

Maria C. COSTA *

HYDROMETALLURGY OF GOLD: NEW PERSPECTIVES AND TREATMENT OF REFRACTORY SULPHIDE ORES

In the last two decades a considerable number of new hydrometallurgical processes have been developed and implemented in gold industry allowing the economical treatment of increasingly complex and lower grade ores as well as refractory ores. As a result, all over the world the production of gold has almost doubled in the last 20 years. In order to overcome the environmental problems caused by cyanidation, new leaching agents have been searched and new leaching techniques, particularly heap leaching, were developed for the treatment of low grade ores. The developments related with gold extraction from pregnant solutions include, carbon-in-pulp, carbon-in-leach processes, the use of resins and solvent extraction techniques. A considerable effort has also been made to treat refractory ores. With that purpose pressure oxidation, bacterial oxidation and more recently electro-oxidation have been investigated with good results as alternative techniques to the classical oxidative roasting. In this paper those developments are revised and considerable attention is given to the electrochemical treatment of refractory sulphide ores.

CYANIDATION

The traditional hydrometallurgical process to recover gold from its ores and concentrates is cyanidation which consists in a cyanide leaching in basic media, described by the following reaction:



followed by zinc cementation according to:



After its first industrial application in 1889 at the Crown Mine in New Zeland (Fleming 1992), the process remained practically unchangeable for 80 years. However, in the last decades there have been developments to the traditional process in order to extend its applicability to different new materials (low-grade and some complex ores) and to turn the process more efficient and economic. Carbon-in pulp

* Universidade do Algarve, UCTA, Campus de Gambelas, 8000 Faro, Portugal.

(CIP), carbon-in-leach (CIL), resin-in-pulp (RIP) and resin-in-leach (RIL) are the examples of those developments, where activated carbon and resins are utilized directly in the pulp, alternatively to zinc, making useless filtration and decantation steps and decreasing capital and operating expenses. Although the advantages presented by resins – high selectivity and efficiency even for very dilute solutions – their use is not widely spread at the moment for economical reasons.

The synthesis of extractants able to combine leach-solvent extraction and electrowinning for the recovery of gold from low grade ores has been attempted. Several projects have been conducted with the aim of developing an extractant which would extract gold from typical cyanide solutions (Fleming 1992; Alguacil et al. 1994, Caravaca 1994; Kordosky et al. 1992) or from other alternative lixivants (Alguacil et al. 1993) and strip the gold into a purified solution from which the precious metal can be electroon. Weak base amines whether alone or modified with organophosphorous esters and/or oxides can extract gold at $\text{pH} < 9$. Quaternary amines show excellent extraction properties for gold at $\text{pH} = 10$. A series of compounds based on the guanidine functionality were specially synthesized for gold recovery from cyanide solutions. Several authors have commented the advantages that solvent extraction for gold recovery could offer over conventional technologies (Wan et al. 1990). The availability of a reagent able to joint successfully extraction and stripping steps may be the key to the successful application of solvent extraction-electrowinning technology.

Table 1. Leaching systems for gold

Leaching agent	Oxidant	Complexes	Ke^*	General conditions
Basic systems				
Cyanide	O_2	AuCN_2^-	2×10^{38}	$\text{pH} > 10$
Neutral systems				
Thiosulphate	O_2	$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	5×10^{28}	$\text{pH} > 7; T = 60^\circ\text{C}$
Bromide	Br_2	AuBr_4^-	10^{32}	$\text{pH} = 7$
Acid systems				
Chloride	Cl_2	AuCl_4^-	10^{26}	$\text{pH} < 2$
Ferric chloride	Fe^{3+}	AuCl_4^-		
Thiocyanate	$\text{Fe}^{3+}, \text{H}_2\text{O}_2$	$\text{Au}(\text{SCN})_2^-$	10^{17}	$\text{pH} < 3$
Thiourea	$\text{Fe}^{3+}, \text{H}_2\text{O}_2$	$\text{Au}[\text{CS}(\text{NH}_2)_2]_2^+$	2×10^{23}	$1 < \text{pH} < 2$

K_e^* - stands for stability constants of the complexes.

The application of heap leaching techniques for gold recovery is a relatively recent innovation which was developed by American researchers in the late 1960s (Fleming 1992; Wall et al. 1987). The process is very simple and consists in spraying dilute cyanide solution onto the top of the heap after piling the ore to a given height (generally between 3 and 18 m). The leach solution flows down through the heap to a collection pound and it is pumped through carbon columns for gold recovery. The pregnant solution containing usually 1–3 ppm of gold can also be treated by zinc cementation although carbon adsorption is more efficient for the treatment of large volumes of low-grade solutions. However refractory ores and ores containing species that consume excess of cyanide or oxygen are not suitable to heap leaching because of difficulties in controlling leaching chemistry within the heap. Heap leaching techniques for gold recovery from low-grade ores have become widespread in recent years (Maki 1989; Anderson 1989) because of their flexibility for small and large scale operation and very low costs.

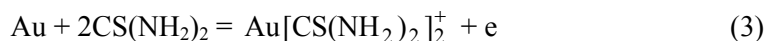
Despite the recognized advantages of cyanidation - simplicity, efficiency and economy – environmental and labour safety requirements, together with the need to treat increasingly low grade and complex sulphide ores, have stimulated the investigation and development of alternative non-toxic leaching agents. Table 1 lists the media usually considered for gold dissolution.

Overall, thiourea leaching has shown to be particularly successful. Due to its high complexing ability, it has long been recognized as an excellent reagent for precious metals leaching (Bruckard et al. 1993; Schulze 1984).

THIOUREA LEACHING

The dissolution of gold with thiourea solutions was first described by Plaksin and Kolkhova (Plaksin et al. 1941) but only in 1976 the process was applied in a French plant (Groenwald 1977). Several studies have been done to clarify the dissolution mechanism and the influence of the experimental parameters involved (Schulze 1984; Groenwald 1977; Deschènes et al. 1988)

Described generically by the following reaction:



the system requires the presence of an oxidizing agent ($\text{Fe}_2(\text{SO}_4)_3$, H_2O_2 , KMnO_4) to promote thiourea oxidation into formamidine disulphide, according to the reaction:



Gold is then oxidized in acid media forming with thiourea a stable complex:



The advantages and drawbacks of thiourea leaching have been extensively reviewed by several authors (Abrantes et al. 1995; Pyper et al. 1981). Fewer hygiene-environmental problems, higher rate of gold dissolution and lower degree of inhibition are the principal advantages. Due to the irreversible decomposition of formamidine disulphide:



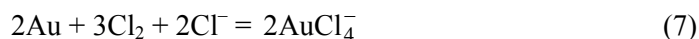
the high reagent consumption has been referred as the main disadvantage. To avoid the decomposition of formamidine disulphide, a strict control of the experimental conditions is required.

OTHER LEACHING SYSTEMS

Halogens

The use of halogens as gold lixiviantes has shown to be very promising considering the stability of the complex formed. Gold form Au (I) and Au (III) complexes with chloride, bromide and iodide, depending on the solution conditions, with the following order of stability: $\text{Cl}^- < \text{Br}^- < \text{I}^-$ (Distin et al. 1985).

Although there are some references to the chlorination of gold ores based on the reaction:



with good results, preference has been done to the use of bromide media.

The first reference of the use of bromide solutions dates from 1982 and the reaction involved is:



Excellent kinetics and high recovery percentages have been referred (Dadgar 1989).

McGraw and Coworkers (McGraw et al. 1985) have suggested the use of iodide electrolytes for sulphide ores leaching. In the last few years there has been a crescent interest for the use of iodide systems. The dissolution process can be described by the following reaction:

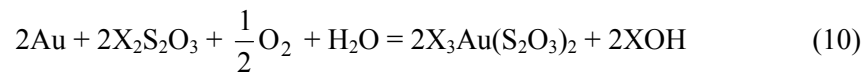


and presents as main advantages the high stability of the solutions and their low oxidation potential (Qi et al. 1991; Ahgelidis et al. 1995).

Thiosulphate

The first reported use of thiosulphate for precious metal extraction dates back to the beginning of the century. In that method, known as Patera's process, the ore was first roasted in a chloride atmosphere and just after a thiosulphate leaching was used to recover gold and silver (Zipperian et al. 1988).

After several decades the importance of thiosulphate was pointed out again by Berezowsky and Septon (Berezowsky et al. 1979) who developed a leaching process using ammonium thiosulphate for the recovery of gold and silver from residues with good results and successful kinetics. The metal dissolution generally occurs in neutral medium in the presence of oxygen:



where X – NH_4^+ or Na^+ , and a severe pH control is required (Berezowsky et al. 1979). The non-toxicity of the solutions involved and the high efficiency for both gold and silver turns the process very promising. The high reagent consumption is the principal obstacle to its industrial application.

Thiocyanate

The first paper reporting the ability of thiocyanate to recover gold dates back to 1905 (White 1905), but only in 1986 Fleming (Fleming 1986) referred again the potentialities of this compound for precious metal recovery.

Metal dissolution with thiocyanate needs acid medium and the use of oxidizing agents. The gold complexes obtained are $\text{Au}(\text{SCN})_2^-$ and $\text{Au}(\text{SCN})_4^-$. Because it is a very recent technique, its kinetics and thermodynamics are not yet well clarified.

Refractory gold ores

Refractory ores are characterized by low recoveries and high reagent consumption when subjected to direct leaching and several attempts have been done to process efficiently those raw materials. In the last few years with the depletion of high grade and free-milling ores and with the development of economic and feasible pre-treatment techniques, there has been an increasing interest by the exploitation and processing of that kind of raw materials (Fleming 1992; Komnitsas et al. 1989; Henley 1989).

The refractory behaviour can be due to several reasons. The most important cause of refractoriness is related with the fact that gold can be finally disseminated in small particles within the mineral layer, usually arsenopyrite or pyrite. In that case gold is called invisible because it is not detected by the usual detection techniques and it is not accessible to the leaching agent. Some tellurides and carbonaceous ores are also

suspected to occlude gold inside their lattice. Other causes of refractoriness are due to chemical reactions between the minerals and the compounds used in the leaching solutions. Minerals such as pyrite (FeS), covellite (CuS) and chalcocite (Cu₂S) as well as native copper can react with cyanide decreasing the efficiency of leaching (Komnitsas et al. 1989). Other species like Fe²⁺, S²⁻, S₂O₃²⁻ and arsenates tend to consume the oxygen vital for the metal dissolution with cyanide and thiosulphate (Iglésias et al. 1993). In these cases changing the leaching agent can be the most practical solution.

During roasting or other metallurgical operations, the formation of insoluble products or the occurrence of passivation phenomena (formation of iron and lead oxides and antimony compounds) can also be responsible for low recoveries.

The presence of carbonaceous materials reduces gold extraction by virtue of their ability to re-adsorb gold once it has been leached, a phenomenon that is known as preg-robbing in the industry. Blinding and deactivation of the carbonaceous ores with organic compounds such as kerosene is a cheap method among others to solve the problem (Fleming 1992).

In order to overcome the refractory character presented by such ores a pre-treatment is required to breakdown the sulphide matrix and renders the gold amenable for recovery prior the application of any conventional treatment. The traditional route to treat these types of raw materials is by oxidative roasting of the sulphides before leaching, generally cyanidation. Alternative viable methods of oxidation have been developed to eliminate pollution problems caused by the emission of toxic gases (SO₂ and As₂O₃) during oxidative roasting. These new methods include pressure oxidation, bio-oxidation and more recently electrooxidation which has shown to be an efficient and promising technique (Costa 1996).

PRE-TREATMENT OF REFRACTORY ORES

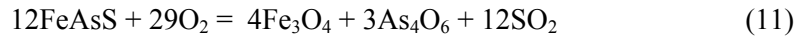
Grinding

Grinding can be the most simple solution for ores that present a suitable granulometric size. For low granulometric sizes, a more drastic treatment is necessary.

Roasting

Roasting is the most popular process for the treatment of refractory sulphide ores and it is practised since 1898 (Fleming 1993). It is also used for carbonaceous materials because it is the only efficient way to eliminate completely the carbon content. The process consists in the transformation of iron sulphides to high porosity iron oxides:

Arsenopyrite



In spite of being a well-established method widely applied, it is expensive and environmentally undesirable considering the present standards for a clean environment. Thus, the pollution problems caused by roasting have stimulated the investigation of new hydrometallurgical treatments based on chemical, biological and electrochemical oxidation.

Pressure oxidation

In recent years there has been an increasing tendency in the industry to use pressure oxidation instead of the traditional roasting methods not only for environmental reasons but also because gold recovery after pressure leaching is generally superior than that achievable from roasted calcines (Fleming 1993). It is a particularly aggressive pre-treatment for highly refractory ores conducted at high temperatures (100–210 °C) and pressure (700–2200 kPa) in oxygen atmosphere. It allows simultaneously the oxidation and dissolution of sulphide compounds, e.g.:

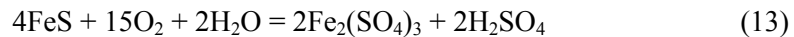
Arsenopyrite:



The solid residue is usually leached with cyanides but thiourea has also been used efficiently (Komnitsas et al. 1989). The process is highly influenced by pH and temperature. The high acidity promotes sulphide dissolution while the temperature can cause the formation of elemental sulphur which can affect the extraction of gold negatively. In spite of its high efficiency and excellent kinetics the application of pressure oxidation is limited by the operating costs (Fleming 1993, Iglésias et al. 1993).

Bacterial oxidation

Bacterial leaching is a biological process in which a bacteria (*Thiobacillus ferrooxidans*) is used to promote the chemical breakdown of the sulphide matrix represented as followed for pyrite:



Despite the large number of Biox plants in operation (Van Aswegen 1993), the process which is environmentally very attractive presents some drawbacks including a poor kinetics and the high dependency of bacterial attack on the type of ore to be treated.

Electrooxidation

The advantages of electroleaching to recover basic metals from sulphide ores (Ngoc 1990; Abrantes et al. 1993) have drawn attention to the possibility of applying a similar process as an alternative pre-treatment to improve the recovery of gold from refractory sulphide ores.

Recent investigation has proved that electro-oxidation is a potential alternative to the traditional pre-treatment of refractory gold ores (Costa 1996; Abrantes et al. 1996). A Portuguese arsenopyrite concentrate showing refractory behaviour was submitted to electrochemical oxidation (+800mV (SCE) applied potential for 1hour) in chloride acidic medium (NaCl 1.9 M + HCl 0.1 M) before leaching the anodic residue with thiourea. The efficiency of electrochemical treatment was emphasized by comparing with the results of direct leaching under the same conditions. After acid thiourea leaching of the electroreacted residue up to 90% of gold was extracted while only 21% was achieved by direct leaching (Abrantes et al. 1996). Previous published studies (Costa 1996; Abrantes et al. 1996) discuss the influence of the operative parameters (temperature, electrolysis time, current and slurry density) on the metal extraction, showing that future improvements can be done by the careful selection of the operating conditions.

Surface spectroscopic techniques were recently used to characterize the altered surface of a mineral sample of arsenopyrite submitted to anodic oxidation (Costa 1997) in order to understand the phenomena responsible for the release of the gold encapsulated inside the mineral layer. According to those studies, electro-oxidation of arsenopyrite at +800 mV in acid media allows the release of the gold occluded in the sulphide matrix by the occurrence of the main following reactions:



and



Although elemental sulphur seems to be the predominant compound in the oxidized surface of arsenopyrite, its formation does not affect the efficiency of the process by passivation phenomena since almost all the gold was subsequently recovered. This fact can be due to the formation of porous layers or due to the use of a slurry system in which the particles are being continuously agitated.

CONCLUSIONS

Although cyanide has been used almost universally until recently there has been a great deal of research for alternative leaching agents in the last 15 years. This is due to concerns related to the ability of the industry to deal with more and more stringent

environmental regulations. At the same time new developments of cyanidation and new leaching techniques were tried.

The increasing demand of gold world-wide and the depletion of the high grade ores turned low grade and/or refractory deposits an increasingly important source of precious metals. Thus, the treatment of refractory ores is a potential niche application while alternative lixivants could become important in the near future.

The extraction of gold from a Portuguese arsenopyrite concentrate exhibiting refractory behaviour proved that electro-oxidation can be a potential alternative pre-treatment to the traditional roasting techniques. In fact, the application of an anodic potential in a chloride acidic media enhance considerably the response of the raw material to the subsequent hydrometallurgical treatment by the sulphide matrix transformation mainly into elemental sulfur and sulfates.

REFERENCES

- ABRANTES L.M., ARAÚJO L.V., 1993, Proc. of Milton Wadsworth Int. Symp. on Hydromet., Hiskey J., Warren G. (eds.), SME-AIME, Littleton, 957.
- ABRANTES L.M., COSTA M.C., 1996, Hydrometallurgy, 40, 99.
- ABRANTES L.M., ZHENG Y.Z., 1995, Min. Eng., 8, 20, 30.
- AHGELIDIS T.N., KYDROS K.A., 1995, Hydrometallurgy, 37, 75.
- ALGUACIL F.J., CARAVACA C., MARTÍNEZ S., COBO A., 1994 Hydrometallurgy, 36, 369.
- ALGUACIL F.J., CARAVACA C., 1993, Hydrometallurgy, 34, 91.
- ANDERSON D.A., 1989, Min. Eng., 1186.
- BEREZOWSKY R.M., SEPTON V.B., 1979, 108th AIME Annu. Meet., New Orleans.
- BRUCKARD W.J., SPARROW G.J., WOODCOOK J.T., 1993, Hydrometallurgy, 33, 17.
- CARAVACA C., Hydrometallurgy, 1994, 35, 27.
- COSTA M.C., ABRANTES L.M., 1997, *A study of the surface oxidation of arsenopyrite by X-ray photoelectron spectroscopy and Raman spectroscopy: Relation to the treatment of refractory gold ores*, submitted to publication.
- COSTA M.C., 1996, Ph.D. Thesis, Faculty of Sciences of Lisbon, Portugal.
- DADGAR A., 1989, J. Metals, 41, 37.
- DESCHÈNES G., GHALI E., 1988, Hydrometallurgy, 20, 179.
- DISTIN P.A., DEMOPOULOS G.D., 1985, J. Metals, 37, 7, 46.
- FLEMING C.A., 1992, Hydrometallurgy, 30, 1-3, 127.
- FLEMING C.A., 1986, Proceed. of the Int. Conf. on Gold, S. Afr. Inst. Min. Metall., Joanesburg, 301.
- GROENWALD T., J. S. 1977, Afr. Inst. Min. Metall., June, 217.
- HENLEY K.J., 1989, Min. Eng., 2, 4, 459.
- IGLÉSIAS N.I., PALENCIA P., CARRANZA F., 1993, Proceed. of EPD'93, ed. J.P. Hager, TMS 99.
- KOMNITSAS C., POOLEY F.D., 1989, Min. Eng., 2, 4, 449.
- KORDOSKY G.A., SIORAKOSKI J.M., VIRNING M.J., MATTISON P.L., 1992, Hydrometallurgy, 30, 1-3, 291.
- MAKI T.D., 1989, Min. Eng., Dec. 1189.
- MCGRAW K.J., MURPHY J., 1985, US Patent 4557759.
- NGOC N.V., SHAMSUDDIN M., PRASAD P.M., 1990, Metall. Trans B, 21B, 611.
- PLAKSIN I.N., KOZHUKHOVA M.A., 1941, Akad. Nauk. SSSR Doklady, 31, 7, 671.
- PYPER R.A., HENDRIX J.L., 1981, Extraction Metallurgy'81, IMM 57.
- QI P.H., HISKEY J.B., 1991, Hydrometallurgy, 27, 47.
- SCHULZE R.G., J. Metals, 1984, 36, 6, 62.

- VAN ASWEGEN P.C., 1993, Proc. of Milton Wadsworth Int. Symp. on Hydromet., J. Hiskey, G. Warren (eds.), SME-AIME, Littleton, 709.
- WALL N.C., HORBY J.C., SETHI J.K., 1987, Min. Mag., May 393.
- WAN R.Y., MILLER J.D., 1990, *Gold Advances in Precious Metals Recovery*, N. Arbiter, K.N.Han (eds.), 143.
- WHITE H.A., 1905, J. Chem. Metall. Min. Soc. S. Afr., 61, 09.
- ZIPPERIAN D., RAGHAVAN S., 1988, Hydrometallurgy 19, 361.

Costa M., Hydrometalurgia z³ota. Nowe perspektywy i przeróbka trudno wzbogacalnych rud siarczkowych. *Fizykochemiczne Problemy Mineralurgii*, 31, 63–72 (w jêz. angielskim)

W ciągu ostatnich dwudziestu lat opracowano i zastosowano wiele nowych procesów hydrometalurgicznych dla rud złota co pozwoliło na ekonomiczną przeróbkę rud niskoprocentowych i rud trudno wzbogacalnych (*refractory ores*). W wyniku tego, w ciągu ostatnich 20. lat światowa produkcja złota uległa podwojeniu. W celu przewycięzenia problemów związanych z ochroną środowiska powodowanych stosowaniem cyjanków poszukiwano nowych odczynników ługujących jak również nowych technik ich przerobu. Opracowano także ługowanie na hałdach rud niskoprocentowych. Zanotowano też postęp dotyczący usuwania złota z roztworu macierzystego, ługowania metodą carbon-in-pulp, metodą carbon-in-leach, użycia żywic oraz ekstrakcji rozpuszczalnikowej. Opracowano szereg metod przerobu trudno wzbogacanych rud jak utlenianie ciśnieniowe, utlenianie bakteryjne, a ostatnio elektrotlenianie jako alternatywne techniki do klasycznych metod prażenia utleniającego. W tej pracy dokonano przeglądu tych zagadnień zwracając szczególną uwagę na elektrochemiczną przeróbkę trudno wzbogacalnych rud siarczkowych.