Effects of lead nitrate and pre-aeration on the departure of base/precious metals in cyanide leaching of a pyritic refractory gold concentrate

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Abstract: This study was undertaken to improve gold and silver extraction from a pyritic gold flotation concentrate, which assayed 11 g/t Au, 42 g/t Ag, 0.21% Cu, 3.57% Zn, and 31% Fe. Direct cyanide leaching of the concentrate at 1.5 g/L NaCN yielded a low gold extraction (37%), confirming its refractory nature. Effects of lead nitrate (200-500 g/t Pb(NO₃)₂) and pre-aeration (24 h) before cyanide leaching at 1.5-3.5 g/L NaCN were investigated. Earlier studies have focused on the impact of these parameters on gold leaching. Besides gold, this study demonstrated the behaviour of silver and base metals (copper and zinc) from the pyritic gold concentrate. Adding lead nitrate had a negligible effect on gold extraction whilst improving silver extraction. Dissolution of copper was substantially suppressed by adding lead nitrate, i.e., from 23% (no Pb(NO₃)₂) to 4% (500 g/t Pb(NO₃)₂) over 24 h. Zinc dissolution was negligible (≤0.01%). Pre-aeration of the concentrate improved the gold and silver extractions by 4-14% and 23-44% at the subsequent cyanide leaching (1.5-3.5 g/L NaCN). However, it did not affect the leaching of copper. Only negligible leaching of zinc (≤0.6%) occurred during cyanide leaching. Pre-aeration also reduced cyanide consumption in subsequent cyanide leaching (1.5 g/L NaCN), i.e., from 2.83 kg/t to 2.03 kg/t NaCN per solids. These results suggested that lead nitrate can improve silver extraction while suppressing copper dissolution, which would be advantageous in the adsorption/circuit (CIP), mitigating the dissolved copper-associated problems. Pre-aeration can also be suitable for improved gold/silver extractions and reduced reagent consumption.

Keywords: gold, cyanide leaching, pyrite, copper, refractory ore, lead nitrate

1. Introduction

Cyanidation is the dominant process for the treatment of gold and silver ores. Under atmospheric conditions, aerated, relatively dilute solutions of cyanide are readily used to dissolve gold present in the ore as an aurocyanide complex. The gold in pregnant leach solution can then be recovered by activated carbon adsorption or zinc dust cementation (Marsden and House, 2006). The production of gold from refractory gold ores receives increasing attention due to the rapid diminution of “easy-to-treat”, free milling gold ores, which allow high gold recoveries. Refractory gold ores often have low amenability to cyanide leaching mainly owing to the occlusion of gold in sulphides such as pyrite and arsenopyrite, the loss of dissolved gold from the solution through adsorption/absorption by inorganic/organic matters present in the ore, high consumption of reagents (i.e., cyanide, O₂) by gangue minerals (e.g., copper minerals, sulphides) and low/slow dissolution of gold due to its occurrence as alloys (e.g., AuSb₂, AuTe₂).

In the refractory ores that contain pyrite and arsenopyrite as gold-bearing minerals, the gold is either in a solid solution or completely encased by the sulphide mineral matrix (La Brooy et al., 1994; Roshan, 1990; Celep, 2015). Similarly, the silver-bearing minerals, including proustite, pyrargyrite, tennantite, tetrachloride, etc., also yield low extractions of silver (as low as 5-10%) in traditional cyanide leaching. Refractory gold (and silver) ores often require pretreatment before cyanidation to eliminate the cause...
of refractoriness and, hence, to achieve acceptable levels of gold extractions from refractory ores/concentrates. Chemical, biological, and physical pretreatments have been developed to decompose the gold and silver-bearing sulphides, thus liberating the locked-up gold and silver ahead of the subsequent cyanide leaching (Iglesias and Carranza, 1994; Gunyanga et al., 1999; Corrans and Angove, 1991).

Flotation is commonly used to upgrade oxide (Feng et al., 2022; Feng et al., 2023) and sulphide ores, including gold-bearing sulphide ores, producing a gold concentrate enriched in sulphides (Dunne, 2005). The presence of sulphide minerals could further adversely affect the cyanide leaching of gold and silver. In this regard, sulphide ion, which is released as a result of the dissolution of sulphide minerals (such as pyrite, arsenopyrite, galena, chalcopyrite, etc.) present in gold ores during cyanide leaching, can lead to the passivation of the surface of gold by reducing its reactivity, and to the increase in cyanide consumption through the formation of thiocyanate (Ceple et al., 2010). The lead nitrate addition in cyanidation is known to ameliorate the adverse impact of sulphide ions, enhancing gold recovery and reducing cyanide and oxygen consumption through the passivation of reactive sulphides (Marsden and House, 2006; Ceple et al., 2015). However, the controlled addition of lead nitrate is required since it can also be detrimental to the gold leaching when added in excess. The detrimental effect of lead nitrate is ascribed to the precipitation of lead on gold, passivating it. In cyanide solutions, lead ions react with gold, leading to the formation of AuPb2, AuPb3 and metallic lead, which can improve the gold dissolution rate (Marsden and House, 2006; Deschênes et al., 2000). Sulphide minerals are reported to behave differently in reaction with lead nitrate, which leads to the formation of a hydroxide layer on the surface of pyrite, passivating it towards reaction with pyrite (Deschênes et al., 2000). It is also pertinent to note that the excessive addition of lead ions could retard the extraction of gold (Deschênes et al., 1998; Deschênes et al., 2003). Deschênes et al. (2005) also reported the beneficial effect of lime treatment in conjunction with lead nitrate on the cyanide leaching of gold tellurides. They also noted that the beneficial effect of lead nitrate addition was more apparent when the ore was subjected to ultrafine grinding.

Copper sulphides present in the ore can also lead to the passivation of the gold surface by forming sulphide film in addition to its consumption of cyanide and oxygen (Deschênes et al., 2000; Marsden and House, 2006; Deveci et al., 2018). Pre-aeration of the ore ahead of the cyanidation is known to be useful to reduce the adverse effect of sulphide minerals during the cyanidation of gold (Kondos et al., 1995; Rajala and Deschênes, 2009). A successful pre-aeration treatment eliminates, to a large extent, cyanide and oxygen consumers present (Rajala and Deschênes, 2009; Bas et al., 2012). These previous studies seem to have focused extensively on the cyanide leaching of gold from various sulphide-bearing ores. This study investigated the effects of lead nitrate addition and pre-aeration on the cyanidation of the pyritic refractory gold concentrate containing sulphides, namely pyrite, sphalerite, galena, and chalcopyrite. The impact of these parameters on the leaching behaviour of silver and base metals was also demonstrated in addition to gold.

2. Materials and methods

2.1. Material

The pulp samples (≈60% solids density by weight) of a pyritic refractory gold concentrate were obtained from the ultrafine grinding circuit of Yıldız Bakır Mining Inc. (Gümüşhane, Türkiye). The particle size (d50) of the concentrate was determined to be 28 µm (d50) using Malvern Mastersizer Hydro 2000MU. A known volume of thoroughly mixed pulp sample was taken from the bulk pulp sample, weighed, and the solid ratios were determined. The chemical analysis of the concentrate sample was carried out at the laboratories of Yıldız Bakır Mining Inc. (Table 1). The sample was found to contain 11 g/t Au and 46 g/t Ag. The XRD analysis of the sample was carried out using PANalytical X-Pert3 Powder (Cu Ka 1.54 Å, detector Pixel 1D, 5-140°, 45 kV, and 40 mA). Pyrite, sphalerite, galena, chalcopyrite, quartz, and clay phases were identified from the XRD profile, as presented in Fig. 1.

2.2. Method

Using a multi-stirrer experimental set-up, leaching tests at 60% w/w pulp density and room temperature were performed for 24 h in 1-L glass reactors, which were packed with pitched-blade
Table 1. Chemical analysis of the concentrate samples

<table>
<thead>
<tr>
<th>Metal</th>
<th>Au, (g/t)</th>
<th>Ag, (g/t)</th>
<th>Zn, (%)</th>
<th>Fe, (%)</th>
<th>Cu, (%)</th>
<th>Pb, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>11</td>
<td>46</td>
<td>3.06</td>
<td>31.0</td>
<td>0.18</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 2. Experimental conditions for cyanidation of the flotation concentrate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCN concentration</td>
<td>g/L</td>
<td>1.5</td>
</tr>
<tr>
<td>Pb(NO₃)₂ concentration</td>
<td>g/t</td>
<td>200 and 500</td>
</tr>
<tr>
<td>Solid ratio (weight)</td>
<td>%</td>
<td>60</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Leach time</td>
<td>hour</td>
<td>24</td>
</tr>
<tr>
<td>Stirring speed</td>
<td>rpm</td>
<td>600</td>
</tr>
<tr>
<td>Particle size (d₈₀)</td>
<td>µm</td>
<td>28</td>
</tr>
<tr>
<td>Air flow rate</td>
<td>L/min.</td>
<td>1.5</td>
</tr>
<tr>
<td>pH (lime)</td>
<td>-</td>
<td>10.5-11</td>
</tr>
</tbody>
</table>

Fig. 1. XRD pattern of concentrate sample showing major mineral phases

turbine impellers at 600 rpm (Table 2). The initial concentration of cyanide was fixed at 1.5 g/L NaCN. If required, sodium cyanide was added to maintain the concentration of NaCN at this level over the leaching period. The consumption of cyanide was recorded in each test. Stock solutions of cyanide (5% NaCN) and lead nitrate (5% Pb(NO₃)₂) were used to prepare leach solutions. Distilled and deionized water was used for the preparation of all test solutions. The concentration of free CN⁻ was determined by silver nitrate titration using p-dimethylamino benzal rhodanine (0.02% (w/w) in acetone) as the indicator. Lime was added to control the pH within ~10.5-11. The pre-aeration ahead of cyanide leaching was carried out by bubbling air into the slurry for 24 h. Samples were taken at predetermined intervals over the leaching period and centrifuged at 4100 rpm for 5 min. to prepare clear aliquots for the analysis of metals. The metal content of the residues was determined by AAS after the solid residue was digested in a hot acid mixture (HCl, HNO₃, HClO₄, and HF) in the laboratories of Yıldız Bakır Mining Inc. Metal extractions were calculated based on the analysis of the leaching residues. Samples of solutions and solids were analysed in replicates, and mean values were presented in the results.

3. Results and discussion

3.1. Effect of the addition of lead nitrate

Effects of lead nitrate addition on the extraction of gold, silver, copper, and zinc by cyanide leaching from the flotation concentrate are illustrated in Figs. 2-3. The direct cyanide leaching of the concentrate resulted consistently in low extraction of Au (37%) and Ag (20%), confirming the refractory nature of the concentrate. The findings have shown that the addition of lead nitrate (200-500 g/t) has a very
limited (adverse) effect on gold extraction (31-36%) (Fig. 2). On the other hand, lead nitrate appeared to enhance the extraction of silver to some extent (Fig. 2). The addition of Pb(NO₃)₂ was found to reduce the release of copper (from 24% to 3%) from the concentrate (Fig. 3). These findings show the beneficial effect of Pb(NO₃)₂ addition for controlling and suppressing copper dissolution, which can have a detrimental impact on the leaching and adsorption circuits. The leaching of zinc was negligible (≤0.01%), with no discernible effect of lead nitrate addition (Fig. 3). Contrary to expectations, cyanide consumption tended to increase with the addition or increasing the level of lead nitrate (Fig. 4).

In a previous study, Celep et al. (2015) reported no significant impact of Pb(NO₃)₂ on the extraction of silver in the cyanide leaching of plant tailings of refractory silver ore. On the other hand, Deschênes et al. (2011) reported the beneficial effect of lead nitrate (0–350 g/t) on the cyanide leaching of gold/silver. Celep et al. (2010) reported a 10% increase in the cyanide leaching of gold from an antimonial refractory ore with the addition of up to 100 g/t. However, these researchers did not observe any effect of lead nitrate addition in the extraction of silver. Sceresini (2005) also showed that the addition of lead nitrate improved the extraction of gold from copper-bearing sulphide ore, presumably due to the alleviation of the adverse effect of sulphides. In the other study, Bas et al. (2012) observed an obvious reduction in the extraction of gold from copper-bearing gold ore in the presence of 100-500 g/t Pb(NO₃)₂.

**3.2. Effect of the pre-aeration**

The pre-aeration of the leach slurry was undertaken to passivate the surface of sulphide minerals present in the concentrate mitigating their potential negative effects on the cyanide leaching process. The results demonstrated that the pre-aeration treatment had a positive influence on the leaching process. A limited
increase in the gold extraction (by 4%) was observed in cyanide leaching (1.5 g/L NaCN) after 24 hours of pre-aeration compared to direct leaching. In the pre-aerated test, 41% of the gold dissolved at 1.5 g/L NaCN (Fig. 5). The gold extraction from the pre-aerated concentrate improved to 51% with increasing the cyanide concentration (3.5 g/L NaCN). Similarly, the pre-aeration treatment also positively affected the leaching of silver. At 1.5 g/L and 3.5 g/L NaCN, the extraction of silver increased from 20% to 43% and 64%, respectively (Fig. 5). On the other hand, the pre-aeration treatment did not have an appreciable effect on the dissolution of copper (Fig. 6). In addition, it was determined that zinc dissolved at a negligible level (≤0.6%) in all tests (Fig. 6). It is pertinent to note that the cyanide consumption decreased from 2.83 kg/t to 2.03 kg/t (by 28%) at 1.5 g/L NaCN, apparently due to the influence of the pre-aeration treatment (Fig. 7).

Bas et al. (2012) reported the positive influence of the pre-aeration ahead of cyanidation on the extraction of gold from copper-bearing gold ore, albeit to a limited extent (i.e. from ~10% to ~30%). This improvement in gold extraction could be linked to the mitigation of the passivation effect of sulphide ions. 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.

4. Conclusions

This study shows the effect of lead nitrate addition during cyanidation and the pre-aeration as a pretreatment prior to cyanide leaching of a pyritic refractory gold concentrate. In direct cyanidation, the extraction of precious metals is limited to 37% Au and 20% Ag, confirming that the concentrate is highly refractory in nature. Sulphur species released from sulphides can react with sodium cyanide and/or...
lead to the passivation of gold and silver surfaces during the leaching of the sulphide ores/concentrate. This could also contribute to the low extent of leaching of gold and silver. The addition of lead nitrate

![Graph](image1)

**Fig. 6.** Leach time versus the effect of pre-aeration (24 hours) on copper (left) and zinc (right) recoveries (pH 10.5-11; air flow rate of 1.5 L/min.)

![Graph](image2)

**Fig. 7.** Effect of pre-aeration (24 hours) on cyanide consumption

(200-500 g/t) was found to have no significant effect on the gold extraction. Notwithstanding this, it improved silver extraction but suppressed copper dissolution. The latter is important to control the undesired impact of soluble copper on the leaching and adsorption processes.

The pre-aeration treatment of the concentrate was shown to have a beneficial effect on the cyanide leaching. It enhanced the gold extraction to 51% at a high cyanide concentration tested (3.5 g/L NaCN). Similarly, silver extraction also reached 64% at 3.5 g/L NaCN. Furthermore, the improved extraction of gold and silver was accompanied by a significant reduction in cyanide consumption by ~28% (at 1.5 g/L NaCN). These findings could be attributed to the passivation of sulphides and the reduction of the deleterious effect of sulphide ions.

It can be inferred from this study that the addition of lead nitrate and pre-aeration can be used to improve the cyanide leaching of the refractory gold/silver ore with the enhanced extraction of precious metals and the reduction of copper release and cyanide consumption.

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**References**


