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 Zn and Cu 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

\[
\begin{align*}
\text{Au} = & \text{Au}^{3+} + 3e^- & E^0 = 1.50 \text{ V} \\
2\text{H}_2\text{O} = & 2\text{H}_2 + 4\text{H}^+ + 4e^- & E^0 = 1.23 \text{ V} \\
\text{H}_2 = & 2\text{H}^+ + 2e^- & E^0 = 0 \text{ V}
\end{align*}
\]

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

\[
\text{Au} + 2\text{CN}^- = \text{Au(CN)}_2^- + e^- & E^0 = -0.60 \text{ V}
\]

The electrode potential of Reaction 4 is much smaller than the value of 1.50 V.
The use of bromine as a leaching agent for gold from ores has been 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 cyanides and bromine leaching tests were performed on two samples of Canadian flotation concentrates. Each sample was dewatered and dried in an oven at 110°C. To make the concentrate 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 of -150 to -200 mesh.

Cyanidation

The bottle-roll-leach technique and agitation of the slurry were used for cyanide and bromine leaching tests. Most of the calcines 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. Head assays of the filtrate, the cake and the concentrate 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 repulped in a volume of water equal to twice the solids weight for ten 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

Explanatory 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 addition. The bromine reagent was added to the leach slurry at the beginning of the test. The pH and oxidation-reduction potential of the solution were monitored during the leach, but no adjustment was made. To establish gold extraction vs. time, complete leach tests were performed at 2, 4, 6, 12, 18 and 24 hr. Head assays of the concentrate and calcines are presented in Table I.

| Table I. Head Assay for Concentrates and Calcines |
|-----------------|----------|
| Material        | Gold (g/tonne) |
| Concentrate I   | 242       |
| Calcine I       | 248       |
| Concentrate II  | 419       |
| Calcine II      | 541       |

Figure 3. The Eh/pH diagram for the Au-Cl-H₂O system at 25°C; [Au] = [Cl⁻] = 10⁻³ M.

Figure 4. The Eh/pH diagram for the Au-Cl-H₂O system at 25°C; [Au] = 10⁻⁶ M, [Cl⁻] = 1.0 M.

given for the Reaction 1. Also, the potential of Reaction 4 is sufficiently lower than the value of 1.23 V for the H₂O₂/H₂O 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-Cl-H₂O are presented in Figures 3 and 4. In Figure 3, Au shows a very small AuCl₃ stability field under even highly oxidizing and acidic conditions. However, the stability field is somewhat expanded, as shown in Figure 4 by increasing the concentration of chloride ions.

The dissolution of gold in a bromide solution is an electrochemical process, as described by Reaction 5.

\[ Au + 4Br⁻ = AuBr₄⁻ + 3e⁻ \]  \[ E^\circ = 0.87 \text{ V} \]  \( (5) \)

Considering the decomposition of water as given in Reaction 2, the dissolution of gold in a bromide solution will be affected by many factors such as bromide and gold concentrations, pH and the electrochemical potentials of anodic and cathodic processes. Although no Eh/pH diagram appears to have been published for the Au-Br-H₂O system, consideration of Figures 1–4 and comparison of the standard electrode potentials for the Au-Br-H₂O system with the corresponding values for the Au-CI-H₂O and Au-CN-H₂O systems, should clearly indicate that the complex ion AuBr₃ must be stable at an Eh value of about 1.0 V with its stability window expanded to pH 7.

Eh/pH diagrams for the Au-Br-H₂O system at 25°C were constructed for [Au] = 10⁻³ M and varying concentrations of bromide and are presented in Figure 5. Also, the stability regions for water according to Reactions 2 and 3 are drawn in Figure 5 by the upper and lower dashed lines, respectively. At a concentration of [Au] = 10⁻³ M, varying the concentration of [Br⁻] from 10⁻⁵ to 1.0 M, the AuBr stability region is expanded as Eh values for Reaction 5 are lowered from 1.20 to 1.0 V. Also, the equilibrium for the AuBr₃/Au(OH)₃ couple moves up from pH 4 to pH 11.

From the Eh/pH diagrams for the Au-Br-H₂O system as presented here, it is possible to write the following reaction for the dissolution of gold in a Geobrom 3400 solution:

\[ 2Au + 3HOBr + 5Br⁻ + 3H⁺ = 2AuBr₃ + 3H₂O \]  \( (6) \)

According to Reaction 6, gold is first oxidized to Au³⁺ by HOBr, then stabilized by the AuBr₃ 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.

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According to Reaction 6, gold is first oxidized to Au³⁺ by HOBr, then stabilized by the AuBr₃ complex ion with bromide. The best experimental conditions are: room temperature, pH 4–6, and an oxidation-reduction potential of 0.7–0.9 V (measured with a platinum/calomel combination electrode).

**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/NaCN reduced the extraction of gold from 242 to 158 g/tonne, with a recovery of 93.5% from 95.5%.

**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>
<td>1.0</td>
<td>5.7</td>
<td>278.0</td>
<td>295</td>
</tr>
<tr>
<td>2</td>
<td>11.9</td>
<td>1.0</td>
<td>24.5</td>
<td>293.0</td>
<td>295</td>
</tr>
<tr>
<td>3</td>
<td>11.0</td>
<td>1.0</td>
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<td>16.5</td>
<td>335</td>
</tr>
<tr>
<td>4</td>
<td>10.6</td>
<td>0.5</td>
<td>81.4</td>
<td>62.3</td>
<td>335</td>
</tr>
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</table>

*Calculated.
†No hot water preleach.