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Assessment of Ammoniacal Ammonium Sulphate Leaching as a Pretreatment Process for Copper Bearing Gold Ores

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ABSTRACT: In the current study, ammoniacal ammonium sulphate leaching (AASL) and pre-aeration as a pretreatment step before the cyanidation of a copper-bearing gold ore was studied. Direct cyanide leaching of the ore resulted in only a ~10% extraction of gold indicating the refractory character of the ore. The ammonia/ammonium sulphate leaching as a pretreatment process was shown to substantially improve the gold extraction (>90%) in subsequent cyanide leaching with a significant reduction in the consumption of cyanide. This could be linked with the ready dissolution/removal of copper in the pretreatment stage by ammonia/ammonium sulphate leaching. The pre-aeration of the ore ahead of cyanidation was also observed to enhance the extraction of gold, albeit, to a limited extent (i.e. from ~10% to ~30%). These findings have demonstrated that ammonia/ammonium sulphate leaching prior to the cyanide leaching can be used suitably for the pretreatment of refractory copper-bearing gold ores.

INTRODUCTION

Cyanide with its peculiarity to form strong complexes with gold is the most effective leaching agent for the extraction of gold from ores. However, cyanide leaching is not particularly selective in that many mineral phases present in the ore may also dissolve under the leaching conditions. To illustrate, most copper minerals are readily soluble in cyanide leaching (Table 1). Dissolution of copper minerals may adversely affect cyanide leaching leading to high consumption of cyanide and poor extraction of gold (Dawson et al, 1997, Alymore and Muir, 2001; Breuer et al, 2005; Muir, 2011; Bas et al., 2012, Kucuk, 2012). Dissolved copper also presents difficulties in downstream processes (Dawson et al, 1997).

Copper-bearing gold ores can consume 30 kg/ton NaCN for every 1% reactive copper present, which may render cyanidation process uneconomic (Muir, 2011). Cyanide consumption can be even higher (e.g. up to 51.5 kg/ton per cent of copper contained) due to the formation of thiocyanate and cyanate in addition to copper cyanide when copper sulphides such as covellite are present (Sceresini, 2005). A copper content of 0.5% Cu is often considered as threshold for cyanide leaching of gold ores (Muir et al., 1991).

Development of alternative processes to cyanide leaching is, therefore, required for the treatment of copper-rich gold ores. In this regard, flotation (Bulatovic, 1998; Forrest et al, 2001), thiosulphate leaching (Bas et al. 2011), leaching of copper ahead of cyanidation (Muir et al, 1991; Dawson et al., 1997; Sceresini, 2005) and cyanide recovery from effluents (e.g. SART process) (Dai et al., 2012) have been proposed for such ores.
Table 1. Solubility of copper minerals (in 0.1% NaCN solutions) (Marsden and House, 2006 after Hedley and Tabachnick (1958))

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>%Cu dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>23°C</td>
</tr>
<tr>
<td>Azurite</td>
<td>2Cu(CO)₃·Cu(OH)₂</td>
<td>94.5</td>
</tr>
<tr>
<td>Malachite</td>
<td>2CuCO₃(OH)₂</td>
<td>90.2</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>Cu₂S</td>
<td>90.2</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>-</td>
</tr>
<tr>
<td>Native copper</td>
<td>Cu</td>
<td>90</td>
</tr>
<tr>
<td>Cuprite</td>
<td>Cu₂O</td>
<td>85.5</td>
</tr>
<tr>
<td>Bornite</td>
<td>FeS₂Cu₂S.CuS</td>
<td>70</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>5.6</td>
</tr>
<tr>
<td>Tetrahedrite</td>
<td>(Cu,Fe,Ag,Zn)₁₂Sb₄S₁₃</td>
<td>21.9</td>
</tr>
</tbody>
</table>

Addition of ammonia as a modifying agent into cyanide solutions has been extensively tested to mitigate copper interferences (Dawson et al., 1997; Sceresini, 2005; Muir, 2011). The role of ammonia is to stabilize Cu²⁺ (1). Otherwise, copper forms strong complexes with cyanide, thus, leading to high consumption of cyanide (2) (Hayes and Corrans, 1992; Breuer et al, 2005; Muir, 2011; Dai et al, 2012). The addition of ammonia allows the selective extraction of gold over copper at a considerably reduced consumption of cyanide (Dawson et al., 1997; Hayes and Corrans, 1992). Muir et al. (1991) showed that the ammoniacal cyanide leaching was an effective system for the treatment of copper containing gold tailings (1.2% Cu, 5 g/ton Au) with a significant decrease in cyanide consumption from 30 kg/ton (in the absence of ammonia) to only 1.6 kg/ton NaCN (and 1.1 kg/ton NH₃ in the presence of 0.3 kg/ton Cu²⁺). They also demonstrated the removal of copper (up to 95%) via ammonia leaching, which also substantially reduced the reagent consumption (down to 6 kg/ton NaCN) in the subsequent cyanide leaching.

$$
Cu^{2+} + 4NH_3 \rightarrow Cu(NH_3)_4^{2+} \quad (1)
$$

$$
Cu^{2+} + 3CN^- \rightarrow Cu(CN)_2^- + 0.5(CN)_2^- \quad (2)
$$

Sulphide ion (S²⁻) that is released from sulphide phases including copper sulphides present in the ore can also lead to the passivation of gold surface in addition to its consumption of cyanide and oxygen (Marsden and House, 2006). Pre-aeration of the ore prior to the cyanidation can be beneficial to mitigate problems associated with sulphide minerals during cyanidation of gold (Kondos et al., 1995; Rajala and Deschenes, 2009). A successful pre-aeration process eliminates a significant proportion of cyanide and oxygen consumers (Rajala and Deschenes, 2009).

In this preliminary study, ammoniacal ammonium sulphate leaching (AASL) as a pretreatment process ahead of cyanidation for the treatment of a copper-rich refractory gold ore was tested. Pre-aeration of the ore prior to cyanidation was also examined. Direct cyanide leaching of gold was tested for comparison.

**MATERIAL AND METHOD**

**Ore Sample**
The ore sample was obtained from sulphide-rich zones of Mandra Gold Mine, located in Gümüşhane, Turkey. The crushed ore sample (down to -4 mm using laboratory jaw and then roll crushers) was ground to 80% passing -75 μm (d₈₀) in a rod mill (Figure 1). The ground ore was riffled and packed as 120 g portions for use in the leaching tests.
The chemical composition of the sample was determined to be 85% SiO₂, 1.1% Cu, 3.1% S, 56 g/ton Au and 10 g/ton Ag (Bas et al, 2012). The XRD analysis of the ore sample indicated the presence of quartz and copper sulphides such as chalcopyrite and covellite (Figure 2). Pyrite, galena and sphalerite were also reported to be detected in the ore (Serbest, 2010; Ozdemir, 2011).

Leaching Tests

Leaching tests were carried out in 1000-ml beakers, which received 480 ml of leach solution and 120 g ore sample (i.e. at 25% wt/vol pulp density) (Kucuk, 2012). Leach solutions were prepared using deionised-distilled water. Cyanide leaching tests were performed at 1.5 g/L NaCN while AASL prior to cyanide leaching was carried out at 0.5 M NH₃/0.5 M (NH₄)₂SO₄. Overhead stirrers were used to agitate the leach pulps at 600 rpm. The beakers were aerated at a flowrate of 2 L per min. The top of the beakers were kept covered during the tests. In the leaching tests, pH was controlled at 10.5-11 by the addition of 1 M NaOH. At predetermined intervals, samples (10 ml) were removed and then centrifuged to obtain clear supernatants for analysis of free cyanide, gold and copper. Free cyanide was determined by titration with silver nitrate using p-dimethylamino-benzal-rhodanine (0.02% w/w in acetone) as the indicator.

Following a leaching period of 24 h, leaching residues were separated by filtration. They were then dried in an oven (at 105°C) and digested in hot aqua-regia for the analysis of metals (gold, silver and copper) using a Perkin Elmer AAnalyst 400 atomic absorption spectrophotometer. Metal extractions in the leaching tests were determined based on the results of residue analysis.
Fig. 3 demonstrates that direct cyanidation of the ore results in poor extraction of gold (i.e. only 4% over 24 h), confirming the earlier findings (Bas et al., 2011; Bas et al., 2012; Ozdemir, 2011). This indicates that the ore is refractory in character. Although the rationale behind the refractoriness of the ore is currently unclear, it is presumed to be associated with the presence of sulphide minerals (copper sulphides in particular) in the ore (Bas et al., 2012). The adverse effect of sulphides on gold extraction could be attributed mainly to the excessive consumption cyanide/oxygen (3), passivating effect of sulphide ion on gold and their pregrobbing characteristics (Sceresini, 2005, Bas et al., 2012; Bas et al., 2012a). Therefore, pre-aeration and ammoniacal ammonium sulphate leaching (AASL) of the ore were tested to improve the extraction of gold.

\[ 2CuS + 8CN^- + \frac{1}{2}O_2 + H_2O \rightarrow 2Cu(CN)_2^{2-} + 2OH^- + 2CNS^- \]  

Pre-aeration of the ore shows an enhancement in the extraction of gold from 4% to 30% (Fig. 3). This improvement could be attributed to the amelioration of the passivation effect of sulphide ion. Previous studies (Lia et al., 2006; Li et al., 2009) have confirmed the benefits of pre-oxidation/aeration on subsequent cyanide leaching of gold ores. Sceresini (2005) also reported that the addition of lead nitrate improved the extraction of gold from a copper bearing sulphide ore presumably due to the alleviation of sulphide effect. However, no enhancement in the gold extraction from the ore sample used in the current study was observed in the presence of 100-1000 g/ton Pb(NO_3)_2 (Bas et al., 2012).

The AASL of the ore was also examined to solubilize copper minerals prior to cyanidation. A significant improvement in the extraction of gold from 4 to 91% was achieved (Fig. 3). This improvement appeared to be consistent with the ready dissolution of copper (54% Cu) in the ammoniacal ammonia leaching stage (Fig. 4). In the ammonia system, the dissolution of copper from oxides/sulphides (5-7) occurs slowly with relatively low copper extractions at low temperatures (Muir et al., 1991). Free ammonia and pH are important parameters controlling the dissolution process and solubility of copper-ammin complexes (Fig. 5) in that high concentrations of free ammonia (>0.45 M) in solution at relatively high pH (i.e. >pH 9.3) should be maintained. In this regard, the test conditions used in the current study was suitable for the dissolution of copper from the ore. Notwithstanding this, further tests are required to optimise dissolution/removal of copper from the ore before cyanide leaching.

\[
\begin{align*}
Cu_SO + 2NH_4^+ + 2NH_3 + \frac{1}{2}O_2 & \rightarrow Cu(NH_3)_4^{2+} + H_2O \\
CuS + 2NH_4^+ + 2NH_3 + \frac{1}{2}O_2 & \rightarrow CuS + Cu(NH_3)_4^{2+} + \frac{1}{2}H_2O \\
CuS + 2NH_4^+ + 2NH_3 + \frac{1}{2}O_2 & \rightarrow Cu(NH_3)_4^{2+} + \frac{1}{2}S_2O_3^{2-} + \frac{1}{2}H_2O
\end{align*}
\]

Figure 3. Effect of pre-aeration (2 L/min) and ammoniacal ammonium sulphate leaching (AASL) (0.5 M NH_3+0.5 M (NH_4)_2SO_4) on the extraction of gold (1.5 g/L NaCN)
**Figure 4.** Dissolution of copper from the ore in preaeration (2 L/min), ammoniacal ammonium sulphate leaching (AASL) (0.5 M NH$_3$+0.5 M (NH$_4$)$_2$SO$_4$) and direct cyanide leaching (1.5 g/L NaCN)

**Figure 5.** pH-dependent stability of copper species in ammonia solution (Medusa, 2004).

**Figure 6.** Effect of ammoniacal ammonium sulphate (0.5 M NH$_3$+0.5 M (NH$_4$)$_2$SO$_4$) leaching pretreatment (AASL) and pre-aeration on the consumption of NaCN (NaCN: 1.5 g/L)

Fig. 6 illustrates the effect of pre-aeration and AASL on the consumption of cyanide. A 16% reduction in the consumption of cyanide after the AASL was recorded (Fig. 6). This was consistent with the earlier studies where more extensive reduction in cyanide consumption (from 30 kg/ton to 2 kg/ton) was reported to occur (Bas et al., 2012; Muir et al., 1991). In contrast, pre-aeration was observed to lead to an increase in cyanide consumption (Fig. 6). This could be attributed to the partial oxidation of sulphides rendering copper readily soluble in cyanide solutions. It should be noted that the solubility of copper (Ksp = [Cu$^{2+}$][OH]$^{-2}$ = 4.8x10$^{-20}$) is limited under the aeration conditions in the absence of cyanide (Fig. 5).
CONCLUSIONS

In this preliminary study, effect of ammoniacal ammonium sulphate leaching (AASL) and pre-aeration on the extraction of gold from a copper-rich ore in subsequent cyanide leaching was demonstrated. Direct cyanide leaching, which yielded poor extraction of gold (4% Au), confirmed the refractory nature of the ore. AASL ahead of cyanidation was found to substantially improve the extraction of gold (from 3.6% to 91.4%) with a concomitant reduction in cyanide consumption, apparently linked with removal of copper present in the ore. Pre-aeration prior to cyanidation was also observed to enhance the extraction of gold though, to a limited extent (i.e. 30%). These findings suggest that AASL and/or pre-aeration ahead of cyanidation could be exploited for the treatment of copper-rich refractory gold ores. Notwithstanding this, further detailed tests are required to develop and evaluate these pretreatment processes.

ACKNOWLEDGEMENT

The authors would like to express their sincere thanks to Assoc. Prof. Dr. I. Alp and Assist. Prof. Dr. O. Celep for their help during the testwork, and Mastra Gold Mine-Koza Gold Operations for kindly providing ore samples.

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