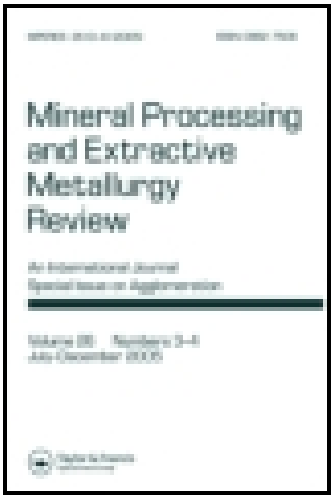

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Dissolution Chemistry of Gold and Silver in Different Lixiviants

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Cyanide has been recognized for a long time as a powerful lixiviant for gold and silver, forming very stable cyano complexes with both metals. While cyanide is very effective in leaching free milling ores, there are certain classes of gold and silver ores (i.e., carbonaceous, pyritic, arsenical, manganiferous, cuperferous) that are considered refractory to conventional cyanidation dissolution. Recently there has been considerable effort directed towards new and improved reagents for leaching these difficult-to-treat ores and concentrates. A large portion of this effort has been devoted to finding alternative lixiviants that might compete with conventional cyanidation. Furthermore, there is a general interest in developing non-toxic environmentally safe substitutes for cyanide.

There are a number of reagents that form stable complexes with gold and silver e.g., thiourea, thiosulfate, halides, malononitrile, acetonitrile and polysulfides. The chemistry of gold and silver dissolution using alternative lixiviants is discussed in this paper. Special emphasis is given to the application of Eh-pH diagrams to interpret the dissolution behavior.

INTRODUCTION

Cyanidation of gold and silver is celebrating its centennial anniversary. The pioneering research of MacArthur and the Forrest brothers and their patents of 1887 and 1889 revolutionized the extractive metallurgy of gold[1,2]. The impact of the Cyanide Process is dramatically illustrated when one compares world gold production for the period 1851–1900 which equalled 9,870 mt to that for the period 1901–1950 which was 34,172 mt (excludes gold production in the USSR after 1928)[3]. The tremendous increase in gold output for

the 1901–1950 period was related directly to the commercial success of the Cyanide Process. This process incorporated two important features. First, it took advantage of the fact that dilute cyanide solutions have a selective dissolution action on gold. Stronger lixiviants like those used in chlorination have a tendency to dissolve numerous impurities. Second, the cyanide process included a convenient method for recovering gold from cyanide solution, i.e., by precipitation with zinc shavings.

The solvent action of potassium cyanide on gold was recognized as early as 1793 by Scheel[4]. However, Agricola[5] in his "De Re Metallica" (1556) indicates that the use of aqua regia to dissolve gold was known centuries before. The Plattner process (1851) was an early hydrometallurgical approach using dissolved chlorine to extract gold from oxidized ores[6].

In recent years with the resurgence in precious metal activity there has been considerable interest in developing lixiviants other than cyanide for gold and silver leaching. Although cyanide leaching remains the overwhelming option for treating gold and silver ores because of its economy and process simplicity, cyanide solutions are still toxic and must be handled carefully to avoid damaging the environment. Furthermore, cyanide it not very effective in treating refractory gold and silver ores and concentrates. Other lixiviants have been examined mainly in an attempt to overcome these problems. Some of the lixiviants that have been recently investigated for the leaching of precious metals are presented in Table I.

As stated above chloride leaching has been applied to precious metal processing for many years. Chloride hydrometallurgy especially the treatment of complex metal sulfide ores and concentrates has been a major area of research during the last few years[7]. In the future, some treatment options for sulfidic gold ores and concentrates will likely involve chloride chemistry. A chlorination process

TABLE I
Alternative lixiviants for the leaching of gold and silver

Lixiviant	Complexing ligand	Oxidants
Thiourea	$CS(NH_2)_2$	Fe^{3+}, O_2, H_2O_2
Thiosulfate	$S_2O_3^{2-}$	O_2, H_2O_2, ClO_3^-
Iodine	I^-	I_2/I_3^-
Malononitrile	$CH(CN)_2^-$	O_2

was developed in the early 1970's[8,9,10] to treat carbonaceous gold ores prior to cyanidation. Alkaline chlorination pretreatment of refractory carbonaceous gold ores accomplished several important results:

1) it eliminated the preg robbing behavior of the carbonaceous matter;
2) it released gold which is chemically combined with the carbonaceous matter;
3) it decomposed associated sulfides which may contain finely dispersed gold which might not be contacted otherwise during cyanidation.

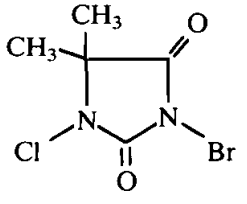
Brunk and Atwood[11] recently reported that during the chlorination of a carbonaceous gold ore as much as 85% of the gold goes into solution. They proposed a "flash chlorination" approach whereby the chlorination chemistry is optimized to achieve maximum gold extraction during this step. Other examples of acid brine leaching have also been reported[12].

Other halogens are gaining attention as lixiviants for the processing of gold and silver ores and concentrates[13,14,15]. One example is the research of McGrew and Murphy[13]. They developed a process involving the iodine dissolution of gold. The process is based on having iodine-reducing species present with the ore (e.g., base metal sulfides) to yield sufficient iodide (I^-). Increasing the I^- concentration greatly increases the overall solubility of I_2 by formation of the tri-iodide complex I_3^-. Gold dissolution occurs according to the following reactions

$$2Au + I^- + I_3^- \rightarrow 2AuI_2^- \quad (1)$$

$$2Au + 3I_3^- \rightarrow 2AuI_4^- + I^- \quad (2)$$

A novel lixiviant for gold is 3-bromo-1-chloro-5, 5-dimethylhydantoin which has the structure



The unique feature of this reagent is its ability to provide complexing ligands and oxidizing power to the system[15].

Thiourea has probably received the most attention as an alternative lixiviant for gold and silver. The strong interest in thiourea is attributed to the extremely fast kinetics associated with acid thiourea leaching of gold and silver. Figure 1 shows a comparison between thiourea and cyanide for dissolution of a rotating gold disk[16]. The rate for the thiourea system is approximately an order of magnitude greater than cyanide.

As early as 1941, Plaskin and Kozhukhova[17] discussed thiourea

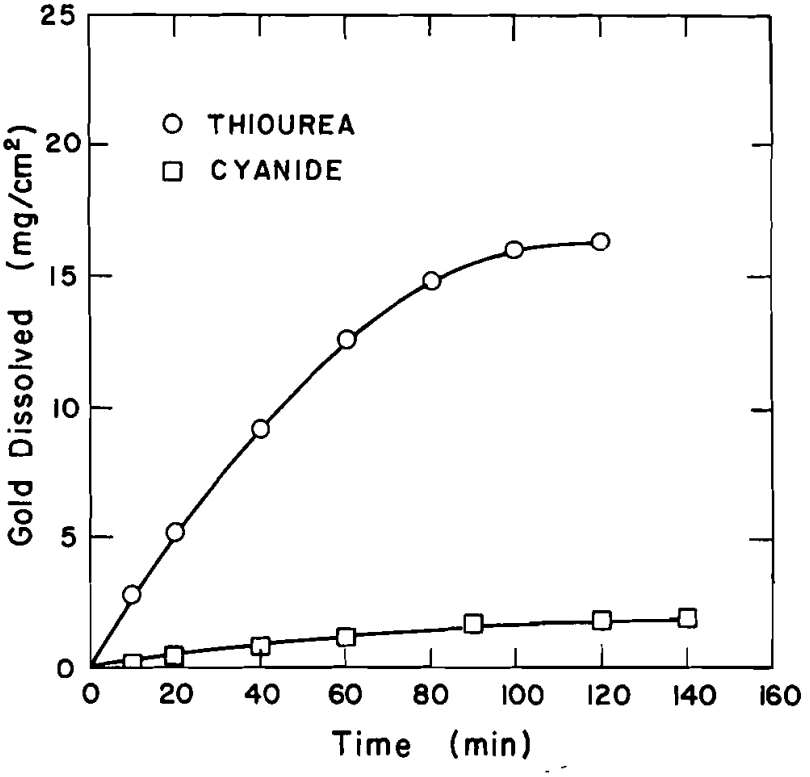


FIGURE 1 Comparison of gold dissolution using acidic thiourea and cyanide solutions. The thiourea system contained 10 g/l $CS(NH_2)_2$, 5 g/l H_2SO_4, and 1 g/l Fe^{3+} and the cyanide system contained 5 g/l NaCN and 0.5 g/l CaO. (After Chen *et al.*[61]).

leaching of gold and silver. Recently, Groenewald[18] and Hiskey[19] reviewed the process chemistry of leaching gold with thiourea solutions. Pyper and Hendrix[20] reported on the leaching of a finely disseminated gold ore using thiourea solutions and Wen[21] discussed the prospects of using thiourea to extract gold from a carbon bearing clayey ore. Bilston and co-workers[22] studied the leaching of an oxidized gold ore with thiourea under controlled conditions. In general, thiourea leaching, besides employing reagents of lower toxicity than cyanide, has the additional advantage of faster gold and silver dissolution kinetics[16,23]. However, high thiourea consumption and problems with passive surface coatings resulted in low leaching efficiencies in many instances. Schulze[24,25] described a procedure that effectively reduces the decomposition of thiourea and avoids the passivation of the feed material. The procedure involves adding SO_2 to the leaching solution thereby controlling the redox couple between thiourea and formamidine disulfide.

A new thiourea leaching process uses a lixiviant containing thiourea, urea and an alkaline lignin sulfonate[26]. The typical solution composition was 2.2 g/l $CS(NH_2)_2$, 2.2 g/l $CO(NH_2)_2$, 3.3 g/l $Fe_2(SO_4)_3$, and 1.1 g/l K-lignin sulfonate. Sulfuric acid was used to adjust the pH to 1.0–1.5. Excellent leaching results have been obtained using this system on a variety of feed materials.

Gold extraction from refractory ores has been the subject of several investigations[27,28,29,30]. Yen and Wyslouzil[27] investigated the dissolution of gold contained in leach residues produced by the pressure oxidation of sulfidic flotation concentrates. Thiourea leaching of the residue yielded gold extractions equivalent to cyandiation in much less time and without an intermediate neutralization step. Moussoulos and others[28] applied thiourea to the extraction of gold and silver from arsenical pyrite concentrate. After roasting, the material was leached with sulfuric acid to remove arsenic, and the leach residue was then leached with thiourea to extract the precious metals. The direct thiourea leaching of a gold bearing pyrite concentrate was investigated by Gabra[29]. A hydrometallurgical process to recover gold and silver from a complex lead-zinc sulfide ore was recently developed by Sandberg and Huiatt at the U.S. Bureau of Mines[30]. Their approach involved thiourea leaching to extract gold and silver from a lead chloride residue containing silver chloride and gold.

An example of a commercial operation using thiourea to recover gold is that of the New England Antimony Mines in Hillgrove, New South Wales[31]. Acid ferric sulfate solutions containing thiourea are used to leach gold from an antimony flotation concentrate assaying 30–40 g/t gold. The dissolution of gold is reported to require less than 15 minutes. The first large scale domestic gold leaching operation to consider thiourea as a lixiviant was the Jamestown project of Sonora Gold Corp[32].

Most of the process development work involving thiourea has focused on the leaching step with only limited work going towards the recovery of gold and silver from thiourea solutions. Deschenes[33] made a comprehensive literature review on the recovery of gold from thiourea solutions and offered a comparison with recovery from alkaline cyanide.

The dissolution of gold and silver with thiosulfate has been recognized for over a 100 years. The solubility of gold and silver in thiosulfate depends on the stability of the representative complex anions $Au(S_2O_3)_2^{3-}$ and $Ag(S_2O_3)_2^{3-}$. A process employing ammonium thiosulfate to recover precious metals from copper bearing metal sulfide concentrates and pressure leach residues was recently developed by Berezowsky *et al.*[34,35]. An important observation of this work is the role of $Cu(NH_3)_4^{2+}$ in promoting the dissolution of gold and silver. It was further recognized that thiosulfate decomposition resulted in the precipitation of copper sulfide which coated gold particles and resulted in an attendant reduction in gold recovery. They compensated for this by using short reaction times. Tozawa, Inui and Umetsu[36] examined the leaching of gold from complex sulfide ores and flotation concentrates using ammoniacal thiosulfate solutions. Enhanced gold recovery was achieved at those conditions which minimized the oxidative degradation of thiosulfate. Kerley[37] improved the stability of the thiosulfate radical by maintaining an alkaline pH and by dilute additions of sulfite ions to the leach liquor. A further improvement of the Kerley patent was made by Perez and Galaviz[38] in which a minimum pH of 9.5 was recommended for the copper-ammonium thiosulfate system.

Numerous other lixiviants for gold and silver have been discussed and/or evaluated in recent years. Heinen and co-workers[39] investigated the use of malononitrile for the extraction of gold from ores. It was shown that malononitrile, $CH_2(CN)_2$, is an effective extractant

under alkaline conditions. Scheiner and Lindstrom[40] proposed the use of malononitrile at concentrations ranging from about .5 to 2.5 g/l and a pH of about 10 to 12 to leach a carbonaceous gold ore. The malononitrile-gold complex was adsorbed on an anion exchange resin having combined weak-base strong-base functional groups. Gold was then eluted from the resin by using a mineral acid like sulfuric acid. Parker[41] has examined in detail the acetonitrile-water system including the solvation chemistry of gold and silver. The thermodynamics of the transfer of $Au(CN)_2^-$ and $Ag(CN)_2^-$ from aqueous solution to mixtures of acetonitrile-water have been reported[42]. Carpenter and Hedley[43] used α-hydroxynitriles to extract precious metals from their ores. The α-hydroxynitriles do not complex gold and silver directly but furnish free cyanide ions by hydrolysis. Schulze[44] investigated the use of N,N′-ethylenethiourea in the extraction of precious metals. Acidic solutions containing 0.1 to 20 g/l N,N′-ethylenethiourea and oxidants like air, nitrate, hydrogen peroxide, and ferric ion were found effective in dissolving precious metals. Finally, it has been reported that polysulfides are capable of dissolving gold under certain conditions[45].

In the present paper we will review the dissolution chemistry of gold and silver in the presence of various lixiviants. Our discussion, when considered appropriate, will utilize Eh-pH stability diagrams to make direct comparisons between the different systems.

CHEMISTRY OF GOLD AND SILVER CYANIDATION

The dissolution of solid metallic materials like gold and silver is best described in terms of an electrochemical model which involves separate anodic and cathodic reactions. Figure 2 shows a schematic of the electrochemical microcell for the process. A mixed potential is developed between the internally short circuited cathodic and anodic sites. The mixed potential establishes the leaching rate. For gold dissolution the anodic step involves oxidation and complexation of the metal according to the following general reaction

$$Au + 2X \rightarrow AuX_2^+ + e \qquad (3)$$

where X is the complexing ligand. This shows Au(I) having a preference to form a linear complex with coordination number two.

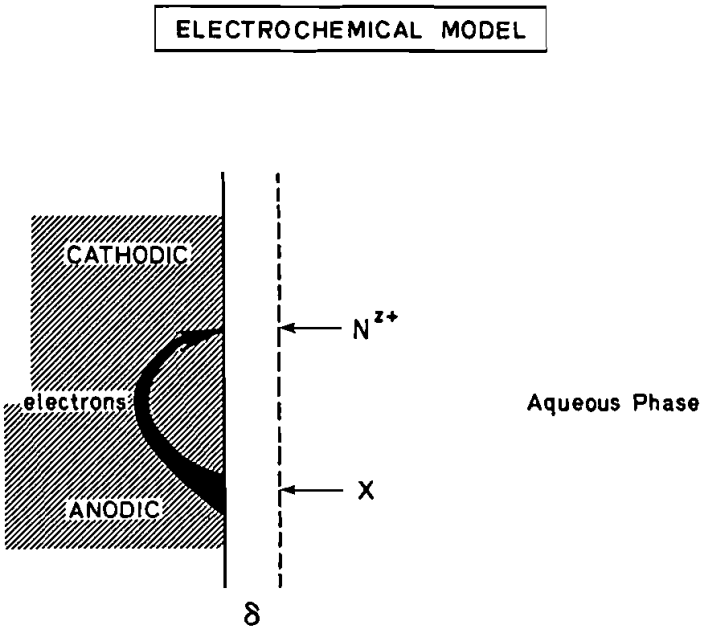


FIGURE 2 Schematic of the electrochemical microcell describing the dissolution of gold.

The cathodic reaction which complements the above reaction involves the reduction of an appropriate oxidant

$$N^{z+} + e \rightarrow N^{(z-1)+} \tag{4}$$

The standard electrode potential for reaction (3) for the oxidation of Au(0) to Au(I) is represented by $E^{\circ}_{0,1}$ (expressed as an oxidation reaction with $\Delta G^{\circ} = nFE^{\circ}$) and can be determined from free energy values for various ligands. It is possible to oxidize Au(0) to Au(III) in the presence of a suitable complexing agent as follows

$$Au + 4X \rightarrow AuX_4^{3+} + 3e \tag{5}$$

The standard electrode potential for reaction (5) is represented by $E^{\circ}_{0,3}$. One must remember that reaction (5) is for the overall process and does not reflect the individual mechanistic steps for the process. It is likely that the overall process involves multiple steps and single electron transfer reactions[46].

Of course, the oxidation of Au(I) to Au(III) in the presence of complexing ligands is possible according to the reaction

$$AuX_2^+ + 2X \rightleftharpoons AuX_4^{3+} + 2e \quad (6)$$

with $E^\circ_{1,3}$ representing the standard potential for reaction (6). It is easy to show that $3E^\circ_{0,3} = 2E^\circ_{1,3} + E^\circ_{0,1}$. Standard potentials corresponding to $E^\circ_{0,1}$, $E^\circ_{0,3}$, and $E^\circ_{1,3}$ for gold with various ligands are listed in Table II.

The stability of the Au(I) complex is related to its apparent tendency to undergo disproportionation.

$$3AuX_2^+ \rightarrow 2Au + Au^{x3+}_4 + 2X \quad (7)$$

The equilibrium constants (K_7) for disproportionation are also given in Table II for the appropriate ligands. Soft polarizable ligands (i.e., CN^-, $CSe(NH_2)_2$, $S_2O_3^{2-}$, I^-, and SCN^-) form complexes of greatest stability. The stability for the gold halide complexes in aqueous solution follow the order $I^- > Br^- > Cl^-$.

In the following sections, the dissolution behavior of gold and silver in the presence of various complexing ligands is examined with the aid of Eh (potential)—pH diagrams. The development and use of these diagrams in hydrometallurgical systems is well documented[47,48]. Various sources of thermodynamic information provided data to calculate standard potentials and equilibrium constants. Latimer[49] and Sillen and Martell[50] represented the basic reference sources for most of species considered. Additional data were obtained from Jorgensen

TABLE II
Standard potentials for reactions involving gold complexes

Ligand	Standard potentials, V SHE $E^\circ_{0,1}$	$E^\circ_{0,3}$	$E^\circ_{1,3}$	K_7
H_2O	1.69	1.50	1.40	6.7×10^9
Cl^-	1.16	1.00	0.92	1.1×10^8
Br^-	0.96	0.87	0.83	2.3×10^4
I^-	0.57	0.57	0.57	1.2
SCN^-	0.67	0.64	0.62	41
NH_3	0.57	0.34	0.23	2.8×10^{11}
thiourea	0.38	—	—	—
selenourea	0.20	—	—	—
$S_2O_3^{2-}$	0.15	—	—	—
S^{2-}	−0.46	—	—	—
CN^-	−0.64	—	—	—

and Pourodier[51]; Hancock, Finkelstein and Evers[52]; and Peschchebitskii, Belevantsev, and Zemskov[53]. The thermodynamic values used throughout this paper are for a temperature of 25°C.

Gold-Water System

The Eh-pH relationships for the Au-H_2O system conveniently illustrate the extremely noble nature of gold in the absence of coordinating ligands. Figure 3 shows the Eh-pH diagram for pure gold at 25°C. The diagram was constructed for dissolved gold species having concentrations equal to 10^{-4} M. The dashed lines delineate

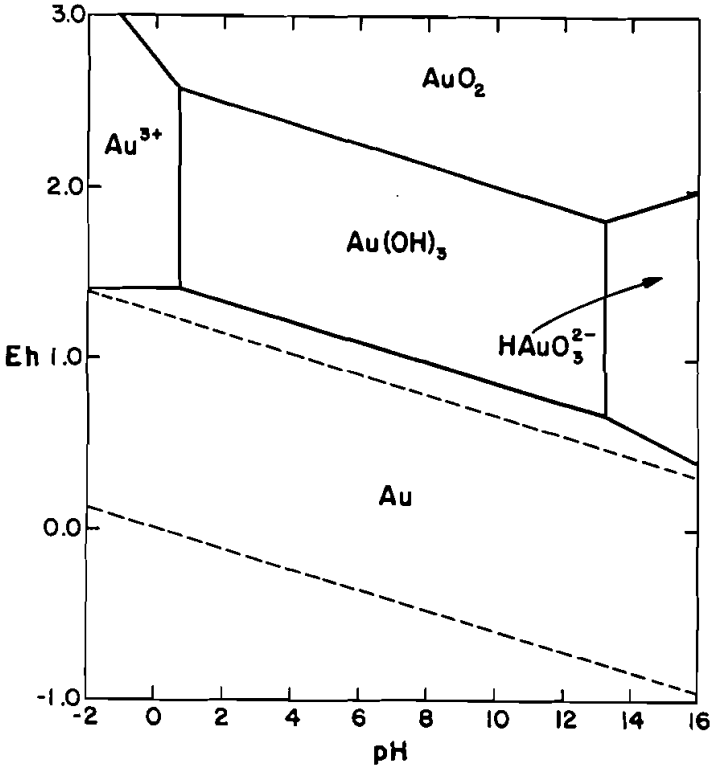


FIGURE 3 Potential-pH equilibrium diagram for the gold-water system for dissolved gold species of 10^{-4} M.

the stability limits of water. Metallic gold covers a very large area of predominance, including the entire domain of water stability. Aurous ion (Au^+) does not appear on the diagram because it disproportionates spontaneously according to the following reaction for the aquo ions

$$3Au^+ \rightarrow 2Au + Au^{3+} \quad (8)$$

The value of the equilibrium constant for this reaction at 25°C is $K = 6.7 \times 10^9$. Auric ion (Au^{3+}) and other oxidized forms of gold only occur at potentials above the upper stability limit of water. However, at these potentials, water will decompose (be oxidized) to oxygen and the various oxidized gold species reduced simultaneously to the metallic state. This means that gold cannot be oxidized in strong acids or strong alkalis in the absence of complexing ligands.

Because gold is completely and perfectly stable in the presence of water, it is found in nature mainly in the native state. As expected very few gold-bearing minerals have been reported[54]. Native gold and electrum are by far the most common forms. Gold is found to occur in a limited number of natural alloys and as tellurides, however, these occurences are considered rare and are of minor significance commercially.

Silver-Water System

Figure 4 shows the Eh-pH behavior for pure silver at 25°C. The diagram was constructed for dissolved silver species having concentrations equal to 10^{-4} M. Silver, like gold, is a very noble metal covering a large portion of the domain of water stability. Metallic silver is fully stable in the absence of oxidizing agents and complexing ligands at all pH values. However, silver can be dissolved under oxidizing conditions in acidic to moderately alkaline solutions to yield Ag^+ and in strongly alkaline solutions to yield AgO^-. The shaded areas in Figure 4 indicate the respective regions for these species at 10^{-4} M.

In natural waters Ag^+ is stable under certain conditions and its existence in aqueous environments allows for the formation of a great many silver-bearing minerals. The silver ion can conceivably precipitate from solution to form sulfides, halogenides, jarosites,

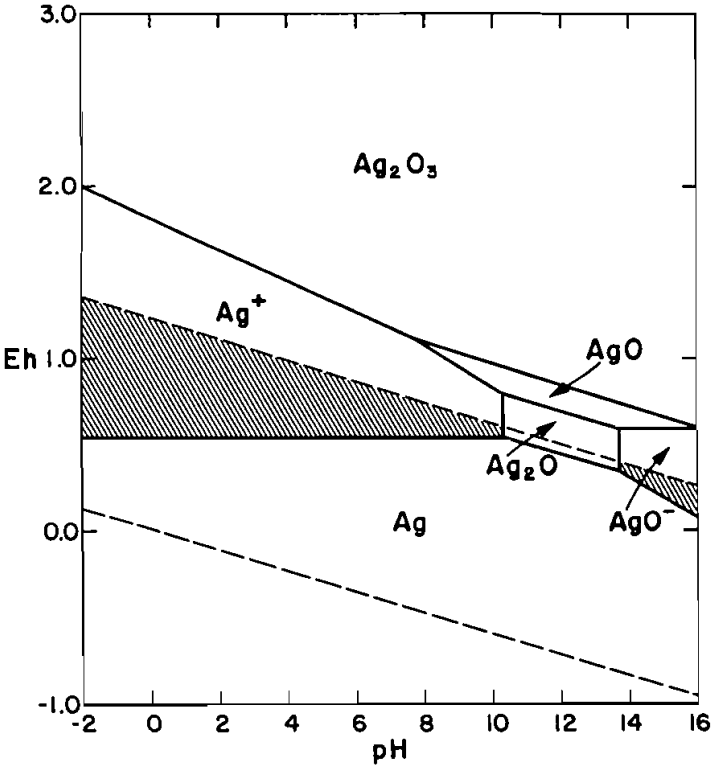


FIGURE 4 Potential-pH equilibrium diagram for the silver-water system for dissolved silver species of 10^{-4} M. Shaded regions show where silver is soluble in the domain of water stability.

selenides, etc. Furthermore, Ag^+ can undergo secondary enrichment type reactions with primary minerals to form silver-bearing minerals. As a result of these factors, silver occurs in approximately 200 different minerals and is characterized by complex mineralogy[55].

Gold-Cyanide-Water System

Gold is readily dissolved in the presence of a complexing ligand and an oxidizing agent, both conditions being necessary for reaction to take place. Aurous ion forms an extremely stable linear cyanide

complex, $Au(CN)_2^-$. There is no evidence for the formation of complex gold(I)-cyano species with higher coordination numbers[56]. The complexation reaction and corresponding formation constant are

$$Au^+ + 2CN^- \rightleftharpoons Au(CN)_2^- \qquad (9)$$

$$\beta_2 = 2.8 \times 10^{39}$$

Figure 5 represents the Eh-pH diagram for the Au-CN-H_2O system at 25°C and at $[CN^-] = 10^{-3}$ M. As illustrated by this diagram, the presence of a strong complexing ligand like cyanide

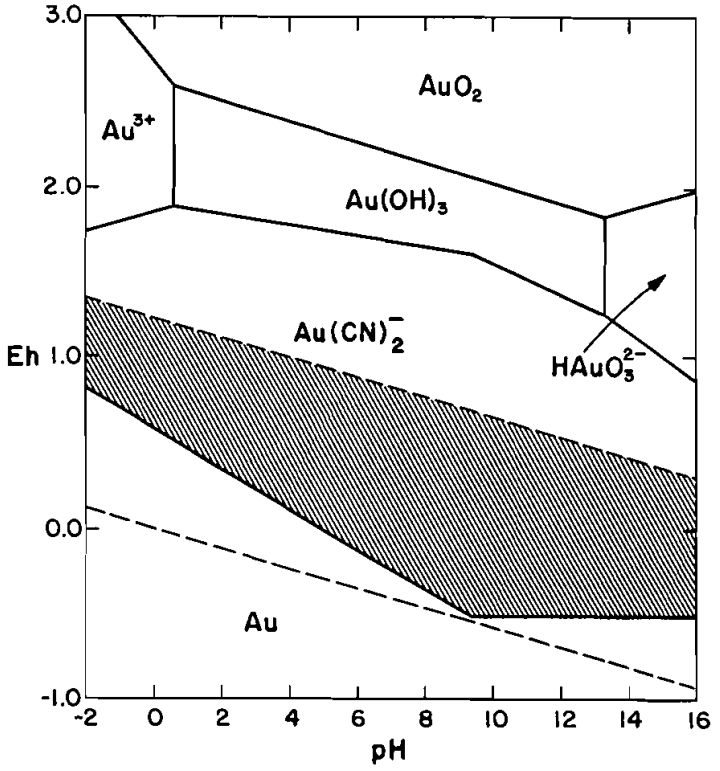


FIGURE 5 Potential-pH equilibrium diagram for the silver-cyanide system for [Au] = 10^{-4} M and [CN] = 10^{-3} M. Shaded region shows where gold is soluble in the domain of water stability.

results in a relatively large region of gold solubility. In alkaline solutions (pH > 10) gold is oxidized to the stable $Au(CN)_2^-$ complex at a potential of about −0.52 V (SHE) for the stated conditions.

Dissolved oxygen is an excellent oxidant for gold dissolution in alkaline cyanide solutions. The overall leaching depends upon the reaction

$$4Au + 8CN^- + 2H_2O + O_2 \rightarrow 4Au(CN)_2^- + 4OH^- \qquad (10)$$

Silver-Cyanide-Water System

As depicted in Figure 6, the Eh-pH behavior of silver in the presence of cyanide is very silmilar to that of gold. In aqueous solution

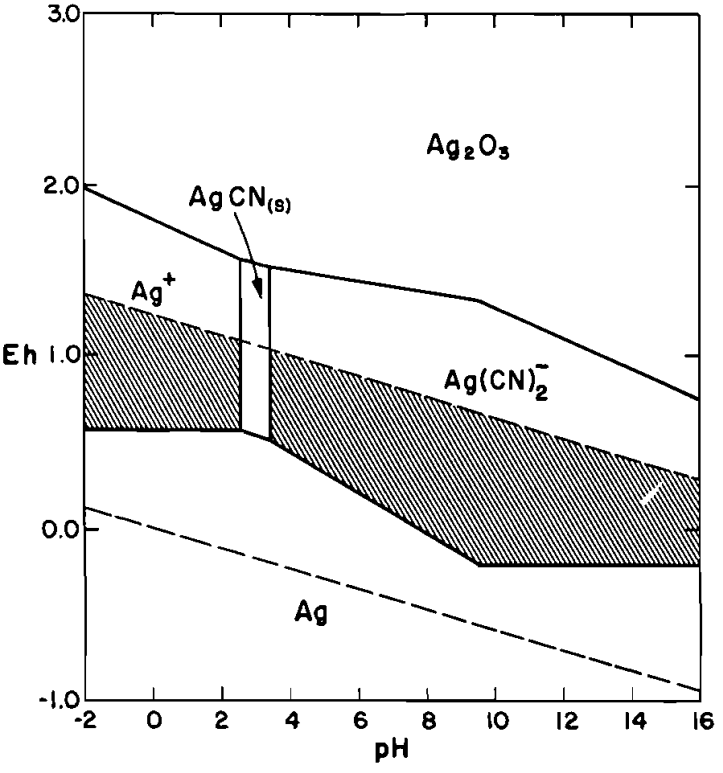


FIGURE 6 Potential-pH equilibrium diagram for the silver-cyanide system for [Ag] = 10^{-4} and [CN] = 10^{-3} M. Shaded regions show where silver is soluble in the domain of water stability.

silver(I) forms a series of complex cyano anions: $Ag(CN)_2^-$, $Ag(CN)_3^{2-}$, and $Ag(CN)_4^{3-}$ [56]. The $Ag(CN)_2^-$ species predominates as indicated by the following thermodyanamic data and the fact that dilute cyanide solutions are normally used during cyanidation

$$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^- \quad \beta_2 = 2.8 \times 10^{20} \tag{11}$$

$$Ag(CN)_2^- + CN^- \rightleftharpoons Ag(CN)_3^{2-} \quad K = 35.5 \tag{12}$$

The behavior of silver in alkaline cyanide solutions is comparable to that of gold, at pH values greater than 10, silver is oxidized to $Ag(CN)_2^-$ at about -0.19 V for 10^{-4} M CN^-. Below pH 4 though, $Ag(CN)_2^-$ reacts with hydrogen ions to form a solid AgCN phase. Under acidic conditions (pH < 2.6) the $AgCN_5$ phase dissolves to yield Ag^+ and HCN.

GOLD DISSOLUTION-ALTERNATIVE LIXIVIANTS

The application of lixiviants other than cyanide to the leaching of precious metals is dependent on the apparent ability of these other ligands to form stable complexes with gold and silver. The following discussion will emphasize the dissolution of gold with halogens, thiourea, thiosulfate, and selected other lixiviants.

Halogens

The halogen complexes of gold are discussed in the order Cl, Br, and I. Au(I) and Au(III) complexes for all three of these halogens have been identified. However, as shown in the individual Eh-pH diagrams for these systems, the relative stability of the various gold halogen complexes is very different. Figure 7 shows the Eh-pH diagrams for the Au-Cl-H_2O system for 10^{-2} M Cl^-. Again, the shaded area shows the portion of the water domain occupied by dissolved gold. The $AuCl_4^-$ complex is the only gold species stable at these conditions. Gold will dissolve in the presence of chloride ion and a strong oxidant when the solution is highly acidic. The existence of $AuCl_2^-$ in aqueous solution under these conditions (i.e., 10^{-2} M Cl^-) is not possible as suggested by the disproportionation equilibrium

$$3\ AuCl_2^- \rightarrow AuCl_4^- + 2Au^0 + 2Cl^- \tag{13}$$

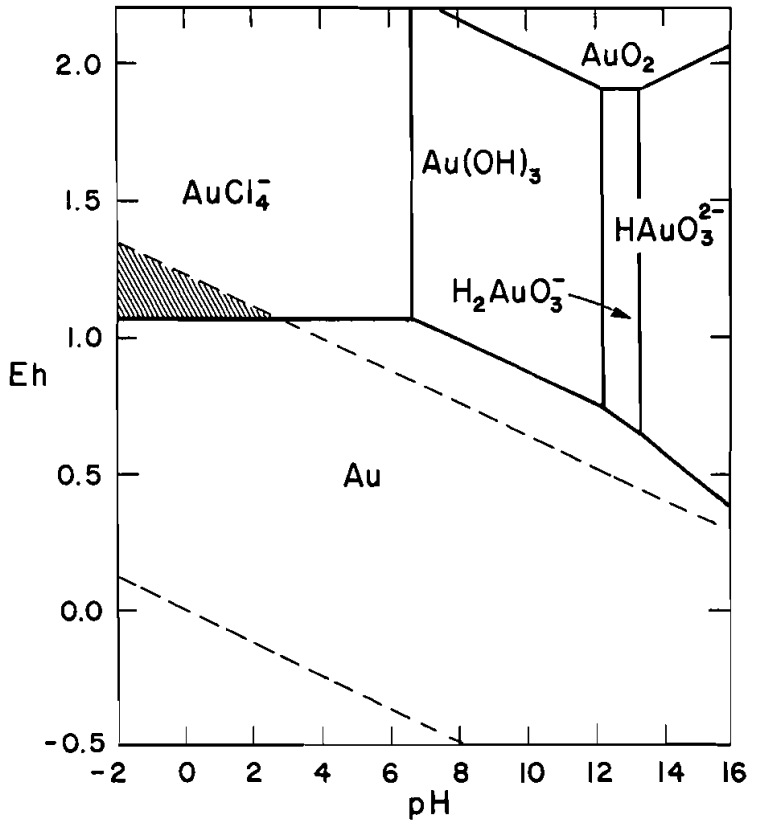


FIGURE 7 Potential-pH equilibrium diagram for the gold-chloride system for [Au] = 10^{-5} M and [Cl] = 10^{-2} M.

The value of the equilibrium constant for this reaction at 25°C is K = 1.3×10^{8}. This value is reasonably close to that reported in an earlier part of this paper for the aquo complexes. By comparison, the extremely stable nature of $AuCN_2^-$ is reflected by its disproportionation constant which is estimated to be about 10^{-25} [57].

Increasing the chloride concentration forces the $Au/AuCl_4^-$ boundardy to lower potentials. At about 0.1 M Cl^- the chloride activity for these conditions is sufficient enough to stablize the $AuCl_2^-$ complex and the Eh-pH diagram would show a region for $AuCl_2^-$. Therefore, in hydrometallurgical and electrolytic systems employing concen-

trated chloride solutions, one would expect $AuCl_2^-$ to be the predominant species. Another example where one would predict the $AuCl_2^-$ species to dominate the system is sea water. In sea water gold is present at very dilute concentrations (0.004 to 0.008 ppb Au) and the dissolved chloride level is very high (18,980 ppm)[58], under these conditions gold is stable as the gold(I)-chloro complex.

In Figure 7, it is shown than gold will dissolve to yield the $AuCl_4^-$ complex ion at about 1.1 V. Nitric acid in aqua regia is a sufficiently powerful oxidant to dissolve gold in the presence of chloride ion.

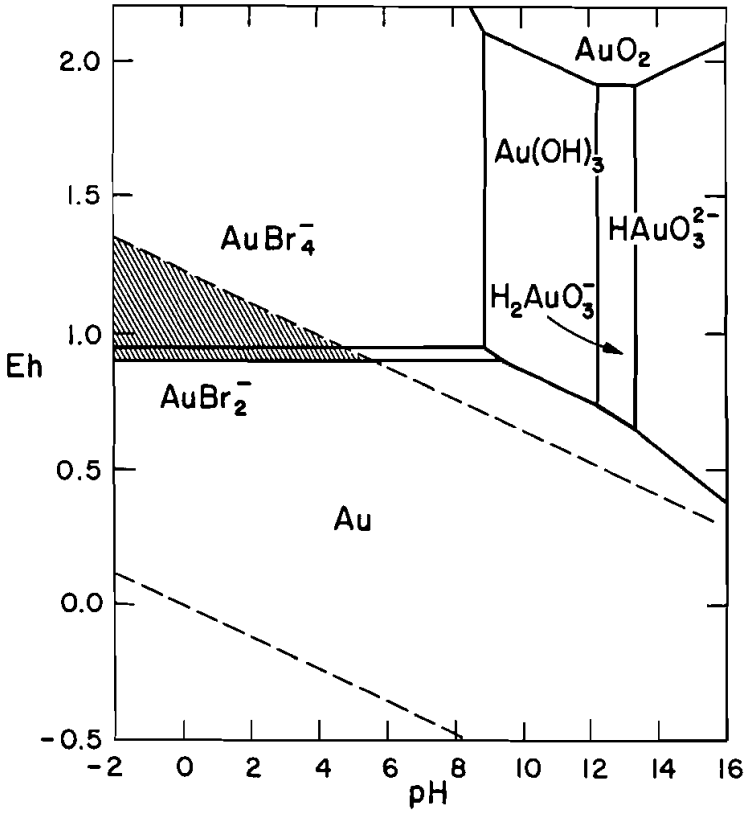


FIGURE 8 Potential-pH equilibrium diagram for the gold-bromide system for [Au] = 10^{-5} M and [Br] = 10^{-2} M.

Dissolved chlorine, hypochlorous acid, and hypochlorite ion are all capable of oxidizing gold in chloride media.

An Eh-pH analysis of the complexation of gold with bromide indicates that the gold(I)-bromo complex is more stable than the chloro complex. Figure 8 depicts the Eh-pH diagram for 10^{-2} M Br^-. The $AuBr_2^-$ complex occupies a very narrow stability field up to about pH 9. Metallic gold is oxidized in the presence of bromide to yield $AuBr_2^-$ at a potential of approximately 0.90 V and the $AuBr_4^-$ complex is formed at about 0.95 V. The overall region of $AuBr_4^-$ stability is greater than that occupied by $AuCl_4^-$. Dissolved gold exists in the shaded area of the diagram. Bromine is an oxidizing substance under acidic conditions and can be considered as an oxidant for the dissolution of gold in the presence of bromide ions.

The Eh-pH behavior of the Au-I_2-H_2O system is expressed in Figure 9 for 10^{-2} M I^-. This diagram illustrates the increased stability of the AuI_2^- complex which occupies a solubility field upto about pH 12. Metallic gold is oxidized in the presence of iodide to yield AuI_2^- at a potential of approximately 0.51 V and above 0.69 V the AuI_4^- complex becomes stable. The overall region of AuI_4^- stability is greater than that of either $AuCl_4^-$ or $AuBr_4^-$. In fact, the $Au(OH)_3$ and $H_2AuO_3^-$ trivalent forms of gold are not present on this diagram because of the strength of the AuI_4^- complex. Of the halogens, the gold iodide complexes are the most stable in aqueous environments.

Bromine and iodine demonstrate the existence of polyhalides. For example, the tribromide ion is formed when dissolved bromine reacts with bromide according to the following chemical reaction

$$Br_2(aq) + Br^- = Br_3^- \tag{14}$$

This allows for the high solubility of bromine in aqueous solutions of bromide ion. Pourbaix[59] reports that Br_3^- ion has a stability region only in solutions whose concentration is greater than about 8×10^{-2} M dissolved bromine. Similarly, iodine reacts with iodide ion as follows

$$I_{2(aq)} + I^- = I_3^- \tag{15}$$

The I_3^- ion is present when solutions contain more than about 1.0×10^{-3} M dissolved iodine. Consequently I_3^- can serve as an oxidant for gold according to the following electrochemical reaction

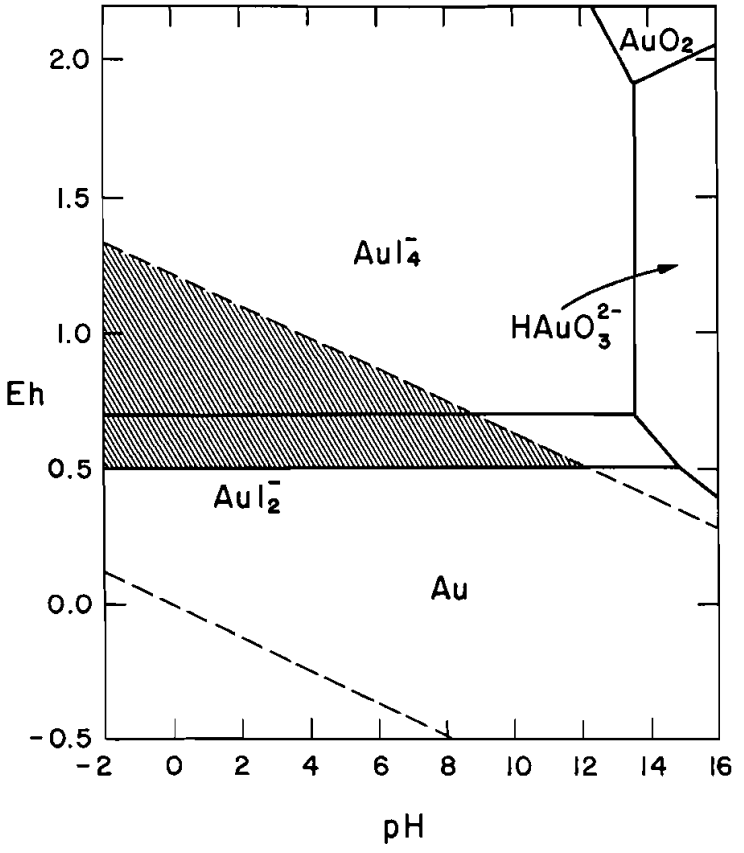


FIGURE 9 Potential-pH equilibrium diagram for the gold-iodide system for [Au] = 10^{-5} M and [I] = 10^{-2} M.

$$Au + 2I^- \rightarrow AuI_2^- + e \qquad \text{anodic} \qquad (16)$$

$$I_3^- + 2e \rightleftharpoons 3I^- \qquad \text{cathodic} \qquad (17)$$

$$2Au + I_3^- + I^- \rightarrow 2AuI_2^- \qquad \text{overall} \qquad (18)$$

The Nernst equation for the I_3/I^- couple is

$$E = 0.54 - 0.03 \log \frac{[I^-]^3}{[I_3^-]} \qquad (19)$$

When $[I^-]$ and $[I_3^-]$ equal 1.0×10^{-3} M, the oxidation potential would be about 0.71 V which is sufficient enough to oxidize gold in the presence of iodine.

Thiourea

Thiourea, $CS(NH_2)_2$, is an organic compound, the crystals of which dissolve in water to yield an aqueous solution stable in acidic solutions. At 298 °K, a saturated solution will contain approximately 142 g/l $CS(NH_2)_2$. The unique feature of thiourea is that in aqueous solution it reacts with gold and silver to form stable cationic complexes. The complexation reaction for gold and silver are shown below with their respective formation constants

$$Au^+ + 2CS(NH_2)_2 \rightleftharpoons Au[CS(NH_2)_2]_2^+ \qquad \beta_2 = 9.1 \times 10^{21} \qquad (20)$$

$$Ag^+ + 3CS(NH_2)_2 \rightleftharpoons Ag[CS(NH_2)_2]_3^+ \qquad \beta_3 = 1.3 \times 10^{13} \qquad (21)$$

The bis(thiourea)gold(I) complex ion is the only known soluble thiourea species of the aurous ion. The predominant argentous thiourea species is the tris(thiourea)silver(I) complex ion, however, there is some evidence of the existence of the bis(thiourea)silver(I) complex[50].

Thiourea solution chemistry will be discussed first. Three species will be considered. They are listed in Table III.

Preisler and Berger[60] have investigated the oxidation-reduction potentials of the thiourea-formamidine disulfide system. In acid solutions the oxidation of thiourea to formamidine disulfide is shown by the following reaction

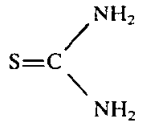
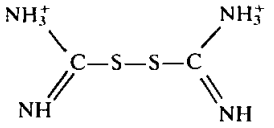
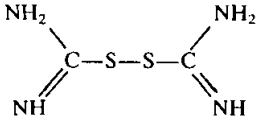
$$2RSH \rightleftharpoons (HRSSRH)^{2+} + 2e \qquad (22)$$

Since this process does not involve H^+, one would expect the Nernst potential to be independent of pH. This was observed to be the case for pH values less than 4.3. The standard potential for the thiourea-formamidine disulfide couple shown in reaction (22) was measured to be 0.42 V SHE. At pH values above 4.3 the following redox reaction characterizes the oxidation of thiourea

$$2\ RSH \rightleftharpoons RSSR + 2H^+ + 2e \qquad (23)$$

In contrast to reaction (22) this process involves H^+ and would yield a Nernst equation containing a pH term. The results of Preisler and Berger[60] suggest a pK value of 4.3 for the reaction

TABLE III
Species considered in the solution chemistry of thiourea

Species	Structure	Formula
thiourea		RSH
formamidine disulfide "protonated"		$(HRSSRH)^{2+}$
formamidine disulfide "unprotonated"		RSSR

$$(HRSSRH)^{2+} \rightleftharpoons RSSR + 2H^{+} \tag{24}$$

From the standard potential for reaction (22) and from the pK value for reaction (24) is possible to construct a simple Eh-pH diagram for the thiourea-water system. Figure 10 shows the stability region for this system. The Eh relationship for reaction (22) may be written

$$Eh = 0.42 + 0.03 \log \frac{[(HRSSRH)^{2+}]}{[RSH]^2} \tag{25}$$

When the formamidine disulfide species and the thiourea equal 0.01 M, the equilibrium potential for the couple would be about 0.48 V. Now the Eh-pH expression for reaction (23) may be written

$$Eh = 0.67 - 0.06\ pH + 0.03 \log \frac{[RSSR]}{[RSH]^2} \tag{26}$$

Potential as a function of pH could not be determined experimentally at pH values greater than 4.3 because of decomposition of the formamidine disulfide. This is an important observation because it illustrates the extreme instability of the formamidine disulfide species. Furthermore, it indicates that formamidine disulfide may

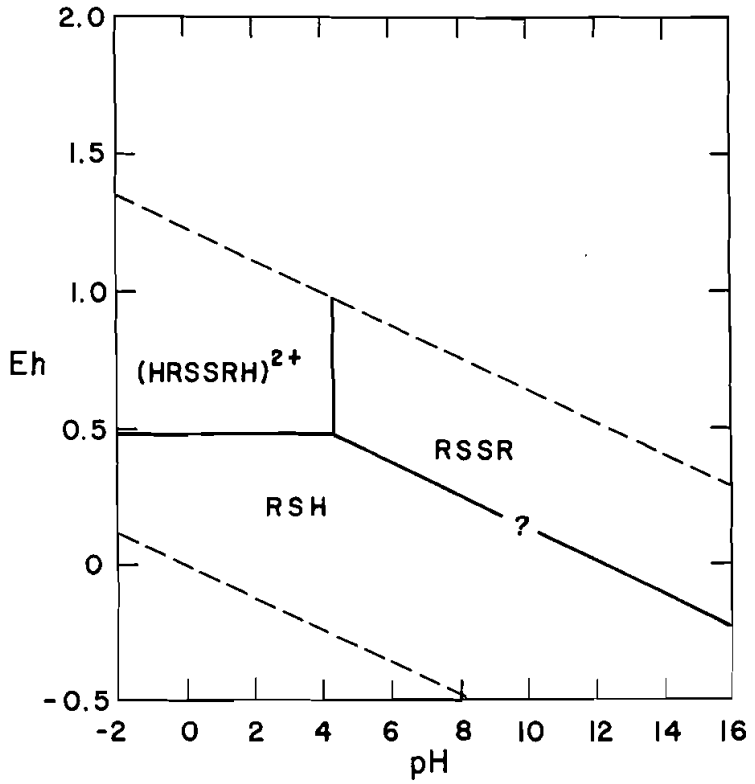


FIGURE 10 Potential-pH equilibrium diagram for the thiourea-water system implied from the data of Preisler and Berger[60].

not have a thermodynamic region of stability and that it is present in aqueous solution only because of kinetic factors.

Gupta[61] has analyzed in detail the decomposition chemistry of formamidine disulfide. Formamidine disulfide undergoes an initial disproportionation step which produces thiourea and a sulfinic acid. The thiourea produced by disproportionation repeats the cycle while the sulfinic acid reacts further to yield cyanamide and elemental sulfur. The elemental sulfur is in a colloidal state and is finally oxidized to sulfate. In alkaline solutions, the cyanamide polymerizes to dicyanamide or cyclic products. In acidic medium, the cyanamide undergoes hydrolysis to form urea

$$H_2NC = N + H_2O \rightarrow CO(NH_2)_2 \quad (27)$$

In the presence of strong oxidants, thiourea is decomposed vigorously to urea and sulfate. The role of urea in the thiourea system proposed by Little[26] is to maintain a stabilizing effect on the thiourea by controlling the decomposition equilibria. Whereas, the addition of K-lignin sulfonate to the system limits the passivating effect of any elemental sulfur produced by thiourea degradation.

Gold is dissolved in the presence of thiourea according to the following anodic reaction

$$Au + 2CS(NH_2)_2 \rightarrow Au[CS(NH_2)_2]_2^+ + e \quad (28)$$

The standard potential for this reaction is 0.38 V (see Table II). This suggests that only mildly oxidizing conditions are required to dissolve gold in thiourea. Potentials near the thiourea/formamidine disulfide couple are considered adequate, in fact there is considerable proof that formamidine disulfide behaves as an internal oxidizing agent for precious metal disslution.

Therefore, the formation of formamidine disulfide in the system need not be avoided. However, strongly oxidizing conditions, from the standpoint of gold dissolution and thiourea decomposition, are considered inappropriate. This is dramatically demonstrated by the electrochemical data of Groenewald[62] who investigated the anodic behavior of gold electrodes in acid thiourea solutions. The effect of potential on the rate of gold dissolution, current density, and current efficiency is shown in Figure 11. As shown gold dissolves with a 100% current efficiency at overpotentials up to 0.3 V. Both current density and gold dissolution rate increase with increasing potential in this region. At overpotentials greater than 0.4 V there is a noticeable decrease in current efficiency, a slight increase in current density and a decrease in dissolution rate. The decrease in current efficiency was attributed to the oxidation of thiourea to formamidine disulfide. The decrease in gold dissolution rate was explained in terms a decrease in thiourea concentration and the poisoning of the gold surface by thiourea oxidation products. Overpotentials up to 0.3 V resulted in a clean gold surface while potentials greater than 0.4 V produced a darkened surface which is believed to indicate the formation of an elemental sulfur surface coating. In a practical sense, the addition of minor amounts of a reductant like SO_2 to the leaching system is an important control measure to stabilize thiourea.

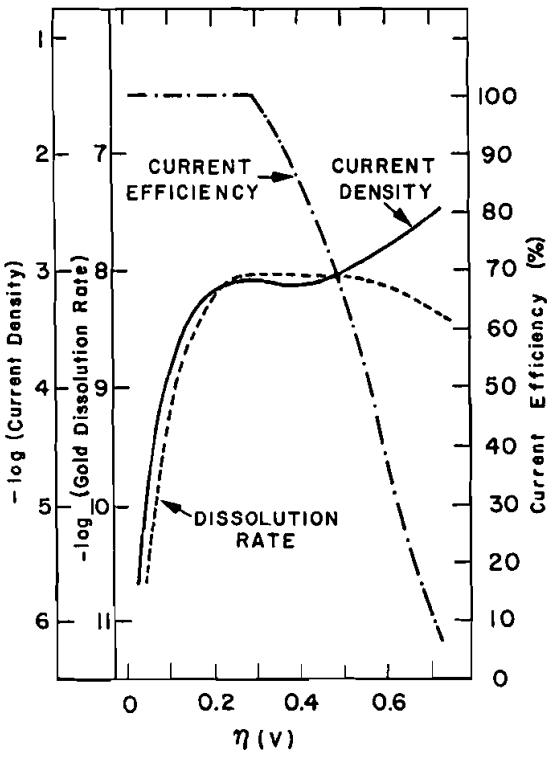


FIGURE 11 Effect of overpotential (η) on the anodic dissolution of gold in 10^{-2} M thiourea and 10^{-1} M sulfuric acid. Current density expressed as A/cm^2 and gold dissolution rate as mole Au/cm^2 sec. (After Groenewald[62]).

In some instances where thiourea is used as a lixiviant in the treatment of refractory gold-bearing sulfides, stronger oxidants may be required to breakdown the sulfide mineral matrix[63]. These systems would dictate the use of high thiourea concentrations.

Thiosulfate

Thiosulfates are compounds containing the group $S_2O_3^{2-}$ which is a structural analog of sulfate with one oxygen atom replaced by a sulfur atom. The unique chemistry of the thiosulfate ion, which has the structure $[S\text{-}SO_3]^{2-}$, is dominated by the sulfide-like sulfur atom

which imparts reducing properties, strong complexing tendencies, and sulfide forming capabilities. Thiosulfates can also be readily reduced to sulfides. The best known reactions of thiosulfate are its oxidation to tetrathionate by iodine, widely used in analytical chemistry, and its ability to dissolve silver halides through complex formation, which is an important step in the development of photographic film[64].

The two most important salts of thiosulfate are sodium thiosulfate (known also as "hypo"), $Na_2S_2O_3$ or $Na_2S_2O_3 \cdot 5H_2O$, and ammonium thiosulfate, $(NH_4)_2S_2O_3$. Sodium thiosulfate is available as colorless long "rice form" crystals or white granules. Ammonium thiosulfate occurs as anhydrous colorless or white tubular crystals belonging to the monoclinic system and is very soluble in water.

Thiosulfate forms complex ions with a variety of metals (e.g., gold, silver, copper, iron, platinum, nickel, cobalt). The chemistry of the thiosulfate leaching of gold and silver has been found to be very complex by previous workers[6,34,35,36,37,65]. Gold and silver dissolve in thiosulfate solutions forming stable complexes according to the following reactions

$$Au^+ + 2S_2O_3^{2-} \rightleftharpoons Au(S_2O_3)_2^{3-} \quad \beta_2 = 1.0 \times 10^{26} \tag{29}$$

$$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-} \quad \beta_2 = 2.2 \times 10^{13} \tag{30}$$

Kakovskii[66] and Tyvrin and Kakovskii[67] have studied the fundamentals of gold and silver dissolution in thiosulfate solutions. In the presence of ammonium thiosulfate, gold is solubilized solely as the thiosulfate complex

$$4Au + 8S_2O_3^{2-} + 2H_2O + O_2 \rightarrow 4Au(S_2O_3)_2^{3-} + 4OH^- \tag{31}$$

while silver reacts predominantly to form the thiosulfate complex

$$4Ag + 8S_2O_3^{2-} + 2H_2O + O_2 \rightarrow 4Ag(S_2O_3)_2^{3-} + 4OH^- \tag{32}$$

with a relatively small portion of the amine complex being formed

$$4Ag + 8NH_3 + 2H_2O + O_2 \rightarrow 4Ag(NH_3)_2^+ + 4OH^- \tag{33}$$

As indicated early in this paper, copper ions exhibit a strong catalytic effect on the rates of dissolution of the noble metals. Tozawa, Inui, and Umetsu[36] have investigated the effect of copper concentration on the dissolution of pure gold plates in ammonical thiosulfate solutions. Gold dissolution was found to be very sensitive

to both thiosulfate and copper concentration, and exhibited a complex dependency on temperature. For thiosulfate concentrations up to 0.25 M, the authors calculated a second order dependency on $[S_2O_3^{2-}]$. The effect of $[Cu^{2+}]$ on the dissolution of gold is much more complex as shown in Figure 12 for 65, 100 and 140°C. Gold dissolution increased with increasing temperature up to 65°C. As shown in Figure 12, at 65°C gold dissolution also increases with increasing $[Cu^{2+}]$ up to approximately 0.40 M then decreases with further increases in copper concentration. The decrease is attributed to depletion of thiosulfate by complexation with copper according to the following reaction

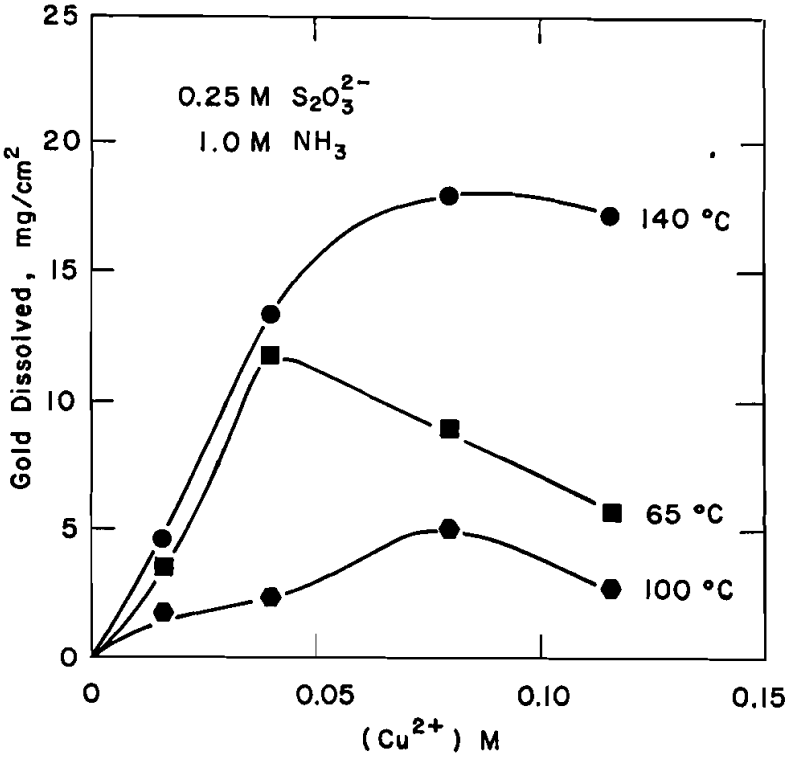


FIGURE 12 Effect of copper concentration and temperature on the dissolution of gold in 0.25 M thiousulfate. (After Tozawa *et al.*[36]).

$$2Cu(NH_3)_4^{2+} + 6S_2O_3^{2-} \rightleftharpoons 2Cu(S_2O_3)_2^{3-} + S_4O_6^{2-} + 8NH_3 \quad (34)$$

where cupric ion is reduced to the cuprous state and complexed with thiosulfate and a portion of the thiosulfate is oxidized to tetrathionate. Gold dissolution decreases between 65 and 100°C for the reasons listed below:

1) Increased oxidation of thiosulfate
2) Reduced levels of dissolved copper because of precipitation as CuS

$$2Cu(S_2O_3)_2^{3-} + \frac{9}{2}O_2 + 6OH^- \rightarrow 2CuS + 6SO_4^{2-} + 3H_2O \quad (35)$$

3) Passivation of the gold surface by CuS

Above 100°C, gold dissolution was found once again to increase with increasing temperature (upto 140°C) due to the instability of copper sulfide at these temperatures. At approximately 140°C, maximum gold dissolution was obtained. The data at 140°C also reflect the decreased stability of the $Cu(S_2O_3)_2^{3-}$ complex resulting in higher levels of free thiosulfate (especially above 0.40 M $[Cu^{2+}]$). However, above 140°C, the oxidation of thiosulfate is extremely rapid corresponding to a decrease in gold dissolution.

Flett and co-workers[65] conducted a fundamental investigation of the ammonical thiosulfate leaching of silver sulfide. The amount of silver leached was observed to increase with increases in both the thiosulfate and the copper concentrations. Their results suggest that in the absence of air the $Cu(S_2O_3)_2^{3-}$ complex (cuprous state) appears to be the stable species. In the presence of oxygen the cupric rather than the cuprous state appears to be favored. Ammonia also helps stabilize the cupric state. These observations are easily supported by the chemical reaction

$$2Cu(S_2O_3)_2^{3-} + 8NH_3 + O_2 + H_2O \rightleftharpoons 2Cu(NH_3)_4^{2+} + 4S_2O_3^{2-} + 2OH^- \quad (36)$$

which has an equilibrium constant of 5.8×10^8 at 25°C. Hence, it can be concluded that at higher concentration of ammonia and increased oxygen pressure, Cu ion is predominantly in the $Cu(NH_3)_4^{2+}$ form. Whereas, at higher concentrations of thiosulfate and at high pH values the $Cu(S_2O_3)_2^{3-}$ species is favored.

Berezowsky and Sefton[35] reported that oxidative degradation of thiosulfate to tetrathionate occurred in the presence of air, parti-

cularly when both soluble copper and sulfides were present and this reduced the efficiency of the lixiviant. The degradation was less when nitrogen purge was used. In some cases, however, in nitrogen at elevated temperatures, copper sulfide precipitated after the initial rapid extraction of gold and silver. They concluded this as the result of a reaction between cupric and thiosulfate ions in solution. Precipitation of appreciable quantities of precious—metal values with the copper were reported. In these cases, mild oxidizing conditions were recommended by them to achieve high extraction of the precious metals.

Other Lixiviants

Malononitrile, a water soluble dinitrile with the formula $CH_2(CN)_2$, will dissolve gold under alkaline leaching conditions[39,40]. The solubility of malononitrile at 20°C is 133 g/l $CH_2(CN)_2$. Heinen et al.[39] analysed the possible reaction mechanism for dissolving gold in the presence of malononitrile. In basic solutions, gold dissolution occurs by two possible routes. According to the first route, the initial step involves the formation of the malononitrile carbanion. The malononitrile carbanion reacts directly with gold to form a gold-malononitrile complex (see route I). The other route proceeds in basic solutions first by dimerization of the malononitrile[68]. This is followed by hydrolysis of the dimer to yield free cyanide ion which reacts with gold. Both routes are illustrated by the reactions shown below

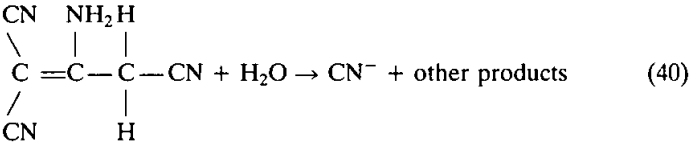
Route I

$$CH_2(CN)_2 + OH^- \rightleftharpoons CH(CN)_2^- + H_2O \tag{37}$$

$$Au + 2CH(CN)_2^- \rightarrow Au(CN(CN)_2)_2^- + e \tag{38}$$

Route II

$$2CH_2(CH)_2 \rightarrow \begin{array}{l} CN \quad NH_2H \\ \backslash \quad | \quad | \\ C = C - C - CN \\ / \qquad | \\ CN \qquad H \end{array} \tag{39}$$



$$\text{Au} + 2\text{CN}^- \rightarrow \text{Au(CN)}_2^- + \text{e} \quad (41)$$

Heinen and co-workers[39] reported results for the leaching of a −100 mesh oxide ore containing 13.7 g/mt gold. Solution pH was shown to have a pronounced effect on gold dissolution. For a solution containing 7.6×10^{-3} M $CH_2(CN)_2$, gold extractions after 24 hrs. of leaching were 95% for pH values above 8. At pH 7, the gold extraction was only 10%. The pH dependence supports the mechanisms described above. By comparison, standard cyanidation using 3.5×10^{-3} M NaCN and 8.9×10^{-3} M CaO also gave 95% gold extraction. However, the gold dissolution rate using cyanide was substantially faster than that with malononitrile. Table IV summarizes leaching results for sodium cyanide, malononitrile, and other malononitrile derivative compounds used in the course of their investigation.

TABLE IV
Comparison of gold leaching using malononitrile related compounds
(Data after Heinen *et al.*)

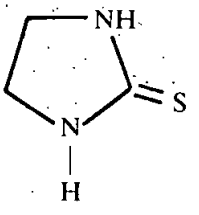
Compound	Lixiviant concentration moles/liter	Gold ext %
Sodium Cyanide NaCN	3.5×10^{-3}	95.0
Malononitrile $CH_2(CN)_2$	7.6×10^{-3}	95.0
Cyanoacetamide $CNCH_2CONH_2$	1.2×10^{-1}	90.0
Ethylcyanoacetate $CNCH_2COOC_2H_5$	8.8×10^{-2}	81.0
Dichloromalononitrile $(CN)_2CCl_2$	7.4×10^{-2}	78.5
Bromomalononitrile $(CN)_2CHBR$	6.9×10^{-2}	75.0

Generally these nitriles are considered stable during the leaching of gold. However, under strongly acidic or basic conditions the hydrolysis of nitriles produces unsubstituted amides[69]. For example, malononitrile will undergo hydrolysis to yield cyanoacetamide in strongly basic solutions. However, hydrolysis of the cyanoacetamide is considered slow[69]. Consequently, the dissolution of gold by malononitrile and the related compounds shown in Table IV is believed to be direct and not by the circuitious formation of free cyanide ions. Furthermore, reasonance stabilization of cyanocarbon anions[70] such as malononitrile-carbanion would favor the direct reaction mechanism.

Carpenter and Hedley[43] proposed the use of α-hydroxynitriles to leach precious metals from their ores. The nitriles examined included: lactonitrile or 2-hydroxy-propanenitrile, $CH_3CH(OH)CN$; mandelonitrile, $C_6H_3CH(OH)CN$; and glycolonitrile. Leaching results indicated that the α-hydroxynitriles yield nearly identical levels of gold extraction as sodium cyanide. For example, the leaching of an arsenical gold ore resulted in about 64% Au extraction at pH 6.6 for both lactonitrile and sodium cyanide. These nitriles do not complex gold directly but furnish free cyanide ions as a result of hydrolysis.

There is an additional reference in the literature to the use of malonic acid dinitrile as a solvent for gold[71].

N,N′-Ethylenethiourea or 2-Imidazolidinethione is a water soluble compound with the structure



Schulze[44] proposed the use of acidic solutions of N,N′-Ethylenethiourea (ETU) to leach gold and silver. The ETU molecule is more stable (more resistant to chemical oxidation) than thiourea, therefore, more aggressive oxidants can be used during leaching.

Aqueous solutions of polysulfides have been employed as lixiviants for gold[45,72]. Latimer[49] reported standard potentials for the following sulfide/polysulfide couples

$$2S^{2-} \rightleftharpoons S_2^{2-} + 2e \qquad E^0 = 0.48 \tag{42}$$

$$S^{2-} + S_2^{2-} \rightleftharpoons S_3^{2-} + 2e \qquad E^0 = 0.49 \tag{43}$$

$$S^{2-} + S_3^{2-} \rightleftharpoons S_4^{2-} + 2e \qquad E^0 = 0.52 \tag{44}$$

The general equation for the overall formation of a polysulfide is

$$nS^{2-} \rightleftharpoons S_n^{2-} + (2n - 2)e \tag{45}$$

Krauskopf[73] provided evidence for gold dissolution in sulfide solutions, presumable as the AuS^- complex. From solubility data, he estimated the free energy of formation for AuS^- as 11.00 kcal/mole. Kakovskii and Tyurin[45] presented data suggesting a ΔG_f° = 11.57 kcal/mole for AuS^-. Based on this value the authors calculated a formation constant for the complexation reaction

$$Au^+ + S^{2-} \rightleftharpoons AuS^- \tag{46}$$

with a $\beta_1 = 2 \times 10^{36}$. This constant is relatively close to the cyanide formation constant of $\beta_2 = 2.8 \times 10^{39}$ (see equation 9). Peshchevitskii and Belevantsev[74] indicate that the Au(I) complex with S_n^{2-} is next to cyanide in relative order of stability. It is important to note that the S_n^{2-} poly anion can react directly with gold as shown for S_2^{2-}

$$2Au + S_2^{2-} \rightleftharpoons 2AuS^- \tag{47}$$

For this reaction ΔG_f° = 1.37 kcal/mole and $K = [AuS^-]^2/[S_2^{2-}] = 10^{-1}$. From most of the available evidence, polysulfide leaching of gold yields the AuS^- complex. However, the possibility of some $Au(S_2)^-$ also forming cannot be ruled out.

An important feature of sulfide/polysulfides is their role in the breakdown of refractory gold-bearing sulfides. For example, ammonium polysulfide, $(NH_4)_2S_n$ was applied to the leaching of a gold-bearing arsenical concentrate[72]. Arsenic was solubilized as the AsS_3^{3-} species. The destruction of the arsencial matrix liberated gold which was dissolved as AuS^- or $Au(S_2)^-$. Consider As_2S_3 (orpiment) dissolution with sulfide/polysulfides to illustrate the leaching chemistry. Orpiment dissolution by sulfide ion can be described by the following equation

$$As_2S_3 + 3S^{2-} \rightarrow 2AsS_3^{3-} \quad (48)$$

Dissolution by polysulfide is described the following general equation

$$As_2S_3 + \left(\frac{2}{n-1}\right)S_n^{2-} + \left(\frac{3n-5}{n-1}\right)S^{2-} \rightarrow 2AsS_4^{3-} \quad (49)$$

where $n \geq 2$ (i.e., a polysulfide anion). A more complex example would be the dissolution of Cu_3AsS_3 (tennantite) in concentrated alkaline sulfide solutions. The leaching of Cu_3AsS_3 with sulfide ion is described by the following equation

$$2Cu_3AsS_3 + 3S^{2-} \rightarrow 3Cu_2S + 2AsS_3^{3-} \quad (50)$$

Leaching with polysulfide anions can be expressed in terms of the following general equation

$$Cu_3AsS_3 + \left(\frac{5}{2n-2}\right)S_n^{2-} + \left(\frac{3n-8}{2n-2}\right)S^{2-} \rightarrow 3CuS + AsS_4^{3-} \quad (51)$$

where $n \geq 2$.

SUMMARY AND CONCLUSIONS

In addition to providing a review of the application of alternative lixiviants for leaching gold and silver, this paper has presented a somewhat detailed discussion of the dissolution chemistry for some of these reagents. Due to the unprecedented rise in the price of gold and silver on the international market over the decade, there has been strong interest in developing new hydrometallurgical processes for recovering gold and silver. Part of this growing interest has been directed at the application of alternative non-cyanide lixiviants. A clear picture of the function and interdependence of these leaching systems has been lacking, and the intent of this review is to help provide a better understanding of the chemistry and to unify what is already known about these systems.

Gold in the absence of a complexing ligand cannot be oxidized to aqueous solution either in strong acid or strong alkalis. However, gold will dissolve in aqueous solutions containing a complexing ligand and a suitable oxidizing agent. Silver on the other hand can be dissolved under oxidizing conditions in acidic to moderately

alkaline solutions to yield Ag^+ and in strongly alkaline solutions to yield AgO^-. Cyanide has been recognized for a long time as a powerful lixiviant for gold and silver, forming very stable cyano complexes with both metals. A basic requirement of any new lixiviant is that it furnishes co-ordinating ligands that form stable complexes with good and very complex process because it involves numerous interrerlated chemical steps and the effectiveness of the lixiviant depends on other important factors. One of the most important is the intrinsic chemical stability of the reagents themselves.

For the information provided by this review along with other observations, a number of principal conclusions can be drawn as follows:

- Cyanide occupies a preeminent position in the hydrometallurgy of gold and silver, and cyanidation because of its economy and process simplicity will remain the principal technique for treating free milling gold ores. While cyanide is very effective in leaching oxidized gold ores, there are certain classes of gold ores (i.e., carbonaceous, pyritic, arsenical, and cupriferious) that are considered refractory to conventional cyanidation.
- The development of alternative non-cyanide lixiviants should certainly address the treatment of refractory ores and concentrates. In many refractory ores, gold is finely dispersed throughout a mineral matrix, and a system that accomplishes both the breakdown of the host mineral and the dissolution of gold seems highly desirable.
- Cyanide is recognized as a very toxic chemical and there is considerable interest in finding non-toxic chemicals and environmentally safe substitutes. Furthermore, maintaining a protective alkalinity condition in the cyanide system dictates the use of high pH solutions. There are certain situations where acidic solutions are required and even preferred.
- The $Au(CN)_2^-$ complex is possibly the most stable form of Au(I) in aqueous solution. Other ligands that form stable Au(I) complexes included: sulfide, thiosulfate, thiourea, and iodide.
- While the halides Cl^-, Br^-, and I^- all form Au(I) and Au(III) complexes, the stability of the complexes increases with the heavier halide ions ($I^- > Br^- > Cl^-$). In aqueous solution,

AuI_2^- and AuI_4^- occupy the largest region of stability. In general there are two important reasons for using this group of elements as lixiviants for gold: (1) the halides are extremely stable in aqueous solution, and (2) the halogens are all to some extent soluble in water and can also serve as an oxidant for gold.

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Appendices

APPENDIX A
Standard free energy data for gold species at 25°C
(kcal/mole)

Formula	State	$\Delta G^\circ_{f,298}$	Formula	State	$\Delta G^\circ_{f,298}$
Au^0	s	0		CYANIDE	
Au_2O_3	s	39.0	AuCN	s	32.5
$Au(OH)_3$	s	−69.3	$Au(CN)_2^-$	aq	64.4
AuO_2	s	48.0			
H_3AuO_3	aq	−61.8		THIOCYANATE	
$H_2AuO_3^-$	aq	−45.8	Au(SCN)	s	35.7
$HAuO_3^{2-}$	aq	−27.6	$Au(SCN)_2^-$	aq	57.9
AuO_3^{3-}	aq	−5.8	$Au(SCN)_4^-$	aq	129.1
Au^+	aq	39.0		THIOSULFATE	
Au^{3+}	aq	103.6	$Au(S_2O_3)_3^{3-}$	aq	−250.9
	HALOGENS				
AuCl	s	−4.2		THIOUREA	
$AuCl_3$	s	−11.6	$Au(CS(NH_2)_2)_2^+$	aq	−9.41
$AuCl_2^-$	aq	−35.98			
$AuCl_4^-$	aq	−56.2			
AuBr	s	−3.7		AMINE	
$AuBr_3$	s	−5.9	$Au(NH_3)_2^+$	aq	0.3
$AuBr_2^-$	aq	−27.1	$Au(NH_3)_4^{3+}$	aq	−2.0
$AuBr_4^-$	aq	−38.1			
AuI	s	−0.76		SULFIDE	
AuI_2^-	aq	−11.47	Au_2S	s	1.04
AuI_4^-	aq	−9.80	AuS^-	aq	11.57

APPENDIX B
Standard free energy data for silver species at 25°C
(kcal/mole)

Formula	State	$\Delta G^\circ_{f,298}$	Formula	State	$\Delta G^\circ_{f,298}$
Ag_2O	s	−2.59			
AgO	s	2.6	AgCN	s	39.2
Ag_2O_3	s	20.8	$Ag(CN)_2^-$	aq	72.05
Ag^+	aq	18.43			
AgO^-	aq	−5.49		THIOCYANATE	
Ag^{2+}	aq	64.1	AgSCN	s	23.3
AgO^+	aq	53.9	AgSCN	aq	33.1
			$Ag(SCN)_2^-$	aq	49.6
	HALOGENS		$Ag(SCN)_3^{2-}$	aq	69.1
AgCl	s	−26.22	$Ag(SCN)_4^{3-}$	aq	90.0
AgCl	aq	−16.8			
$AgCl_2^-$	aq	−50.7		THIOSULFATE	
$AgCl_3^{2-}$	aq	−82.5	$Ag(S_2O_3)^-$	aq	−121.3
$AgCl_4^{3-}$	aq	−115.0	$Ag(S_2O_3)_2^{3-}$	aq	−254.2
AgBr	s	−22.93	$Ag(S_2O_3)_3^{5-}$	aq	−382.6
AgBr	aq	−11.80			
$AgBr_2^-$	aq	−40.41		THIOUREA	
$AgBr_3^{2-}$	aq	−66.13	$Ag(CS(NH_2)_2)_3^+$	aq	−26.9
$AgBr_4^{3-}$	aq	−91.98			
AgI	s	−15.85		AMINE	
AgI	aq	−4.64	$Ag(NH_3)_2^+$	aq	−4.16
AgI_2^-	aq	−20.83			
AgI_3^{2-}	aq	−37.00			
AgI_4^{3-}	aq	−50.23			

APPENDIX C
Standard free energy data for other species at 25°C
(kcal/mole)

Formula	State	$\Delta G^\circ_{f,298}$	Formula	State	$\Delta G^\circ_{f,298}$
H_2O	l	−56.69		THIOCYANATE	
OH^-	aq	−37.6	SCN^-	aq	21.2
H^+	aq	0			
				THIOUREA	
	HALOGENS		$CS(NH_2)_2$	aq	−9.14
Cl^-	aq	−31.35			
Cl_2	g	0		AMMONIA	
Br^-	aq	−24.57	NH_3	aq	−6.36
Br_2	l	0			
Br_3^-	aq	−25.27			
I^-	aq	−12.35			
I_2	s	0			
I_3^-	aq	−12.31			
	SULFUR				
$S_{(r)}$	s	0			
S^{2-}	aq	22.1			
S_2^{2-}	aq	21.8			
S_3^{2-}	aq	21.1			
S_4^{2-}	aq	19.4			
SO_3^{2-}	aq	−116.1			
$S_2O_3^{2-}$	aq	−127.2			
	CYANIDE				
HCN	g	28.7			
HCN	aq	26.8			
CN^-	aq	39.6			