Precious metals have traditionally been recovered from ores by leaching with an alkaline cyanide solution. While widely practiced on a commercial scale, cyanide leaching suffers from several well-known disadvantages: low leaching rates (contact times of 24-72 hr. are common for gold ores); the high toxicity of cyanide; and severe environmental restrictions. Process purge streams must be carefully monitored and controlled, and spent cyanide leaching solutions must be treated before being discharged to the environment.

Extraction of gold and silver from two refractory concentrates using cyanide and bromine reagents was reported at the 12th International Precious Metal Conference. Other processes have been developed for the use of halogens, halides or other halogen-bearing compounds for the extraction and recovery of precious metals from ores. This article compares the extraction, recovery and economics of gold from two refractory concentrates using sodium cyanide and a new proprietary liquid bromine carrier (Geobrom™ 3400).

### THERMODYNAMIC DATA

Dissolution of metals or minerals in an aqueous solution is determined by considering the free energies involved for the particular reactions. Therefore, thermodynamic data may be used to predict the general conditions likely to be favored in the dissolution processes. These thermodynamic data are best presented in the form of stability, or oxidation-potential/pH (Eh/pH), diagrams. The concept of stability diagrams based on chemical thermodynamics has been set forth by many investigators. Most of the data necessary to calculate the free energy of a given reaction are available in the published compilations.

Eh/pH diagrams for zinc and copper in water indicate that in acidic conditions (i.e., pH < 6) both Zn²⁺ and Cu²⁺ are thermodynamically stable. Gold, on the other hand, is more noble than zinc and copper. The standard electrode potential for gold is more positive even than that of the decomposition of water, as given by

\[
\text{Au} = \text{Au}^{3+} + 3e^- \\
2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4e^- \\
\text{H}_2 = 2\text{H}^+ + 2e^- \\
\]

Therefore, gold is highly stable in an aqueous solution, as shown in Figure 1 by its Eh/pH diagram. However, gold can form stable complexes with different ligands in aqueous solution. As a result of complexation, considerable modification takes place in the Eh/pH diagram of the Au-H₂O system. The complexation of gold with cyanide, thiourea, chloride and bromide is used to expand the domain of dissolution of gold compared to that given in Figure 1. The standard electrode potential for the complexation of gold with cyanide is given by

\[
\text{Au} + 2\text{CN}^- = \text{Au(CN)}_2^- + e^- \\
E^o = -0.60 \text{ V} 
\]

The electrode potential of Reaction 4 is much smaller than the value of 1.50 V.


**EXPERIMENTAL PROCEDURES**

The use of bromine as a leachant for gold ores is reported in the literature as far back as 1882. To overcome the problems of handling and use (high vapor pressure and corrosion) inherent with liquid bromine, a liquid bromine carrier of considerably lower vapor pressure than liquid bromine has been developed. To demonstrate the effectiveness of this bromine carrier as a leaching reagent for gold, leaching tests have been performed using two refractory concentrates. Due to the high concentrations of carbon (10–13%) and sulfur (12–15%) in these concentrates, it was necessary to pretreat them prior to leaching. Pressure oxidation and roasting, among other methods, are commonly used to oxidize carbon and sulfur in carbonaceous and refractory ores before the actual leaching. The concentrates were roasted to compare bromine leaching with the standard cyanidation.

The cyanide and bromine leaching tests were performed on two samples of Canadian flotation concentrate. Each sample was dewatered and dried in an oven at 110°C. To make the concentrates amenable to both cyanide and bromine leaching, they were roasted at temperatures of 650–750°C. Samples of concentrates and calcines used for head assay or gold leaching were 47–80 mesh.

**Cyanidation**

The bottle-roll-leach technique and agitation of the slurry were used for cyanide and bromine leaching tests. Most of the calcine samples were leached with hot water prior to the cyanide leach. The hot water leach removed most of the soluble compounds, mainly magnesium and sulfate, from the calcine, hence reducing the high lime consumption. During the standard cyanidation leach (24–48 hr), sodium cyanide and lime were added to maintain the desired cyanide and pH levels. In kinetic tests, intermediate gold extractions were obtained by analyzing samples taken from the bottle over time. Fresh water was added to the leach bottle to compensate for solution lost due to sampling. At the end of the test, the leach slurry was filtered. The filter cake was washed with a volume of water equal to twice the solids weight for 10 minutes. The repulped slurry was filtered, and the cake was washed with a volume of water equal to the solids weight. Samples of the filtrate, the wash, and the residue were analyzed for gold.

**Bromine Leaching**

Exploratory bromine leach tests indicated that prewashing the calcine would not affect the bromine leach results; therefore, hot water calcine preleaching was not necessary. Other test procedures for bromine leaching were similar to the cyanide leaching; the exception was reagent concentration. The bromine reagent was added at the beginning of the test, and the bromine leaching tests were performed on samples of concentrates and calcines in 47–80 mesh.

**CYANIDATION TESTS**

Exploratory tests were conducted on Calcine I to investigate the recovery of gold by cyanidation. In all tests except Test 2, the calcine was preleached at 80°C for 1 hr. with water. It was then filtered and repulped in a cyanide solution. The tests were performed in bottles on rolls for 48 hr. Table II summarizes the results. The high pH in Tests 1 and 2 resulted in lower gold recoveries. Reducing the cyanide concentration from 1.0 to 0.5 g/l NaCN reduced the extraction of gold from 24.5 to 22.3 g/t (Table II).

![Eh/pH diagram for the Au-CI-H2O system at 25°C; [Au] = [Cl-] = 10^-3 M.](image1.png)

![Eh/pH diagram for the Au-CN-H2O system at 25°C; [Au] = [CN-] = 10^-3 M.](image2.png)

Given for the Reaction 1. Also, the potential of Reaction 4 is sufficiently lower than the value of 1.23 V for the H2O/O2 couple, so that water decomposition acts as the cathodic process for gold dissolution. The Eh/pH diagram for the Au-CN-H2O system is presented in Figure 2. Notice that for gold in the presence of cyanide, the solubility window for the complex ion Au(CN)3^- is expanded in both the acidic and basic regions. Because of the high pK value of 9.36 for HCN and its poisonous nature, cyanidation is generally carried out between pH 10.5 and 12.0.

Eh/pH diagrams for the system Au-CN-H2O are presented in Figures 3 and 4. In all tests except Test 2, the calcine was preleached at 80°C for 1 hr. with water. It was then filtered and repulped in a cyanide solution. The tests were performed in bottles on rolls for 48 hr. Table II summarizes the results. The high pH in Tests 1 and 2 resulted in lower gold recoveries. Reducing the cyanide concentration from 1.0 to 0.5 g/l NaCN reduced the extraction of gold from 24.5 to 22.3 g/t (Table II).

**Table I. Head Assay for Concentrates and Calcines**

<table>
<thead>
<tr>
<th>Material</th>
<th>Gold (g/tonne)</th>
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<tbody>
<tr>
<td>Concentrate I</td>
<td>242</td>
</tr>
<tr>
<td>Calcine I</td>
<td>268</td>
</tr>
<tr>
<td>Concentrate II</td>
<td>419</td>
</tr>
<tr>
<td>Calcine II</td>
<td>541</td>
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</table>

**Table II. Calcine I Exploratory Cyanidation Results**

<table>
<thead>
<tr>
<th>Test</th>
<th>pH</th>
<th>NaCN (g/l)</th>
<th>Au Extraction (%)</th>
<th>Au in Residue (g/tonne)</th>
<th>Au Head* (g/tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.9</td>
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<td>9.7</td>
<td>278.0</td>
<td>295</td>
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<td>24.5</td>
<td>253.0</td>
<td>295</td>
</tr>
<tr>
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<td>1.0</td>
<td>95.1</td>
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<td>81.4</td>
<td>62.3</td>
<td>335</td>
</tr>
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</table>

* Calculated.
† No hot water preleach.