal sulfides.
In this work, the leaching behaviour of freibergite-tetrahedrite concentrate from the Asgat polymetallic ore with potassium dichromate acidic solution was studied. The influence of variables such as sulfuric acid and dichromate concentrations, temperature, leaching time on the dissolution rate of silver, copper, antimony and iron from the concentrate were investigated.

**EXPERIMENTAL**

**Materials and methods:** In this study was used sample of freibergite-tetrahedrite concentrate, which was prepared by using flotation (80g/t butylxanthate, 40g/t pine oil and liquid glass 160g/t) of Asgat silver-polymetallic ore. The chemical composition of the concentrate was determined by physical-chemical methods and ICP-OES, which is presented in Table 2. The mineralogical composition of the concentrate was determined by XRD (Enraf Nonius Delft) and SEM-EDS (HITACHI TM-1000), these figures are showed in Fig. 1 and Fig. 2.

The dissolution experiments were carried out in a 1 L, three-necked round bottomed glass reactor equipped condenser, thermometer in a heating Mantle and placed in a magnetic stirrer at a constant rate of 400 rpm. To each leaching solution, 500 ml of leaching solution was used. The leaching solution was first added to the reactor and when the desired temperature was reached, the solid sample was added. The solution samples were timely taken from reactor for analysis of dissolved metals which was carried out by AAS (AA-650iF). In each experiment, the solid residue was filtered, washed with distilled water, dried and their phase content was determined by X-ray analysis using diffractometer. The influence of each variable was determined by keeping all other variable constant.

Dissolution tests of minerals in the freibergite-tetrahedrite concentrate were using by acidic potassium dichromate solutions, to determine the effect of the following parameters: potassium dichromate (K$_2$Cr$_2$O$_7$) concentration (0.02M, 0.05M, 0.1M), sulfuric acid (H$_2$SO$_4$) concentration (0.2M, 0.3M, 0.4M), leaching temperature (40$^\circ$C, 80$^\circ$C, 95$^\circ$C), and leaching time (15, 30, 60, 120, 180 and 240 minutes).

Chemicals used in the experiments were of analytical reagent grade. The leaching solution was prepared by dissolving the proper chemicals in distilled water to the required concentration. A weighed amount of potassium dichromate (K$_2$Cr$_2$O$_7$) was dissolved in water, then the desired volume of sulfuric acid (98%) was added.

**RESULTS AND DISCUSSION**

**Mineralogical and elemental composition:** Fig. 1 shows the result obtained from XRD analysis performed on concentrate. The major mineralogical phases identified in the diffractogram were tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$), freibergite ([Cu$_6$Fe$_2$Zn$_2$Ag]$_{12}$Sb$_4$S$_{13}$), stromeyerite (AgCuS), chalcopyrite (CuFeS) and siderite (FeCO$_3$).

![Fig. 1. XRD diffractogram of freibergite-tetrahedrite concentrate](image)

Minerals content of the polysulfide (freibergite-tetrahedrite-stromeyerite-chalcopyrite) concentrate by XRD analysis was calculated and shown in Table 1.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical formula</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freibergite</td>
<td>(Cu, Fe, Zn, Ag)$_{12}$Sb$<em>4$S$</em>{13}$</td>
<td>60.90</td>
</tr>
<tr>
<td>Tetrahedrite</td>
<td>(Cu$_{12}$Sb$<em>4$S$</em>{13}$)</td>
<td>18.07</td>
</tr>
<tr>
<td>Stromeyerite</td>
<td>Ag, CuS</td>
<td>13.09</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS$_2$</td>
<td>3.34</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO$_3$</td>
<td>4.58</td>
</tr>
</tbody>
</table>

37
XRD result shows the concentrate is rich in freibergite and silver is also found in freibergite and stromeyerite. The freibergite-tetrahedrite concentrate was examined under SEM-EDS and the resulting spectra is presented in Fig. 2.

It can be seen grain of copper and antimony sulfide minerals and no line of other elements was detected by EDS spectrum analysis that are hosted in the tetrahedrite structure. The elemental composition of the polysulfide concentrate is presented in Table 2.

Table 2. Chemical composition of the polysulfide concentrate from the Asgat deposit

<table>
<thead>
<tr>
<th>Component</th>
<th>Ag</th>
<th>As</th>
<th>Zn</th>
<th>Cu</th>
<th>Sb</th>
<th>Pb</th>
<th>Fe</th>
<th>Bi</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0.905</td>
<td>&gt;1.0</td>
<td>5.51</td>
<td>38.75</td>
<td>28.67</td>
<td>0.09</td>
<td>10.6</td>
<td>&gt;0.2</td>
<td>10.0</td>
</tr>
</tbody>
</table>

**Effect of leaching time on dissolution metals from the concentrate:** The effects of leaching time on silver, antimony, copper and iron dissolution from the concentrate were investigated at various leaching times at 95°C in solutions containing 0.1M K₂Cr₂O₇, 0.4M H₂SO₄ and experimental results are presented in Fig. 3. The leached antimony initial 15 min was 96%, and when the leaching time was increased, antimony dissolution was reached until 99.86%. Silver dissolution was increased with increasing of the leaching time and reached 64.09% at 240 min. Also 63.56% copper was leached after 15 min, with increasing of the leaching time copper dissolution rate was slightly increased (68.13%) until 180 min. After this time copper dissolution rate decreased. The iron reached the highest value (84%) in initial 15 min, and then decreased.

**Influence of acid ion and dichromate ion and concentrations:** In the experiments to study the influence of sulfuric acid (H₂SO₄) concentration on silver, antimony, copper and iron dissolution, H₂SO₄ concentration was varied in the range of 0.2 - 0.4M at 95°C while the K₂Cr₂O₇ concentration was kept constant at 0.1M. It is illustrated in Fig. 4 that the except iron metals dissolution rates all valuable metals were reached maximum at 0.4M of sulfuric acid concentration (Sb - 99.94%, Ag - 95.69%, Cu - 93.86%).

The results indicate that the oxidizing potential of Cr₂O₇²⁻ ions increased with the increase of solution acidity, which contributed to the dissolution of copper, silver and antimony. Hydrogen ions concentration on the reduction potential of Cr₂O₇²⁻ ions was highly influenced.
In order to study the effect of dichromate ion concentration on metals dissolution, the leaching conditions were maintained the same described above except that the concentration of \( \text{H}_2\text{SO}_4 \) was constant at 0.4M while the concentration of \( \text{K}_2\text{Cr}_2\text{O}_7 \) were 0.02 M to 0.1M.

The result is illustrated Fig.5 that the silver dissolution increased from 87.40% to 95.69%, when the concentration of dichromate was increased from 0.02M to 0.1M. Also, dissolution rate of antimony was increased from 97.99% to 99.84% with increasing dichromate concentration. After 4h leaching, 43.13% of copper was extracted at a concentration of 0.02M \( \text{K}_2\text{Cr}_2\text{O}_7 \) and when the concentration increased to 0.05M, 95.54% of copper was dissolved from polysulfide concentrate. In contrast, iron is not influenced by changes in dichromate concentration. **Effect of temperature on metals dissolution:** The influence of reaction temperature on the metals \( \text{Sb}, \text{Ag}, \text{Cu}, \text{Fe} \) dissolution, under following fixed conditions: leaching time 4h, 0.1M \( \text{K}_2\text{Cr}_2\text{O}_7 \), and 0.4M \( \text{H}_2\text{SO}_4 \). Then temperature was varied in the range 40\(^\circ\)C - 95\(^\circ\)C (Fig.6). At 40\(^\circ\)C, 62.48%, 58.64% and 55.84% Sb, Ag and Cu were dissolved respectively, and when the reaction temperature was increased to 95\(^\circ\)C, about 99.81%, 95.65%, 93.85% and of Sb, Ag and Cu were dissolved. Whereas iron reached the highest value (69.25%) at 80\(^\circ\)C, and it decreased to 30.18% at 95\(^\circ\)C. However the temperature has a strong influence on the dissolution rate. At 95\(^\circ\)C temperature were observed reducing of dissolution rates of the Fe and Cu and it thought to be caused by formation of elemental sulfur that precipitated at the particle surfaces of minerals. **Characterization of the solid residues:** The solid residue was remained under the following leaching conditions: stirring speed 400 rpm, 0.1M \( \text{K}_2\text{Cr}_2\text{O}_7 \), and 0.4M \( \text{H}_2\text{SO}_4 \) at 95\(^\circ\)C reaction temperature and 4h leaching time. The recoveries of antimony, silver and copper and iron from the concentrate were 99.84%, 95.69%, 93.85%, 30.18% respectively. Characterization of this solid residue was determined by X-ray analysis (Fig.7).
In the XRD pattern was detected an elemental sulfur phase which confirms the breakdown of the freibergite-tetrahedrite crystal structure with the simultaneous liberation of all its components. These minerals are dissolved in the acidic dichromate solution due to the following reaction:

$$\text{Cu}_{12}\text{Sb}_4\text{S}_{13} + 4\text{K}_2\text{Cr}_2\text{O}_7 + 26\text{H}_2\text{SO}_4 + 5\text{SO}_2 = 12\text{CuSO}_4 + 4\text{K}[\text{Sb(OH)}_6] + 2\text{K}_2\text{SO}_4 + 4\text{Cr}_2(\text{SO}_4)_3 + 13\text{S}_0 + 14\text{H}_2\text{O}$$

(1)

$$[\text{CuFeZnAg}]_{12}\text{Sb}_4\text{S}_{13} + 4\text{K}_2\text{Cr}_2\text{O}_7 + 62\text{H}_2\text{SO}_4 + 23\text{SO}_2 = 12\text{CuSO}_4 + 6\text{Fe}_2(\text{SO}_4)_3 + 12\text{ZnSO}_4 + 6\text{Ag}_2\text{SO}_4 + 4\text{K}[\text{Sb(OH)}_6] + 2\text{K}_2\text{SO}_4 + 4\text{Cr}_2(\text{SO}_4)_3 + 13\text{S}_0 + 50\text{H}_2\text{O}$$

(2)

CONCLUSIONS
Dissolution behaviour of freibergite-tetrahedrite concentrate from the Asgat polymetallic ore by acidic dichromate solutions was investigated at bench scale. The composition of concentrate was determined by X-ray diffraction and consist of 60.90% freibergite ((Cu,Fe,Zn,Ag)_{12}Sb_{4}S_{13}), 18.09% tetrahedrite (Cu_{12}Sb_{4}S_{13}), 13.09% stromeyerite (AgCuS), 3.34% chalcopyrite (CuFeS_2) and 4.58% siderite (FeCO_3). The concentrate contains 9050g/t silver, 38.75%copper, 28.67% antimony and 10.6% iron which determined leaching polysulfide concentrate with dichromate acidic solution at optimal condition resulted total amount of leaching 95.69% silver, 93.85% copper, 99.84% antimony and 30.18% iron (K_2Cr_2O_7:0.1M, H_2SO_4:0.4M leaching time 4h, leaching temperature 95°C).

REFERENCES