Hydrometallurgical recovery of gold from arsenopyrite refractory concentrates

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ABSTRACT

Hydrometallurgical methods for preparation of refractory arsenopyrite concentrates to cyanidation using bacterial leaching and chemical decomposition have been investigated. After cyanide or non-cyanide gold dissolution, the complexes of gold can be selectively recovered on acrylic or styrene anion exchangers.

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1. INTRODUCTION

In 1960-2001, rich gold raw materials were getting scarce, and that entailed the substantial changes in gold production technologies (Lodeyshchikov, 1999). It can be said that during this period the gold mining industry has passed through three following stages:

- Cyanide leaching of gold with subsequent filtration of pulp, followed by electrolytic precipitation of gold from solutions and its smelting with subsequent refining
- Cyanide dissolution and sorption recovery of gold (sorption technology), followed by electrolytic isolation of gold
- Improvement of sorption cyanide leaching of gold (closely grouped, buried, using novel types of ion exchangers) together with treatment of refractory gold-containing ores and concentrates (moving from pyrometallurgical towards hydrometallurgical methods of preparing ores and concentrates to gold recovery by dissolution in cyanide solutions). At the same time, the investigation of gold leaching by non-cyanide reagents from mineral and secondary raw materials, industrial application of these reagents (e.g. thiosulfate closely grouped leaching) is carried out.

Gold in refractory arsenopyrite ores and concentrates of Siberian Region of Russia exists in the form of fine patches mainly in sulfide minerals (pyrite, arsenopyrite) and, to a lesser extent (no more than 5%) in non-sulfide materials (Kuzina et al., 2000). It should be noted that only 23-84% of gold can be recovered from such refractory arsenopyrite concentrates (RAC) without a hydrometallurgical preparation (Lodeyshchikov, 1999; Kuzina et al., 2000; Kholmogorov et al., 2000). The present paper is devoted to the problem of gold recovery by cyanide leaching from RAC containing 13-14% of FeAsS and FeS2 (As – up to 5%, S ~7.6-7.9%, Au – 51-103g/t). The content of organic matter was ~12% in different types of concentrates.

2. RAC PREPARATION METHODS FOR CYANIDE GOLD LEACHING

The composition of concentrate and gold distribution in it were determined by mineralogical, X-ray graphical and thermographical methods. We have found that arsenopyrite and pyrite exist separately in
concentrate and their joints are rare. The organic matter schists are spread in all the mineral part, causing a problem for their selective isolation by physical beneficiation methods. Such distribution of gold and minerals hinders a choice of technological schemes.

The thermographical data of breakdown of sulfide concentrate shows that at the initial stage (up to 150-180°C) water and other volatile compounds (for instance, flotation reagents) are withdrawn. In the range of 450-480°C, the losses in mass of weighed samples are minor, i.e. organic matter compounds are not removed to a considerable extent. At the temperature higher than 480°C, pyrite and arsenopyrite start actively to oxidize, and organic matter schists – to burn out. Therefore, it is ineffective to use thermal processes for selective recovery of carbon from concentrate.

The hydrometallurgical methods of RAC preparation to cyanidation are based on the chemical breakdown of arsenopyrite and pyrite, enabling the access of cyanide reagent to gold (Lodelshchikov, 1999; Kuzina et al., 2000; Kholmogorov et al., 2000; Sokolov et al., 2001).

The bacterial leaching was carried out using ground concentrate (~95% species of this concentrate have 44µm size) at the temperature 28-32°C. The oxidizing culture *Thiobacillus ferroxidans* was used for this purpose. The process time was about 90h at pH 1.7-2.5. Under these conditions, the oxidation degrees ~92-99% and ~70-73% were reached for FeAsS and FeS₂, respectively. A negative factor for bacterial leaching is the formation of jarosite and other arsenites. That leads to decrease in gold recovery during the cyanidation process.

In order to improve the rate of bacterial leaching of the arsenopyrite concentrates, we propose to carry out this process at ~10-15% density of the mechanically activated concentrate (instead of 45-50%) and to implement a depression of reaction ability of carbon by chemical and bacterial means. Moreover, this process should be divided into two stages, where the first stage is the isolation of oxidized part of pulp by flotation method (Kuzina et al., 2000; Kholmogorov et al., 2000).

The chemical preparation of RAC was carried out in aqueous nitric acidic solutions or in HNO₃–Fe(NO₃)₃–H₂O systems (Kuzina et al., 2000; Kholmogorov et al., 2000). The salt composition of pulp during the oxidation of arsenopyrite and pyrite changes in accordance with the following processes:

\[ MS^n \xrightarrow{2\Delta H} M^{n+} + nSO_4^{2-} \]  \hspace{1cm} (1)

\[ MS^n \xrightarrow{90-93°C} M^{n+} + nS^0 \]  \hspace{1cm} (2)

The decrease of process temperature to 70-85°C (instead of 90-93°C) causes the formation of sulfate ions. If the species size of the concentrate used is on a level of 0.044-0.060mm, then the rate of this process will be high. After chemical preparation, pyrite and arsenopyrite are decomposed and removed during pulp filtration. Gold is concentrated in cake, from which it is recovered by cyanidation or by thiosulfate leaching (Kononova et al., 2001; Kholmogorov et al., 2001).

3. CYANIDE AND NON-CYANIDE DISSOLUTION OF GOLD

The cyanide dissolution of gold proceeds according to the following reaction:

\[ 2Au + 4CN^- + 2H_2O \rightarrow 2Au(CN)_2^- + 4H^+ + 2e^- \]  \hspace{1cm} (3)

This process depends on cyanide concentration as well on content of oxygen in solution. The gold dissolution is carried out, as a rule, at cyanide concentration of 6.5x10⁻³mol/l in the presence of NaOH (or KOH) with concentration 0.001-0.005mol/l. During the cyanidation, hydrogen peroxide or calcium peroxide serve as a carrier of the active oxygen (instead of air), especially for closely grouped leaching of gold, where the concentration of cyanide is 0.3-0.8g/l at pH=9.5-11.0.

It is possible to use non-cyanide reagents for the recovery of gold from products of chemical preparation as well as during closely grouped leaching of gold from oxidized mineral raw materials. The comparative kinetic dependencies for gold leaching by cyanide and non-cyanide reagents are given in Table 1, which shows that the recovery degree of gold after leaching of sodium cyanide is 83-91% during 85-97h. The same recovery degree is reached within 2.9-3.3h after gold leaching by thiocarbamide solutions and within 4-5h – by Na₂S₂O₃ solutions. The rate of gold leaching decreases in the following row: (Thio + H₂SO₄) > Na₂S₂O₃ > KSCN >> (NaCN + NaOH).

It should be noted that the change in leaching temperature from 20-22°C to 50-60°C does not lead to appreciable increase in the rate of gold recovery. Moreover, the formation of films from elemental sulfur is possible because of reagent (thiosulfate or thiochyanate) decomposition. Therefore, the thiosulfate solutions are recommended for gold leaching under the industrial conditions. They are also used for the processes of closely grouped leaching (Zipperian and Raghavan, 1988; Zhuchkov and Bubeev, 1990; Lukomsksaya and Piletsky, 1998).

The gold recovery from cyanide and thiosulfate solutions can be carried out by electrolytic precipitation as well as extraction and sorption. The sorption methods using anion exchangers are efficient for the
concentration and complete recovery of gold. Table 2 contains the physico-chemical characteristics of such ion exchangers and Table 3 shows dependence of gold recovery by these sorbents on pH value of Na$_2$S$_2$O$_3$ contacting solution.

Table 1
Dependence of gold leaching from chemically prepared product of RAC

<table>
<thead>
<tr>
<th>Leaching reagent</th>
<th>Time, h</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
<td>3.0</td>
<td>4.0</td>
<td>5.0</td>
<td>20</td>
<td>40</td>
<td>60</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>Thio* (0.5M) + H$_2$SO$_4$ (0.5M)</td>
<td>29</td>
<td>63</td>
<td>82</td>
<td>116</td>
<td>121</td>
<td>129</td>
<td>133</td>
<td>133</td>
<td>133</td>
<td>133</td>
<td>133</td>
<td>133</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3$, pH=6.5</td>
<td>14</td>
<td>39</td>
<td>57</td>
<td>74</td>
<td>109</td>
<td>117</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>126</td>
</tr>
<tr>
<td>KSCN, pH=2.2</td>
<td>7</td>
<td>16</td>
<td>39</td>
<td>52</td>
<td>66</td>
<td>89</td>
<td>97</td>
<td>129</td>
<td>129</td>
<td>129</td>
<td>129</td>
<td>129</td>
</tr>
<tr>
<td>NaCN+NaOH, pH=11.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>10</td>
<td>12</td>
<td>49</td>
<td>67</td>
<td>89</td>
<td>101</td>
<td>114</td>
</tr>
</tbody>
</table>

* Thio – Thiocarbamide

Table 2
Physico-chemical characteristics of anion exchangers investigated

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Trade name</th>
<th>AN-85-10P</th>
<th>AN-106-7P</th>
<th>AP-2-12P</th>
<th>Purolite A-100/2412</th>
<th>AV-17-10P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional groups</td>
<td>–(NH)$_2$(CH$_2$)$_2$</td>
<td>–NH(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$</td>
<td>–$\tilde{N}$(CH$_3$)$_2$CH$_2$</td>
<td>–$\tilde{N}$(CH$_3$),</td>
<td>–$\tilde{N}$(CH$_3$)$_2$</td>
<td>–$\tilde{N}$(CH$_3$)$_3$</td>
</tr>
<tr>
<td>Total exchange capacity to Cl$^-$ (mmol/g)</td>
<td>6.2</td>
<td>8.9</td>
<td>3.7</td>
<td>3.9</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>Exchange capacity for strong basic groups (mmol/g)</td>
<td>–</td>
<td>–</td>
<td>1.1</td>
<td>0.7</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Total pore volume (cm$^3$/g)</td>
<td>0.57</td>
<td>0.69</td>
<td>0.59</td>
<td>1.2</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Specific surface (m$^2$/g)</td>
<td>46</td>
<td>54</td>
<td>37</td>
<td>29</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Exchange capacity for Au during sorption from thiosulfate solutions (pH=6.0) (mg/g)</td>
<td>3.3</td>
<td>3.7</td>
<td>4.2</td>
<td>4.6</td>
<td>4.9</td>
<td></td>
</tr>
</tbody>
</table>

* Ac – acrylic, St – styrene

We have tested the poly-functional anion exchangers Purolite A-100/2412 and AP-2-12P in various ways. The resins exhibited a high selectivity to gold cyanide complexes. In comparison with these sorbents, the interaction between gold cyanide complexes and the functional groups of the strong basic anion exchanger AV-17-10P does not lead to a necessary saturation of this resin with gold from industrial solutions, because together with these complexes, the sorption of CN$^-$ as well as of cyanide complexes of iron, copper and nickel takes place (contents of the latter ions are higher than concentration of gold complexes).
The efficiency of anion exchangers investigated in thiosulfate solutions is high (Table 3). Gold elution is possible by ammonium thiosulfate solutions at pH>10. The experimental data obtained allow us to conclude that hydrometallurgical processes are effective for gold recovery from refractory arsenopyrite concentrates, and technological developments using non-cyanide reagents for gold dissolution are slightly dangerous for environment.

Table 3
Gold recovery on anion exchangers of different structure from thiosulfate solutions

<table>
<thead>
<tr>
<th>Anion exchanger</th>
<th>lg D* at pH of contacting solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11.0</td>
</tr>
<tr>
<td>AV-17-10P</td>
<td>2.3</td>
</tr>
<tr>
<td>Purolite A-100/2412</td>
<td>2.1</td>
</tr>
<tr>
<td>AN-106-7P</td>
<td>–</td>
</tr>
<tr>
<td>AP-2-12P</td>
<td>1.9</td>
</tr>
<tr>
<td>AN-85P</td>
<td>–</td>
</tr>
</tbody>
</table>

\[ D^* = \frac{[Au]}{[Au]_0} \]

where \([Au]\) and \([Au]_0\) are equilibrium gold concentrations in anion exchanger (mmol/g) and in solutions (mmol/ml), respectively.

REFERENCES


Zipperian, D. and Raghavan, S., Gold and silver extraction by ammonical thiosulfate leaching from a rhyolite ore. Hydrometallurgy, 1988, 19, 361-375.