Gold Recovery from its Flotation Concentrate using Acidic Thiourea Leaching and Organosilicon Polymer

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The method for the recovery of gold from its flotation concentrate using acidic thiourea leaching followed by adsorption on an organosilicon polymer (PSTM-3C) was discussed in the present study. The study had allowed identification of the effect of thiourea, oxidizer and acid concentration, leaching time, temperature and pulp density on gold dissolution in thiourea solution. The results showed that the vast majority of gold (93.6%) from the gold concentrate was dissolved in nitric acid solution with thiourea under the optimum conditions. Whereas some accompanying elements like Se, Te, V, Cr and Ni in the concentrate were insoluble in the acidic thiourea solution. Gold was recovered from the leach liquor by adsorption on the organosilicon polymer PSTM-3C. The influence of acid concentration, adsorption time and temperature was studied for gold recovery using the polymer. The result showed that about 94.4% of gold was adsorbed on the polymer from the liquor after the optimization of the experimental conditions. The FT-IR analysis revealed that when the polymer adsorbed Au from the liquors, a new IR band appeared at 1703 cm⁻¹ which observed in the IR spectrum of the pure polymer was disappeared.

Key Words: Gold leaching, Flotation concentrate, Thiourea, Organosilicon polymer

1. Introduction

Increasing demand for gold in many countries all over the world per year requires the rational utilization of gold resource and effective protection of the environment [1, 2]. Alkaline solution of cyanide commonly uses for the recovery of gold from ores by leaching, however due to the environmental problems of the cyanide leaching, there is need to find practical alternative reagents to cyanide [1-3]. The alternative reagents are thiourea, halide (chloride, bromide and iodide) systems that can be used for this purpose. The main advantages of chlorine which is one of the alternative systems are faster dissolution rate of gold and no passivation of gold surfaces than cyanide leaching process. However, the major disadvantages of the chlorine systems are highly corrosive nature, highly reactive with the sulphate and gangue minerals and instability of gold chloride complex formed etc [2-4]. Therefore main two of the alternative reagents are thiourea and iodide leaching systems due to the lower standard redox potential of their complexes with gold and stability of the resulting complexes in the solution. The standard potential of the half-reaction of gold in the solution with thiourea and iodide is \( E_{\text{AuCl}^+}^{0} = 0.38 - 0.42 \text{V} \) and \( E_{\text{AuI}^+}^{0} = 0.53 - 0.57 \text{V} \) respectively [5-7]. Among them, thiourea \( [\text{SC(NH}_2)_2] \) leaching was extensively studied as a potential substitute to cyanide leaching due to its lower toxicity and faster initial reaction kinetics for gold and silver with an appropriate oxidant [5, 6, 8]. Due to the development of the thiourea gold leaching system, various methods have been proposed for the recovery of gold from its leach solution by cementation [9], carbon adsorption [10], electrowinning [11] and ion exchange/solvent extraction [12, 13]. However, there is limited information on the recovery of gold from thiourea pregnant solution using organosilicon polymer with ion exchange. Due to the efficient recovery of gold from gold ore and concentrate, it is necessary to clarify thiourea leaching system and extraction system.

The aims of this study were: (i) to find optimum conditions for gold leaching in acidic thiourea solution; (ii) to study the effect of acid concentration, adsorption time and temperature on the recovery of gold from its pregnant solution by organosilicon polymer (PSTM-3C).

2 Experimental

2.1. Materials and methods

The study had been conducted on the flotation concentrate obtained from gold-bearing ore in Mongolia. The samples of the concentrate were prepared for the experiments, chemical analysis and mineralogical characterization. The chemical contents and mineral composition of the concentrate were determined by ICP-MS, XRD, chemical and physical-chemical methods and results are summarized in Table 1. Sulfide minerals could not revealed in
the sample by the XRD analysis due to detection limit of XRD for sulphides. However, some sulphide compounds such as FeS$_2$, PbS, ZnS and CuS were revealed by microscopic analysis. Analytical grade thiourea (SC(NH$_2$)$_2$), nitric acid (HNO$_3$) and ferric sulfate (Fe$_2$(SO$_4$)$_3$) were used in this study. The solid residues were separated by filtration and the filtrate solutions were analyzed by spectrophotometric methods. Organosilicon polymer PSTM-3C used in this study was received from Irkutsk Institute of Chemistry, Siberian branch, Russian Academy of Sciences.

2.1.1. Thiourea leaching of gold from the concentrate

The effects of thiourea, oxidant and HNO$_3$ concentration, leaching time, temperature and pulp density on the thiourea gold leaching process were examined and the results obtained are presented in the following sections, respectively. On the other hand, influence of the accompanying metals as Ag, Cu and Sb on the Au leaching was examined under the conditions.

Thiourea can effectively dissolve of gold in acid solutions with the presence of oxidant (Fe$_2$(SO$_4$)$_3$):

\[ \text{Au} + 2\text{CS(NH}_2\text{)}_2 + \text{Fe}^{3+} = [\text{Au(CS(NH}_2\text{)}_2)_2]^+ + \text{Fe}^{2+} \quad \text{Eq.(1)} \]

Ion Fe$^{3+}$ is the best oxidizer and accelerates the reaction of the dissolution of gold in acid solutions of thiourea [3-5].

Table 1. Chemical contents and mineral composition of the gold concentrate

<table>
<thead>
<tr>
<th>Compounds</th>
<th>wt.%</th>
<th>Elements wt.%</th>
<th>Mineral composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>77.8</td>
<td>Cu</td>
<td>0.306</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.15</td>
<td>Zn</td>
<td>0.163</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>5.84</td>
<td>Pb</td>
<td>0.872</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.90</td>
<td>Ni</td>
<td>0.008</td>
</tr>
<tr>
<td>CaO</td>
<td>3.64</td>
<td>Sb</td>
<td>0.044</td>
</tr>
<tr>
<td>MgO</td>
<td>0.89</td>
<td>Sc</td>
<td>0.010</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.25</td>
<td>As</td>
<td>0.071</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.85</td>
<td>Bi</td>
<td>0.029</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.15</td>
<td>SO$_2$</td>
<td>1.360</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
<td>Au</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag</td>
<td>0.242</td>
</tr>
</tbody>
</table>

SIO$_2$  
TiO$_2$  
Fe$_2$O$_3$  
Al$_2$O$_3$  
CaO  
MgO  
P$_2$O$_5$  
K$_2$O  
Na$_2$O  
MnO

2.1.2. Recovery of gold from the pregnant solution

Organosilicon polymer PSTM-3C was used in the process for the recovery of gold from its pregnant solution. The effects of acid concentration (HNO$_3$), adsorption time and temperature on the recovery of gold were studied. The PSTM-3C as an ion-exchange sorbent is a white powder with particle size distribution between 0.7-2.0 mm, which is insoluble in water and organic solvents and unswollen. Fraction of monomer in the PSTM-3C is represented by following formula as given in Eq. (2) [14]. Organosilicon polymer used in this study was synthesized at the Irkutsk Institute of Chemistry, Siberian branch, Russian Academy of Sciences [14].

\[ = \text{Si-O-Si(CH}_3\text{)}_3\text{NH-C(Si(CH}_3\text{)}_3\text{)-Si-O-Si} \quad \text{Eq.(2)} \]

3. Results and Discussion

3.1. Thiourea leaching of gold from the concentrate

3.1.1. Effect of acid concentration

Effect of nitric acid concentration on gold (Au) dissolution from gold concentrate was studied using various concentration of HNO$_3$ ranged from 0.5 N to 4 N under thiourea concentration of 0.2%, pulp density of 1:10, temperature at 20°C, leaching time at 3 hours without oxidant. The effect of the dissolution of Ag, Cu and Sb as accompanying metals on the Au leaching rate was examined. The leaching rates of the metals in the thiourea solutions are shown in Figure 1.

The highest Au and Ag leaching rate was 79.3% and 99%, respectively, when the concentration of HNO$_3$ was 2 N. The gold leaching rate in the thiourea solution was decreased further up to 59.3% with increasing the acid concentration until 4 N, whereas the leaching rate of Sb was increased up to 81% from 57.5% and stabilized in further within the concentration range. Almost 97.7%-99.6% of Ag and 37.8%-44.8% of Cu dissolved in the thiourea solution showing no significant influence on the gold leaching.

3.1.2. Effect of oxidant

The effect of ferric sulfate (Fe$_2$(SO$_4$)$_3$) as an oxidant on the gold leaching rate was examined under identical condition with oxidant concentration from 1% to 4% at HNO$_3$ concentration of 2 N as shown in Figure 2.

As can be observed, the gold leaching rate drastically increased from 8% to 71.4% with increasing an oxidant concentration from 1% to 3%, but the gold dissolution rate slightly decreased up to...
63% when the oxidant concentration was further increased to 4%. Increasing of the gold leaching rate with increasing of the oxidant concentration might be controlled by mass transfer of free ferric ion in the solution forming of complexes such as $[\text{FeSO}_4\text{SC(NH}_2\text{)}_2]^+$ or $[\text{Fe}2\text{SC(NH}_2\text{)}_2]^+$ [3].

3.1.3. Effect of thiourea concentration

In this experiment, the influence of thiourea concentration from 0.2% to 2% on the leaching rate of Au, Ag, Cu and Sb was investigated with the concentration of HNO$_3$, oxidant and thiourea of 2 N, 3% and 0.2%, pulp density of 1:10, temperature of 20°C, leaching time of 3 hours. The leaching rates of Au and accompanying metals (Ag, Cu and Sb) were found from data presented in Figure 3. The results showed that the gold leaching rate was rapidly increased with increasing of thiourea concentration from 0.2% to 2%, whereas the rate of Ag dissolution was insensitive under the condition investigated. The accompanying metals (Ag, Cu, Sb) were readily dissolved with high leaching rate at lowest thiourea concentration. The assumption was made that the increment of gold leaching rate up to 67% was maybe related to slow reaction between thiourea and ferric ion to form relatively stable metal complexes such as $[\text{Au(SC(NH}_2\text{)}_2\text{)}_2]^+$, $[\text{Ag(SC(NH}_2\text{)}_2\text{)}_2]^+$ and $[\text{Cu(SC(NH}_2\text{)}_2\text{)}_2]^+$ $(n=2, 3, 4)$ as well as $[\text{Sb(SC(NH}_2\text{)}_2\text{)}_2]^+$ in the solution with increasing the consumption of thiourea [2-5].

![Figure 3. Effect of thiourea concentration on the rate of Au, Ag, Cu and Sb dissolution. 2 N HNO$_3$, 3% Fe$_2$(SO$_4$)$_3$, pulp density (S:L) 1:10, leaching temperature: 20°C, leaching time for 3 h.](image)

3.1.4. Effect of temperature

The effect of temperature on gold leaching in thiourea solution was investigated at the initial concentration of HNO$_3$, thiourea and oxidizing agent (Fe$_2$(SO$_4$)$_3$) of 2 N, 2% and 3%, pulp density of 1:10, leaching time of 3 hours with variation of temperatures ranging from 20°C to 80°C, respectively. The experimental results obtained were summarized in Figure 4. It was shown that the gold (Au) and antimony (Sb) leaching rates were decreased to 50% from 77.3% and to 83% from 89%, respectively with increasing the temperature from 20°C to 80°C. Copper (Cu) leaching rate was increased in the range of 50% to 70% under the fixed condition. The rate of Ag dissolution in thiourea solution was more stable. The results suggested that the increment of the temperature gave a significant effect on the gold dissolution in acidic thiourea solution. It may be assumed that the effect was appeared due to the thermal decomposition of thiourea, oxidizing agent and redox reaction between them.

![Figure 4. Effect of temperature on the dissolution of Au, Ag, Cu and Sb. 2 N HNO$_3$, 3% Fe$_2$(SO$_4$)$_3$, 2% CS(NH$_2$)$_2$, pulp density (S:L) 1:10, leaching time 3 h.](image)

3.1.5. Effect of leaching time

The experiments were conducted at an initial HNO$_3$ concentration of 2 N, thiourea concentration of 2%, oxidant concentration of 3% and temperature of 20°C, pulp density of 1:10 with different time range between 1 to 6 hours. The experimental results obtained are shown in Figure 5.

![Figure 5. Effect of leaching time on the rate of Au, Ag, Cu and Sb dissolution. 2 N HNO$_3$, 3% Fe$_2$(SO$_4$)$_3$, 2% CS(NH$_2$)$_2$, pulp density (S:L) 1:10, 20°C.](image)

It can be seen that the rates of Ag, Sb and Cu dissolution in the acidic thiourea were faster than Au within 1 h as 98%, 91% and 42%, respectively whereas at the same time 12% Au was leached in the solution. However, leaching rate of gold reached to 66% when leaching time was further increased to 6 hours. The results indicated that the leaching time is higher significant effect on the Au leaching with thiourea and is independent for the dissolution of accompanying metals. The leaching time of Au in the thiourea solution was much rapid than that dissolution with cyanide [1-5].

3.1.6. Effect of pulp density

The effect of pulp density was investigated to find a condition with the highest rate of gold leaching from the concentrate in the thiourea solution when keeping the optimum conditions determined in previous experiments. The variation of the pulp density in the study was in the range of 1:2 to 1:20 as shown in Figure 6. It was observed that the lower pulp density (S:L=1:20) lead to enhance the rate of gold dissolution up to 68% in the acidic thiourea solution while at higher pulp density (S:L=1:2) the leaching rate of gold was 7% which due to the availability of the quantities of thiourea.
reactants. The accompanying metals (Ag, Cu and Sb) dissolved with the highest grade in the solution at the pulp density of 1:2 and the variation of the pulp density gave not particularly effect on the dissolution of the Ag and Cu. It was concluded that the pulp density must be fixed at 1:20 for the more effective gold leaching from the concentrate in the thiourea solution.

As a results of the experiments, optimum conditions were found for leaching of gold in nitric acid solution with thiourea and summarized in Table 2.

Table 2. Optimum conditions of gold leaching by nitric acid solution of thiourea

<table>
<thead>
<tr>
<th>Factor</th>
<th>Optimum condition</th>
<th>Leaching rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃ concentration</td>
<td>2 N</td>
<td>79.3</td>
</tr>
<tr>
<td>Oxidant concentration</td>
<td>3 %</td>
<td>71.4</td>
</tr>
<tr>
<td>Thiourea concentration</td>
<td>2 %</td>
<td>67.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>20 ± 1°C</td>
<td>77.3</td>
</tr>
<tr>
<td>Leaching time</td>
<td>6 hs</td>
<td>66.0</td>
</tr>
<tr>
<td>Solid-Liquid ratio</td>
<td>1:20</td>
<td>68.4</td>
</tr>
<tr>
<td>Thiourea leaching</td>
<td>One-stage</td>
<td>41.4</td>
</tr>
<tr>
<td></td>
<td>Two-stage</td>
<td>93.6</td>
</tr>
</tbody>
</table>

The gold flotation concentrate was dissolved in the acidic thiourea solution by a two-stage leaching under the established optimum conditions (Table 2). As a result, about 93.6% of Au from the concentrate was dissolved in the acidic thiourea solution forming strong cationic complex [Au(S=CS(NH₂)₂)]⁺ as shown in Eq.1. The content of accompanying elements (Ag, Cu, Sb, Zn, Pb, As, Te, Se et al) were determined by X-ray fluorescent spectrometer. The accompanying elements of 78.3% K, 57.0% As, 89.5% Mn, 49.3% Cu, 30.0% Pb, 21.4% Zn and 100% Sb, Bi were dissolved in the thiourea solution from the flotation concentrate, whereas some of them like Ni, Cr and Se were insoluble in the solution. It can be seen from our experimental results that the silver dissolves in thiourea solution more easily than gold. It related to the higher amount of silver in the concentrate and is may related to solubility of Au-TU complex [Au(TU)₂]⁺ under acidic condition. Mineev & Panchenko have determined the solubility of metal-thiourea (Me-TU) complexes under acidic conditions and revealed following solubility characteristics [15].

This order suggested that the [Ag(TU)₂]⁺ complex formed has higher solubility in acidic medium than that of [Au(TU)₂]⁺ complex. Therefore, the silver leaching rate is higher than gold in the medium. It also obvious that [Ag(TU)₂]⁺ complex is more soluble than [Cu(TU)₂]²⁺ complex which has a lower leaching rate compared to gold and silver.

The solution obtained from thiourea leaching under optimum conditions is used as a pregnant solution for the recovery of gold using an organosilicon polymer (PSTM-3C).

3.2. Recovery of gold from the pregnant solution by organosilicon polymer (PSTM-3C)

The application of the organosilicon polymer as an ion-exchange sorbent PSTM-3C for the recovery of gold from the pregnant solution has also been described in this paper. The PSTM-3C polymer was synthesized by immobilization of N, N'-bis(3-triethoxysilylpropyl)thiocarbamide on the surface of silica [16]. The sorption property of the sorbent was studied as a function of acid concentration, adsorption time and temperature.

3.2.1. Effect of acidic concentration of the pregnant solution

The optimum concentration of the pregnant thiourea solution in the adsorption was examined using varying concentration of nitric acid from 0.1 N to 3 N. In each experiment, 0.1 g polymer (PSTM-3C) was added to a 100 ml pregnant solution which contains 1.513-1.519 g/L gold. The experiments were carried out at temperature of 20°C, adsorption time of 1 hour and stirred at 500 rpm (see Figure 7).

As shown in Figure 7, the results indicated that the polymer PSTM-3C can be adsorbed up to 99.5% gold from the pregnant solution at 1 N, therefore the optimum acidic concentration of the pregnant solution was established at 1 N for adsorption. It assumed that the complex cation [Au(CS(NH₂)₂)]⁺ formed in the pregnant solution was decomposed in the acidic condition releasing gold cation or aurous thiourea complex created in the solution. The released gold from the complex cation in the solution is adsorbed on the polymer PSTM-3C.

3.2.2. Effect of adsorption time

Gold recovery with variation of adsorption time from 0.5 hour to 2 hour is shown in Figure 8. As shown in Figure 8, the results indicated that the polymer PSTM-3C can be adsorbed up to 99.5% gold from the pregnant solution at 1 N, therefore the optimum adsorption time was established at 1 hour for adsorption.
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3.2.3. Effect of temperature

The rate of gold adsorption on the organosilicon polymer was investigated at the HNO₃ concentration of 1 N and the adsorption time of 1 hour while the temperature ranged from 20°C to 75°C (see Figure 9).

The correlation between gold adsorption rate and temperature shows that 90.6%-95.6% gold can be adsorbed by the polymer PSTM-3C within the temperature range between 20°C-75°C. The maximum adsorption of gold on the polymer is 95.6% at the temperature of 40°C as an optimum temperature. The results indicated that the effect of temperature on gold recovery is not much significant as presented in Figure 9.

According to the selected optimum conditions, experiment on adsorption of gold from the pregnant solution was done in parallel using the organosilicon polymer. The result of this study showed that 93.06%-95.86% gold (94.46% average recovery achieved) can be adsorbed from the pregnant solution on the polymer PSTM-3C under the optimum conditions as shown in Table 3.

### Table 3. Gold recovery from the pregnant solution on the organosilicon polymer PSTM-3C at optimum conditions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Optimum conditions</th>
<th>Recovery, average (Rₑₓₘₖ %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSTM-3C</td>
<td>HNO₃ (N)</td>
<td>Time (h)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

3.3. FT-IR measurement

The difference FT-IR spectrum of both pure and Au adsorbed polymers is shown in Figure 10. Main feature of the IR spectrum are at 800.74 cm⁻¹ (Si-C stretching vibration) and at 1079.8 cm⁻¹ (Si-O-Si stretching vibration). Due to deeper and large width of the Si-O-Si stretching band in the organosilicon polymer PCTM-3C, it is not possible to observe any obvious change of the C-N and C=S stretching and bending vibrations in the FT-IR spectrum.

The peak at 1554.5 cm⁻¹ in IR spectrum of the pure polymer corresponds to N-H bending vibration, however that band disappeared in the IR spectrum of a polymer adsorbed gold. It was also observed from the difference IR spectrum that the weak peaks due to N-H bending vibration at 1620 cm⁻¹, C-H asymmetric stretching at 2930 cm⁻¹ and N-H stretching vibration at 3350 cm⁻¹ in the IR spectrum of the pure polymer were shifted slightly to 1639 cm⁻¹, 2935 cm⁻¹ and 3262 cm⁻¹ in the spectrum of Au-adsorbed polymer, respectively. A new peak appeared at 1703 cm⁻¹ in the spectrum of the Au-adsorbed polymer. It is suggested that this new band respects to the saturation of the polymer by gold.

Thiourea has to be taken care for handling reported as [17], however it acts faster dissolution rate and without a harmful environmental effect than the conventional cyanide leaching. Therefore thiourea is an effective lixiviant of gold in acidic media.

The organosilicon polymer PSTM-3C has a high chemical and thermal stability as well as high adsorption activity of gold that is confirmed by FT-IR spectrum of the gold-adsorbed sorbent in which a new band appeared at 1703 cm⁻¹ attributable to the Au adsorption.

In near future, a process for desorption of gold from Au-loaded organosilicon polymer and the reusability of the polymer will be investigated using acidic thiourea solutions as the eluents.
4. Conclusions

Thiourea leaching and an organosilicon polymer PSTM-3C are used in the process for recovery of gold from its flotation concentrate. It can be concluded that the vast majority of gold (93.6% Au) from the gold flotation concentrate was dissolved in nitric acid solution with thiourea forming strong cationic complex $\text{Au}[\text{S=C(NH}_2]_2]_2^+$ under the optimum conditions. The gold in the concentrate was rapidly leached in the thiourea-iron sulfate system than that of the conventional cyanidation method. It was observed that some accompanying elements such as Se, Te, V, Cr and Ni in the concentrate were insoluble in the acidic thiourea solution.

The result showed that about 94.4% of gold was adsorbed on the organosilicon polymer PSTM-3C from the liquor after the optimization of the experimental conditions. It suggested that released gold from the complex cations into the acidic gold-thiourea solution by decomposition or aurous thiourea complex as $\{\text{Au}[\text{S=C(NH}_2]_2]_2\}^+\text{NO}_3$ formed in the solution is adsorbed on the organosilicon polymer PSTM-3C. The FT-IR analysis revealed the appearance of a new band at 1703 cm$^{-1}$ and the disappearance IR band at 1554.5 cm$^{-1}$ in the IR spectrum of the gold-adsorbed polymer.

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References