

ALTERNATES TO GOLD RECOVERY BY CYANIDE LEACHING

Ömer E. Kuzugüdenli* and Çetin Kantar**

*Erciyes Üniversitesi Fen-Ed. Fakültesi Kimya Bölümü Kayseri, TURKEY

**Dept. of Environmental Science Colorado School of Mines Golden CO, USA

ABSTRACT

Cyanide leaching has been the most widely applied technique to recover gold for over a century. Growing environmental and health concerns about the use of cyanide have resulted in legislation of stringent rules or prohibitions, as well as public pressure against cyanide use in gold processing worldwide. There is an increasing interest in finding new alternatives or improving previously tried processes. This paper evaluates the alternates to gold recovery by cyanide leaching.

SİYANÜRLE ALTIN ELDESİNE ALTERNATİFLER

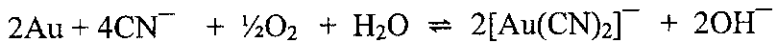
ÖZET

Altın üretiminde siyanür kullanımı yüz yılı aşkın bir süredir en yaygın uygulamadır. Siyanürün aşırı derecede toksik olması ve çevreye kalıcı zarar verebilmesi nedeniyle, siyanürle altın üretimine karşı gittikçe artan yasal sınırlamalar ve toplumsal direnç oluşmaktadır. Bu durum siyanürle altın üretimine alternatif güvenli yöntemler geliştirilmesi ihtiyacını doğurmuştur. Altın üretiminde kullanılacak alternaif yöntemler derlenerek bu çalışmada sunulmuştur.

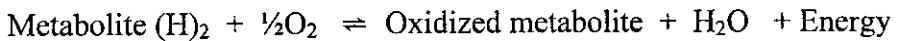
INTRODUCTION

Gold is called a noble metal for it possesses some exceptional properties such as resistance to chemical attacks, heat and moisture. Mankind has tried to find ways to produce gold throughout the history. These includes converting other metals into gold (no success yet), gravity techniques and chemical extraction [1-8]. While various gravity techniques have been applied to recover gold for thousands of years, the techniques are not suitable or economical for gaining the metal from most gold deposits. This metal's attractiveness mainly comes from its resistance to chemical attacks. The same reason, at the same time, makes the extraction of this metal from its ores very difficult. There are few solvents to dissolve gold, and the chemicals that have been used in gold extraction efficiently are known to be extremely corrosive, toxic and hazardous to the environment.

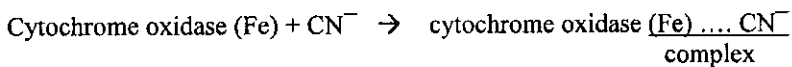
Cyanide is one of the few chemicals known to form a complex with gold and the reaction can be written as



The cyanide ion, CN^- , is a toxic agent. Some cyanide salts such as sodium cyanide have found applications in several processes like electroplating and gold recovery. It can be produced by nature, also. The natural sources of cyanide ions include the seeds of cherry, plum, peach, apple and apricot fruits, and peach leaves. There are even a few recorded instances of humans poisoned by eating large numbers of apple seeds [9]. Cyanide poisons by asphyxiation, and it works very rapidly. Cyanide interferes with oxidative enzymes, such as cytochrome oxidase. Oxidases are enzymes containing a metal, usually iron or copper. They catalyze the oxidation of substances such as glucose.



The iron atom in cytochrome oxidase is oxidized from Fe^{2+} to Fe^{3+} to provide electrons for the reduction of O_2 . The iron regains electrons from other steps in the process. The cyanide ion forms stable cyanide complex with the metal ion of the oxidase and renders the enzyme incapable of reducing oxygen or oxidizing the metabolite.



Since the electrons of iron are “frozen”, the mechanism by which the oxygen is used in the support of life is stopped. As a result, the cells start to die, and if this occurs fast enough in the vital centers, the victim dies [9].

Gold usually exists as fine particles disseminated within the ore. The ore usually needs to be crushed and ground to fine sizes to liberate the gold particles before a recovery process applied. The cyanide leaching became a popular process in the late nineteenth century. The use of cyanide presented a number of problems both during and after the recovery process since it is an extremely poisonous chemical to work with. However, the basic chemistry regarding gold mining worldwide has changed little in over one hundred years and cyanide continues to be the method of choice by far. There is another significant health hazard from the use of cyanide that remains a problem long after the initial cyanide toxicity dissipates. During processing, toxic heavy metals, such as lead and mercury, are released from the ores geochemical matrix. These can leach from tailings years after mining operations have stopped, to contaminate ground water, rivers and the

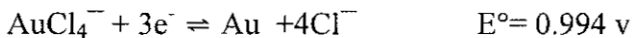
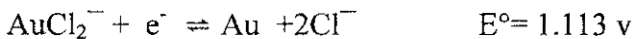
land. Reports on accidents, harms to wildlife or spills related to present day cyanide operations are seen frequently, and many abandoned operations continuous to contaminate the environment.

Because of its toxicity and environmental concerns, there is an increasing interest in finding alternates to gold recovery by cyanide leaching. In this study these alternative techniques are presented.

ALTERNATE PROCESSES

Chlorination

Before the cyanidation process was introduced, industry extensively applied chlorination in the 1880's to treat gold ores containing sulfides, for these ores were found to be not suitable for gravity concentration and amalgamation [1,4]. Gold dissolves in aqueous chloride solutions to form both Au(I) and Au(III), chloride complexes. The dissolution of gold occurs in two stages: first, the formation of Au(I) chloride on the gold surface, and the formation of AuCl_2^- during the second stage. This species, in turn, is either diffuses into the solution as AuCl_2^- or oxidized further to form AuCl_4^- , depending on the oxidizing potential of the solution [3]. The process needs very oxidizing conditions for gold dissolution, followed by the precipitation of metallic gold.



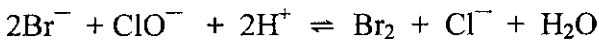
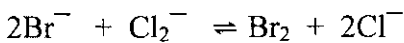
Gold dissolves extremely fast under acidic conditions and the passivation of gold is not expected [1]. When Au species are compared, the Au(III) complex is expected to be more stable in Au-Cl-H₂O systems.

According to the experiments conducted by Filmer and friends [1] using NaCN, thiourea and chlorine, the rate of dissolution with chlorine was the best, while the total extractions values of gold were found to be similar. The leaching and extraction processes can be influenced by the composition of the ores. For example, both silver and lead react with chlorine to form insoluble chlorides in chlorine-chloride solutions. This can reduce the solubility of gold because of the formation of an insoluble passivation layer, resulting in the loss of gold recovery. On the other hand, carbonates and other acid-soluble minerals will be dissolved in acidic chlorine-chloride media, and gold extraction may be enhanced with the decomposition of

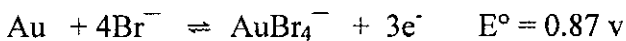
these minerals to expose locked gold [4]. The principal disadvantage of chlorine as a lixiviant for gold is the high reagent consumption in the presence of oxidisable material in leaching. Sulfides such as pyrite can dissolve faster (to form sulfates) than gold in chlorine solution, resulting in high reagent consumption. As sulfide content of an ore increases, this process becomes costlier and less attractive compared to the others. Incomplete dissolution of sulfides will result in reduction of the soluble gold. The application of chlorine leaching commercially is considered more difficult than that of cyanide for a number of practical reasons, too. The process requires very acidic conditions. Therefore, in addition to the safety concerns, complications arise in material selection, constructions and maintenance. The recovery of gold from chloride solutions by activated carbon requires very high loadings (greater than 50 kg/tonne). The carbon at these loadings is used for recovery of gold bullion. The gold that precipitates on activated carbon is, however, in a metallic form, resulting in significant losses due to abrasion [1]. Another restriction to commercial application of the process comes from the difficulties and health risk related to the transportation, storage and handling of the chlorine gas.

Bromine Leaching

Bromine was first introduced as a solvent for gold in 1846 [6]. A protonic cation, like NH_4^+ , and an oxidizing agent, when added to the solution, may enhance the rate of leaching by bromine. Bromide can be added to leaching solution along with chlorine and hypochlorite (as oxidant), converting bromide to bromine [6].



Daggar [5] conducted a series of experiments to recover gold using bromine. The complexation with bromine was used to expand the domain of gold dissolution. The dissolution of gold in bromide is an electrochemical process

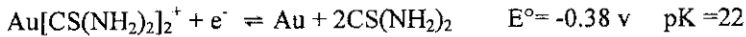


Many factors affected to dissolution of gold by bromine leaching such as bromine and gold concentration, pH and electrochemical potential of anodic and cathodic processes. Carbon adsorbtion, ion exchange, solvent extraction and precipitation by zink can be used to recover gold from the

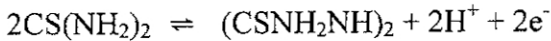
pregnant solution. He suggested that the bromine process had the potential to be a good and economic alternate to the cyanide leaching.

Thiourea Leaching

Thiourea is another reagent capable of extracting gold and is less toxic than cyanide [4,6]. It offers several advantageous properties such as high gold recovery and low sensitivity to base metals (Pb, Cu, Zn, As, Sb) and sulphur. The dissolution of gold is strongly affected by pH, and thiourea and oxidant concentration. Thiourea and gold form a single complex anion in acidic media.



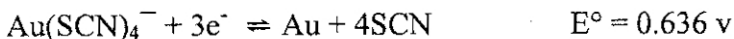
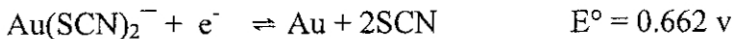
Thiourea has also several disadvantages in gold recovery. It can dissolve heavy metals in addition to gold, creating problems in handling and disposal of the effluent. It can easily be oxidized and consumed very rapidly under leaching conditions, giving rise to high reagent consumption [1,4]. The oxidation of thiourea to formamidine disulphide occurs as follows:



The oxidation of thiourea not only causes the loss of reagent, but also causes the generation of elemental sulphur in fine adhesive form, possibly from decomposition of formamidine disulphide, and this sulphur may cover the gold surface resulting in passivation of gold (6). Despite its low toxicity, thiourea is not a safe reagent at all. It is a potent thyroid poison for humans, and recognized as potentially carcinogenic [8].

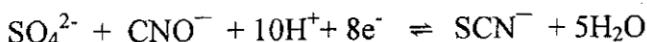
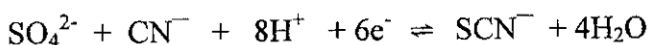
Thiocyanate Leaching

The thiocyanate ion, SCN^- , is considerably less harmful than cyanide ion [9]. Acidified thiocyanate in aqueous solutions can dissolve gold to form both Au(I) and Au(III) complexes, depending on the solution potential [4].



The thiocyanate ion has a linear structure with the carbon atom in the centre and is capable of forming covalent compound and complexes. The linearity of its structure is based on two resonance forms, $^- \text{S}-\text{C}-\text{N}$ and $\text{S}=\text{C}=\text{N}^-$, the combination of which can be regarded as the free ion. Thiocyanate is a

pseudohalide, forming the pseudohalogen thiocyanoge and thiocyanic acid. The oxidation of thiocyanate can occur in three redox systems [3]:



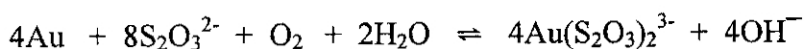
The first reaction is irreversible so that it can not be reduced back to SCN^- either chemically or electrochemically. The second reaction is an irreversible oxidation step resulting in the production of cyanate, CNO^- , or cyanic acid, HCNO , depending on the pH. The third reaction is the irreversible decomposition of metastable oxidation products (cyanate and cyanic acid) into carbondioxide and ammonia. Cyanic acid, which has a pKa of 3.91, is very unsatable in aqueous solutions. In a Au-SCN- H_2O system, below pH 3.9 HCNO is predominant, which leads to rapid decomposition into $\text{CO}_2 + \text{NH}_4^+$, whereas above pH 3.9 the cyanate ion predominates. Although it is more stable than cyanic acid, the cyanide ion is meta-stable, too, ultimately decomposing into carbonate and ammonia. According to Barbosa and Monhemius [3], in acidic media (pH range 1-3) the thiocyanate is an effective leaching chemical for gold, and Fe(III)-thiocyanate system can be used for treatment of ores. However, for good results, conditions less desirable for safety and the stability of the reagents, like low pH and very high temperature (85°C), are required.

Malononitrile

Malononitrile, $\text{CH}_2(\text{CN})_2$, can be used to leach gold under alkaline conditions. However, malononitrile is known to be a toxic chemical. Besides, this reagent is unsatable under strong acidic or basic conditions to produce unsubstituted amides. Its hydrolytic decomposition products, such as acetamide and cyanoacetamide, are suspected to be carcinogens [7].

Thiosulphate Leaching

Thiosulphate, $\text{S}_2\text{O}_3^{2-}$, is another reagent frequently mentioned in the literature on gold leaching. It is also reported that the process is enhanced by the presence of copper ions (6). Gold dissolves slowly in alkaline thiosulfate solution and usually dissolved oxygen is used as the oxidant to form the Au(I) complex [4]



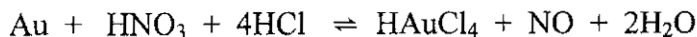
The process temperature and the concentrations of thiosulphate and dissolved oxygen are the major factors affecting the rate of dissolution. A process for the treatment sulfidic gold ores has been proposed whereby thiosulphate ions are generated in situ under alkaline oxidation conditions.

The use of thiosulphate in gold process commercially prevented by various reasons, such as high reagent consumption due to several oxidation and associated reactions, unfavorable effects resulted from the presence of other metals, and slow reaction rate.

USE OF OTHER CHEMICALS

Aqua Regia

Aqua Regia is a concentrated mixture of hydrochloric and nitric acids. This reagent, known as royal water or eau r'egale for it can solubilize gold, is frequently used to attack high gold alloys in places where nitric acid and sulphuric acid are not effective. Although gold forms stable complexes with chlorine ion, hydrochloric acid alone is not sufficiently strong oxidant to dissolve gold. Aqua regia is required to provide both strongly oxidizing and complexing components [2,4,6]. The dissolving action is due to the formation of chlorine and nitrosyl.



Aqua regia is used in small batch processes for refining gold. The steps usually go as leaching, boiling, settling, reduction, filtration and washing, followed by drying, melting and casting. However, the process will be excessively costly for treating ores. Besides, aqua regia is a toxic and extremely corrosive agent. These dangerous properties put further restrictions to its widespread use.

Selenic Acid

Selenic acid, H_2SeO_4 , can be used to leach gold. However, this compound is highly corrosive, costly and toxic. These factors combine to exclude its use in commercial gold extraction [8].

Mercury

Mercury can be combined with gold easily, and then removed by vaporization, leaving the gold as the residue. Mercury amalgamation was a popular way of extracting gold in the past. From the process the mercury

vapor enters the environment as long term toxic contamination. Mercury is acutely hazardous substance as a vapor and in water-soluble salts: Mercury is a quite volatile metal. It is easily inhaled and passes through the skin. The body has no quick means of ridding itself of this toxic element and there tends to be a build-up of the toxic effects leading to chronic poisoning [9]. It can cause irreversible brain, liver and kidney damages. Still, it has a rather peculiar fascination for many people and some even love to touch it. Although its use in gold recovery is banned now, it is believed that the process is not eradicated completely.

CONCLUSIONS

The information on chemicals and processes mentioned above comes from lab-scale investigations or literature work on related fields. Therefore, any suggested process needs to be refined further and tested for industrial viability. As alternatives to cyanide, aqua regia, selenic acid and mercury can be ruled out for they are more hazardous. The halogen using systems appear to be less toxic and much safer than cyanide usage for people and the environment. Other chemicals also are not very toxic compared to the cyanide and are not stable in the environment for extended period of time. However, they usually have other shortcomings relating to the processes or safety. For example, thiourea is known to be a potential carcinogen. One can find other lixivants suggested for gold recovery in the literature. For example, Haber Inc. offers a lixiviant that, according to them, acts more efficiently than cyanide with regard to speed and gold recovery, and is nonhazardous environmentally [8]. However, the composition of the lixiviant is not disclosed, and those claims have not been proven to be valid by an industrial application yet. Since there is no well-developed alternative for gold recovery yet, it seems that the cyanide leaching process will remain around at least for a while.

REFERENCES

- [1] Filmer, A.O., Lawrence, P.R. and Hoffmann, W., "A Comparison of Cyanide, Thiourea and Chlorine as Lixiviant for Gold," Gold: Mining, Metallurgy and Geology, The Australian Institute of Mining and Metallurgy, p.279. (1984)
- [2] Habashi, F. A Text Book of Hydrometallurgy, Metallurgie Extractive Quebec Enr., Quebec City, p209. (1993)

- [3] Barbosa, F.A. and Monhemius, A.J., "Leaching of Gold in the Thiocyanate Solutions," Institute of Mining and Metallurgy, London, Transactions, sec. C, vol.102, pp, 105-125. (1994)
- [4] Marsden, J. and House, L., The Chemistry of Gold Extraction, Ellis Horwood Limited, New York. (1992)
- [5] Daggar, A., "Extraction and Recovery of Gold from Concentrated by Bromine Leaching," Precioue Metal, Ed. by Jha, M.C. and Hill S.D., The Minerals, Metals and Materials Society, pp 227-239. (1988)
- [6] Yannapoulus, J.C., The Extractive Metallurgy of Gold, van Nonstrand Reinhold, New York. (1991)
- [7] Hiskey, J.B. and DeVries, F.W., "Environmental Considerations for Alternates to Cyanide Processing," Ed. by Chander, S., Proc. of Symposium on Emerging Process Technologies for a Cleaner Environment. Feb. 24-2, 1992, Phoenix, Arizona, AIME, Littleton, Colorado. (1992)
- [8] Haber Gold Processing, Information Brochure, Haber, Inc., New Jersey. (1999)
- [9] Jones, M.M., Netterville, J.T., Johnston, D.O., and Wood, J.L., Chemistry, Man and Society, Sec. Ed., W.B. Saunders Co., Philadelphia, pp 426-432. (1976)