NON-CONVENTIONAL METHODS FOR SOLUBILIZING MINERALIZATIONS WITH PRECIOUS METAL CONTENT

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Abstract: *There is an increasing trend worldwide to replace cyanide-based technologies with alternative gold and silver recovery technologies from minerals and mining concentrates containing precious metals, which have a low risk of environmental pollution surrounding. Gold recovery processes have been improved over the years. The latest improvements to extraction technologies are not only about economic issues - by increasing efficiency and reducing costs, but also about environmental issues, especially with regard to the emissions of gas and liquid effluents discharged from gold mining facilities.*

1. Introduction

Cyanide is still widely used in the mining industry, either as a complex reagent for the recovery of gold and silver, or as a depressant reagent in flotation circuits. According to the data provided by DuPont (SUA), approximately 570 tons of sodium cyanide is consumed annually in mining, the most used cyanide [D. Clifford, 1991].

At present, there are over 460 mining units in the world that process the ores by cyanide to extract gold and silver. In recent years, new gold recovery processes have been investigated from ores or mining concentrates based on the use of less reactive reagents than cyanide.

Below are some examples of alternative cyanide reagents, along with the advantages and disadvantages of possible technologies based on them [*Alternative lixiviants for gold recovery*, *www.cyplus.com*, S. Gos, A. Rubo, www.degussa-huels.de].

Table 1. *Solubilizing agents. Advantages and disadvantages*

″Alternative″ reagent	Possible advantages	Disadvantages	Applications mentioned in the literature
THIOUREA $Au + 2CS(NH_2)_2 = Au(CS(NH_2)_2)_2^+ + \bar{e}$	Proven, technology Availability Recommended for refractory ores High velocity of dissolution of gold	• Limited recyclability due to decomposition • Considerable costs for effluent decontamination • Difficulties in controlling process parameters • Limited applicability	Industrial scale application in: Australia, China, France (*Miner Eng. 1999, vol. 12, No. 6)*
THIOSULFATE $Au + 2S_2O_3^{2-} = Au(S^1{}_2O_3)_2^{3-} + \bar{e}$	Proven, technology Availability Recommended for refractory ores Gold solubilisation performance (> 99%)	• Limited recyclability due to decomposition • Considerable costs for effluent decontamination • Difficulties in controlling process parameters • Limited applicability	Pilot scale application in Nevada, USA *(Hunter R. et al. Yes Technologies, Process Brochure)*
THIOCYANATE $Au + 2SCN^- = Au(SCN)_2^- + \bar{e}$	It can act on a wide range of pH Partially recyclable	• Limited availability • Appreciable costs for effluent decontamination • Requires higher temperatures (85^0C)	There are no applications at the industrial scale

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″Alternative″ reagent	Possible advantages	Disadvantages	Applications mentioned in the literature
DISULFIDE $Au + H_2S + HS^- = Au(HS)_2^- + ½ H_2$	Availability Recommended for bio oxidized pulps, where bacteria can use sulphate ions and hydrogen to reformulate the bisulfide ⇒ Recyclable reagent	• Very low dissolution velocity (about 50% after 80 h) • High costs for decontamination • Limited applicability	There are no applications at the industrial scale
AMMONIA $Au + 2NH_3 = Au(NH_3)_2^+ + \bar{e}$	Availability Recyclable Recommended for refractory ores	• It can't be neutralized - it needs to be recycled • Requires high temperatures and pressures for acceptable performance • Selective uncertainty	There are no applications at the industrial scale
HALOGENS / HALIDES $Au + 2X^- = AuX_2^- + \bar{e}$ $Au + 4X^- = AuX_4^- + \bar{e}$ X = Cl, Br, I	Technology confirmed Availability Recommended in most types of ores Good performance solubilisation	• Handling and difficult process control • Requires an oxidant, most often halogen halide used	The use of chloride for gold refining is a proven technology There are no applications at the industrial scale

Table 2. *Optimal solubilisation conditions for different solubilizing agents*

Solubilisation agent	Oxidizing	Complex	Ke*	General conditions
Bazic systems				
Cyanide	O_2	$AuCN_2^-$	$2 \cdot 10^{38}$	pH > 10
Neutral systems				
Thiosulfate	O_2	$Au(S_2O_3)_2^{3-}$	$5 \cdot 10^{28}$	pH > 7; T = 60˚C
Bromide	Br_2	$AuBr_4^-$	10^{32}	pH = 7
Acid systems				
Chloride	Cl_2	$AuCl_4^-$	10^{26}	pH < 2
Iron chloride	Fe^{3+}	$AuCl_4^-$		
Thiocyanate	Fe^{3+}, H_2O_2	$Au(SCN)_2^-$	10^{17}	pH < 3
Thiourea	Fe^{3+}, H_2O_2	$Au[CS(NH_2)_2]_2^+$	$2 \cdot 10^{23}$	1 < pH < 2

Ke = stability constant of complex formed*

All reagents presented have the property of forming, under certain conditions, complexes of water-soluble gold but having different stability constants (Ke) [Costa C. Maria, 2007].

The presented ones show that there is an increasing trend worldwide to replace cyanide-based technologies with alternative gold recovery technologies from mines and mining concentrates, which have a low risk of environmental pollution.

2. Unconventional techniques for treating ores containing gold and silver

The aim of these processes is the solubilisation of gold and silver from the original material or oxidized in advance by treatment with unconventional / alternative cyanide complexing reagents.

2.1. Solubilisation with thiourea

Of the cyanide alternative complexing agents, thiourea has been most closely watched due to the following advantages over cyanide:

- is a non-toxic reagent for the environment;
- ensures high solubilisation velocity of gold and silver and consequently a much shorter leaching time for precious metals;
- the dissolution rates of precious metals are influenced to a much lesser extent by the presence of "cyanide" metals, such as Cu, As, Fe, Zn.

Due to its high complexity capability, thiourea has been recognized as an excellent leaching agent for precious metals (Thiourea, World Health Organization Geneva, 2003).

Approximately 25% of the annual thiourea produced worldwide is used as a leaching agent, especially for extracting gold and silver. (W. T. Yen and D. M. Wyslouzil, 1985)

The process of dissolving gold in acidic thiourea solutions is based on the following chemical reaction:

$$Au^{+} + 4\,CS(NH_2)_2 + 2\,Fe^{3+} \rightarrow 2\,Au[CS(NH_2)_2]_2^{+} + 2\,Fe^{2+}$$

The presence of moderate oxidizing agents such as Fe^{3+} ions, perhydrol or dissolved oxygen is obligatory for the solubilisation of gold, which causes the conversion of a certain quantity of thiourea to formamidine-disulfide protonated, the main ionic species that complexes and dissolves the precious metal from the leached material:

$$2CS(NH_2)_2 \xrightarrow{H2O2} [(NH_2)_2\,C\text{-}\,S - S - C\,(NH_2)_2]^{2+} + 2e^{-}$$

This reaction takes place rapidly, the subsequent oxidation reactions being much slower. In sulphate medium and containing Fe^{3+} ions, the oxidation is due to the presence of Fe^{3+} / Fe^{2+} couple:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}\ ;\ E^{0} = +0{,}77\ V$$

In parallel with the dissolution process, a secondary decomposition reaction of the formamidine-disulfide protonated occurs with the formation of colloidal sulphur.

The kinetics of the leaching process being controlled by the rate of diffusion of the reagents into the ore granule, the presence of colloidal sulphur may inhibit or even inhibit dissolution by forming an insoluble film on the ore surface.

Maintaining an acidic pH (≤ 4), a suitable temperature (t = 20 - 25^{0}C), as well as adding substances that maintain a relatively constant potential of the solution ($NaHSO_3$, Na_2SO_3) and implicitly a constant concentration of Fe^{3+} in the system, ensures that the effects of the secondary reaction are diminished.

The main parameters influencing the liquefaction of precious metals with thiourea in acid environment are:
- fineness of grinding of the material;
- the addition of ferric sulphate and the concentration of Fe^{3+} ions in lees;
- acid concentration in the leaching solution;
- the concentration of thiourea in lecithin
- the liquid / solid ratio ie solution / ore;
- addition of Na_2SO_3;
- the solubility temperature;
- solubilization time;

2.2. Solubilisation in acidic solutions of sodium chloride and hypochlorite

Gold is dissolved in chlorine-rich aqueous solutions (pH ≤ 2) and oxidizing, and the complex ion of trivalent gold, $[AuCl_4]^{-}$ is the only stable species present [J.B.Hiskey 1984]

Under the above-mentioned conditions, the existence of the $[AuCl_2]^{-}$ ion in aqueous solution is not possible, since this ion suffers a disproportion:

$$3[AuCl_2]^{-} \leftrightarrow 2\,Au^{0} + [AuCl_4]^{-} + 2\,Cl^{-}$$

In solutions obtained from hydrometallurgical and electrolytic processes using concentrated chloride solutions, it is expected that $[AuCl_2]^{-}$ is the predominant species. In the presence of strong enough oxidants, such as nitric acid, dissolved chlorine, hypochlorous acid or sodium hypochlorite, in chloride solutions the gold will be in the form of $[AuCl_4]^{-}$ [J.B.Hiskey 1984].

In dilute sodium chloride solutions, silver chloride is hypothetically insoluble; but when the chloride concentration increases, appreciably increases the solubility of silver chloride.

Hypochlorite reacts with sulphides from ores after the following reactions:

$$ClO^{-} + S^{2-} + H_2O = S^{0} + Cl^{-} + 2\,OH^{-}$$
$$2\,ClO^{-} + S^{0} + H_2O = SO_4^{2-} + 2\,Cl^{-} + 4\,H^{+}$$

Secondarily, sodium hypochlorite can decompose, decomposition which is favoured by the presence of metallic oxides from ores. The decomposition process of NaClO can be inhibited by the addition of cyanuric acid, but also a decrease in the rate of solubilisation occurs.

Although the mixture of NaCl and NaClO was originally designed for in-situ leaching of precious metals, he soon found a wide range of applications, especially in the landfill process.

The process is similar to cyanide as a complex reagent: the NaCl and NaClO mixture is added to the top of the ore dump and as it passes through it, the precious metals are dissolved.

The rich solution is collected in a basin and first led into an activated charcoal column for gold retaining and then to an electrolysis cell for regeneration of NaClO for recirculation.

2.3. Solubilisation with ammonium salts (thiosulphate, etc.)

Han Keneth and MengVinhui 1994, propose a process for the extraction of gold and silver from ores and other materials with ammonia. The process comprises the step of pulverizing the gold ore in an aqueous ammonia solution with one of the ammonium salts: $((NH_4)_2SO_4$, NH_4I, $(NH_4)_3PO_4$,

NH_4Br,$(NH_4)_2CO_3$)in a concentration of 0.1-2 mol/l and an oxidant O_2, O_3, hypochlorite or H_2O_2.

Heat the suspension at 100-300 ° C and 100-1000 psi to form a solution containing a gold and silver amine (complex) followed by the recovery of gold and silver in this solution. The process is efficient for refractory ores in cyanide, including for coal. This process does not use cyanide, being cheaper, less dangerous and has a wide domain of application.

Bacterial pre-treatment and solubilisation with thiosulfate of a sulphur-containing ore containing refractory gold

Experimental tests were performed on a sulphide ore [Irena I Spasova et al, 2012], pyrite being the main mineral sulphide in ore containing gold, but mineralogical analysis also revealed galena, chalcopyrite. The total sulphur content of the ore was about 2%.

The first stage consisted in the release of gold and silver from the sulphide matrix as a result of sulphide oxidation using acidophilic chemolithotrophic bacteria.

The gold and silver released were solubilized in the second step using solutions containing thiosulfate and amino acids as complexing agents.

Approximately 90% of gold and 70% of silver were extracted in this way, the bacterial solubilisation time being 20 days.

The various acidophilic chemolithotrophic bacteria can oxidize sulphides in soluble sulphates and release this gold. The oxidation is carried out in dilute sulphuric acid solutions in which the exposed gold is not soluble. Gold remains in solid residues after bacterial oxidation and is subjected to the percolation process with suitable reactants such as cyanide, thiosulfite and thiourea [Livesey-Goldblatt et al., 1983; Groudev and Groudeva, 1993; Neale et al., 2011).

At present, most industrial operations for the bacterial pre-treatment of gold-containing sulphuric concentrations use mixed mesophilic chemilotrophic bacteria, especially Acidithiobacillusferrooxidans, Acidithiobacillusthiooxidans and Leptospirillumferrooxidans.

Some moderate thermophilic bacteria, especially the Acidithiobacilluscaldus species and several species of the Sulfobacillus species, as well as some extremely thermophilic bacteria of the genus Sulfolobus and Acidianus, are capable of oxidizing sulphuric minerals.

Pyrite and arsenopyrite are usually the main sulphur-containing minerals that contain gold. Extracting gold and silver from the bacterial pre-treated concentrations depends on the degree of oxidation of the pyrite.

However, in some cases, it is necessary to oxidize only a relatively small quantity of pyrite to succeed in large extractions of gold and silver. This is due to the fact that in some mineralogical species of pyrite, these precious metals are located especially in places where the pyrite crystalline network is defective and these places are mostly attacked by chemolithotrophic bacteria.

In most industrial operations, solubilisation of gold is achieved with cyanide solutions. Cyanides, however, are particularly toxic reagents and can cause serious environmental problems.

At the same time, it has been shown that gold and silver are efficiently solubilized by means of ammonium thiosulphate solutions. In some cases, amino acids were added to these solutions [Groupev et al., 1996].

Amino acids have the ability to complex heavy and precious metals [Gillard et al., 1973] and stabilize thiosulphate. It has been found that the addition of some amino acids to the thiosulphate solutions increases the extraction of gold and silver and decreases the consumption of thiosulfate [Groudev et al., 1993; Michel and Frenay, 1998; Freg and van Deventer, 2011].

The source of the amino acids to be used in such solubilisation systems may be different. The most economically attractive is the use of protein hydrolysates obtained from various protein-rich wastes, including microbial biomass, and containing mixtures of various amino acids in suitable proportions.

2.4. Solubilisation in acidic solutions of calcium chloride and hypochlorite

The HCl-CaCl2 leaching process is an effective way of recovering precious metals, especially from hematite residues containing plumbo-jarosite [J.Viñals, C.Nuñez, J.Carrrasco 1991].

Experiments performed by J.Viñals on samples of such residues from southern Spain (3.1 g / t Au, 62 g / t Ag, 0.03% As, 2.2% Pb, S 1.8% S) shows that the solubilisation of the gold proceeds in 90-95% yields when working under the following conditions: 300 g / l CaCl2, 0.3-0.5 M HCl, t = 85-900C, solution / ore ratio = 1 / 2.5, solubilisation time = 1h.

2.5. Solubilisation with sodium chloride in dilute nitric acid medium

The HYDROCOIL process is a one-step recovery process of Au and Ag in which sodium chloride is used in dilute nitric acid media to mobilize precious metals in solution [A.W. Morrison, L.F.Robinson, M.N.Anderson, 2010].

Company H.M.C. Technology PLC in England has focused its research on the reaction of dilute nitric acid and alkaline metal chlorides with refractory gold minerals. The method is fast and does not require expensive investment or special equipment for working under pressure. Experimental tests with 10% NaCl leaching solution containing 35% HNO_3 resulted in 99% gold solubility at temperatures between 95^0 and 100^0C after only 30 minutes of reaction.

Oxidation with HNO_3 to Au associated in sulphide ore is a complicated phenomenon. The reaction of metal sulphide with HNO3 produces sulphate, nitrogen oxide and water. However, in the presence of NaCl, the "nitro" ions form nitrosyl chloride, which quickly attacks gold.

The other metals in the ore - As, Sb - are also oxidized in this strongly oxidizing environment. It follows that the nitric acid requirement can't be calculated solely on the basis of the reaction stoichiometry, but an excess must be added to compensate for its consumption in the oxidation reactions with the accompanying metals.

3. Conclusions

In Romania, precious metals are not recovered, on an industrial scale, by unconventional processes, with a low environmental risk. The gold mining concentrates are cyanurate and solubilized precious metals are recovered by adsorption on activated carbon (CIL technology), followed by elution with concentrated sodium cyanide solution, electrolysis or Zn dusting (Merrill Crowe process) and then refining in order to obtain gold in ingot.

Although the ores cyanation has a number of advantages (simplicity, efficiency and economy), environmental requirements, coupled with the need to extract gold as efficiently as possible from poor, complex or refractory ores, require the replacement of cyanide-based processing technologies and stimulate investigations for the development of processes using non-toxic, alternative, solubilising agents.

As a result, only those reagents should be selected to ensure the formation of complexes with a stability constant high enough to achieve the highest economic performance (a high degree of gold recovery and recirculation of lean waste, energy consumption and reagents as small as possible). In the same time, we must to achieve the most environmentally friendly impact through the emission of compounds whose degradation products are not toxic to animal or plant organisms.

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Scientific reviewer:
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