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New Technology for Recovery of Gold and Silver by Pressure Cyanidation Leaching and Electrocoagulation

José R. Parga¹, Jesús L. Valenzuela² and José A. Díaz¹

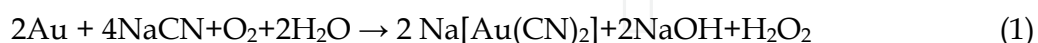
¹*Department of Metallurgy and Materials Science Institute
Technology of Saltillo, Saltillo Coahuila*

²*Department of Chemical Engineering and Metallurgy
University of Sonora, Hermosillo, Sonora
México*

1. Introduction

The present chapter describes a new technology of pressure oxidation/cyanidation leaching for the dissolution of gold and silver and the recovery of the precious metals by using the electrochemical process of Electrocoagulation (EC). The novel method demonstrates that the oxidation and dissolution of gold and silver in alkaline cyanide solution can be conducted simultaneously in the same reactor in less than 90 minutes with a recovery that exceeds 96%. Then, the pregnant cyanide solution with gold and silver is sent for recovery of precious metals by using a very promising electrochemical technique (EC) that does not require high concentrations of silver and gold in cyanide solutions.

Gold is classed as a noble metal because of its inertness to most chemical reactions under ordinary conditions. At the present time, cyanidation has superseded all previous leaching processes, particularly chlorination, because of its ability to effectively and economically treat ores containing as little as 1-3 g/ton gold. Cyanidation processes are especially suitable for treatment of gold/silver-bearing sulphidic materials. Gold cyanidation has been reported to involve the chemical reactions shown in Eqs. (1) and (2). Silver is accomplished in the same fashion (Senanayake, 2008; Parga et al., 2007).



The Equation (1) proposed by Elsner is stoichiometrically correct but does not describe the cathodic reactions associated with the dissolution. The stoichiometry of the process shows that 4 moles of cyanide are needed for each mole of oxygen used. At room temperature and std. atmospheric pressure, approximately 8.2 mg of oxygen are present in one liter of water. This corresponds to 0.27×10^{-3} mol/L. Accordingly, the sodium cyanide concentration (molecular weight of NaCN = 49) should be equal to $4 \times 0.27 \times 10^{-3} \times 49 = 0.05$ g/L or approximately 0.01%. This was confirmed in practice at room temperature by a very dilute

solution of NaCN of 0.01% - 0.5% for ores, and for concentrates rich in gold and silver of 0.5 % -5 % (Parga et al., 2007). Details of this electrochemical reaction have received considerable attention and under certain circumstances the reaction is limited by the coupled diffusion of CN⁻ and O₂ to the gold surface. Lime or sodium hydroxide (caustic) is added to keep the system at an alkaline pH of 10-11. This protective alkalinity is required to counteract the generation of acid during cyanidation, thereby preventing cyanide degradation and the formation of the deadly HCN gas.

Gold and silver ores are classified as refractory when a significant portion of the precious metals cannot be extracted by the conventional cyanidation process. The refractoriness may be of a physical or chemical nature. The former type is usually due to sub-microscopic particles of gold being locked within mineral particles, for example in sulphides or silicates. Refractory gold-silver ores contain precious metals locked up in a matrix of pyrite and/or arsenopyrite (Parga et al., 2007). Such ores are not amenable to cyanidation. To liberate the gold-silver from the sulfide matrix and render it accessible to cyanidation. It is a common practice to subject them to a preoxidation in order to enhance the recovery of the precious metals. Although effective, these techniques result in the production of large quantities of environmental hazardous substances such as sulphur dioxide gas or sulfuric acid, which can cause difficulties in compliance with environmental pollution regulations. After review of the literature (Parga et al., 2007), it was shown that roasting is currently the most cost effective means of oxidizing refractory pyrite and arsenopyrite concentrates to produce a product amenable to the cyanidation process. However, the major drawback of roasting is that it produces large quantities of SO₂ gas which is released into atmosphere and this is not acceptable. The sulphur dioxide must be collected, or an alternative technology used. One such alternative process that has previously been used successfully around the world, is that of pressure aqueous pre-oxidation of the sulphide minerals. Pressure oxidation has been the most popular method for the treatment of refractory gold concentrates (see Table 1); This process utilizes oxygen or air at high pressures and temperatures to oxidize an aqueous slurry of the ore or concentrate to produce hematite, iron sulphates and considerable quantities of free sulphuric acid. Because of this, before the cyanidation process excessive lime or caustic soda must be used in order to the pH of the pulp to 10 or 11.

This process, which is used in many commercial plants around the world, involves the recovery of the precious metals by oxidation pretreatment followed by traditional cyanidation. By consequence the saving in time for the gold and silver dissolution from ore or concentrates is limited by the conventional cyanidation leaching step, a process which requires 48 to 72 hours. It should be remembered that the pressure aqueous pre-oxidation technology is not used to leach the gold but only to make the cyanide ions accessible to the gold in the host mineral.

2. Extraction of gold and silver from the argentopyrite / argentite ore

2.1 Pressure oxidation / cyanidation chemistry

The oxidation of gold and silver is a prerequisite for its dissolution in the alkaline cyanide lixiviant. Pyrite along with arsenopyrite, argentopyrite, sphalerite and covellite are the most common host minerals of gold, silver and electrum. It is important from a process optimization standpoint to understand the behavior of each of these minerals during alkaline pressure oxidation/cyanidation which leads to dissolution/destruction and

subsequent liberation of gold and silver which would then be available for the cyanide ions. Pressure oxidation of pyrite and argentopyrite at low temperature (70°C) and oxygen pressure (60 lb/in²) involves reactions yielding ferrous ion, sulfate ion, and elemental sulfur as products (Anderson and Nordwick, 1996; Chander and Briceño, 1987).

The primary reactions are:



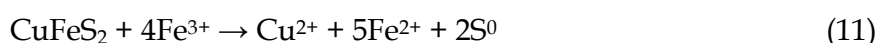
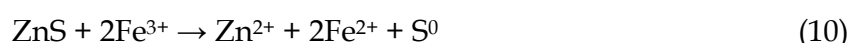
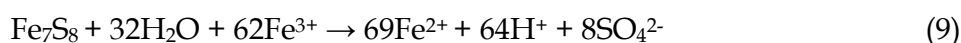
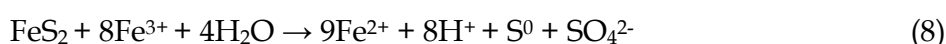
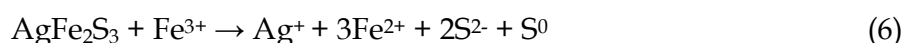
Plant Location	Feed	Medium	Capacity T/d	Operation Data		
				T (°C)	P (psi)	t (min)
McLaughlin, California USA	Ore	Acid	2700	180	401	90
São Bento Brazil	Concentrate	Acid	240	190	230	90
Barrick Mercur Utah, USA	Ore	Alkaline	790	225	473	70
Getchell USA	Ore	Acid	3000	210	420	130
Goldstrike Nevada, USA	Ore	Acid	1360	225	439	75
Goldstrike Nevada, USA	Ore	Acid	5450	225	400	75
Porgera, Papua New Guinea	Concentrate	Acid	1350	190	258	180
Campbell Canada	Concentrate	Acid	70	195	305	120
Barrick USA	Ore	Acid	2000	220	450	100
Goldstrike Nevada, USA	Ore	Acid	11580	200	200	140
Santa Fe Pacific Gold Nevada, USA	Ore	Acid	4000	225	460	50
Sunshine Mining & Co Idaho, USA	Ore	Acid	1000	120	90	60
Porgera, Papua New Guinea	Concentrate	Acid	2700	190	250	150

Table 1. Commercial plants using pressure aqueous pre-oxidation (Adams M.D., 2005; Parga et al. 2007).

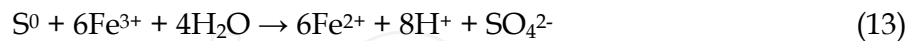
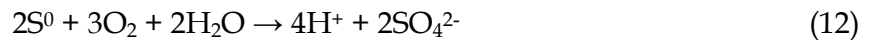
Ferrous ions produced by reaction (3, 4) are subsequently oxidized to ferric ions.



And contribute to the leaching of sulfides only as a source of ferric ions. The ferric ions can also contribute to the oxidation of argentopyrite, argentite, pyrite, pyrrhotite, sphalerite and chalcopyrite:



Of course silver has been shown to activate the oxidation and dissociation of chalcopyrite because a porous sulfur layer is formed (Parga et al., 2007). Then, elemental sulfur may also be further oxidized to sulfate by oxygen or by ferric sulfate:



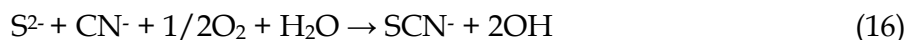
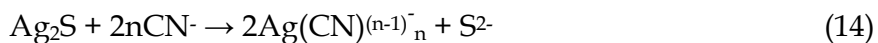
This results in the formation of a porous, but nonprotective, elemental sulfur layer, thus allowing cyanide and dissolved oxygen to access to the previously locked gold, silver and electrum. It was thought that by maintaining high concentrations of CN^- ions in the pressure leach reactor it would be possible to complex gold and silver (Eq. 14) as they became liberated and thus achieve both objectives, i.e. decomposition of refractory minerals and leaching the Au/Ag with the cyanide ions, simultaneously in a single stage. Also, two of the main advantages of this cyanidation process are the selectivity of free cyanide for gold and silver dissolution and the extremely high stability of the cyanide complex as illustrated in Table 2.

Reaction	K	Reaction	K
$Au^+ + 2CN^- = Au(CN)_2^-$	$10^{38.3-10^{39.3}}$	$Ag_2S = 2Ag^+ + S^{2-}$	$10^{-53.5^f}$
$Au(CN)_2^- = AuCN + CN^-$	$10^{-7 a}$	$H^+ + S^{2-} = HS^-$	10^{17m}
$Au^+ + 2HS^- = Au(HS)_2^-$	$10^{30.1 b}$	$HS^- + H^+ = H_2S$	10^7
$Au^+ + HS^- = Au(HS)$	$10^{24.5 b}$	$2S + HS^- + OH^- = S_2S^{2-} + H_2O$	$10^{2.2}$
$Au^+ + 2OH^- = Au(OH)_2^-$	$10^{22.0 c}$	$3S + HS^- + OH^- = S_3S^{2-} + H_2O$	$10^{3.9}$
$Au^+ + OH^- = Au(OH)$	$10^{20.6 c} - 10^{10.2 d}$	$4S + HS^- + OH^- = S_4S^{2-} + H_2O$	$10^{4.6}$
$Au^+ + OH^- + CN^- = Au(OH)(CN)^-$	$10^{23.3 e}$	$5S + HS^- + OH^- = S_5S^{2-} + H_2O$	$10^{4.6}$
$Au^+ + 2CH_3CN = Au(CH_3CN)_2^*$	$10^{1.6 n}$	$6S + HS^- + OH^- = S_6S^{2-} + H_2O$	$10^{2.3}$
$Au_2S = 2Au^+ + S^{2-}$	$10^{-72.8^f}$	$Cu^{2+} + 4CN^- = Cu(CN)_4^{2-}$	10^{25}
$Ag^+ + 2CN^- = Ag(CN)_2^-$	$10^{20.1}$	$Fe^{3+} + 6CN^- = Fe(CN)_6^{3-}$	$10^{43.6}$
$Ag^+ + 3CN^- = Ag(CN)_3^{2-}$	$10^{21.4} - 10^{21.8}$	$3Ag^+ + Fe(CN)_6^{3-} = Ag_3Fe(CN)_6(s)$	$10^{18.2}$
$Ag^+ + 2OH^- = Ag(OH)_2^-$	$10^{3.6} - 10^{4.2}$	$Au^+ + 2S_2O_3^{2-} = Au(S_2O_3)_2^{3-}$	10^{26}
$Ag^+ + OH^- = AgOH$	$10^{2.3} - 10^{3.9}$	$Ag^+ + S_2O_3^{2-} = AgS_2O_3^-$	$10^{8.80}$
$Ag^+ + OH^- + CN^- = Ag(OH)(CN)^-$	$10^{12.8} - 10^{13.2}$	$Ag^+ + 2S_2O_3^{2-} = Ag(S_2O_3)_2^{3-}$	$10^{13.7}$
$AgCN = Ag^+ + CN^-$	$10^{-15.7^*}$	$Ag^+ + 3S_2O_3^{2-} = Ag(S_2O_3)_3^{5-}$	$10^{14.2}$

Table 2. Equilibrium constants (Marsden and House, 1960).

For this argentopyrite concentrate, both gold and silver extractions achieved were in fact greater than 96%.

Since silver in Mexican ores occurs as argentite the cyanidation and sulfide oxidation reaction are as follows:



According to the above equations, sulfide ions are oxidized to thiosulphate and can contribute with the dissolution of gold. Also Graham et al. (Graham and James, 1995) showed that an alkaline or near neutral solution of thiosulphate dissolved gold metal slowly in the presence of a mild oxidant. The dissolution of the gold can be written as in Equation (19), where oxygen is the oxidant and thiosulphate is the ligand.

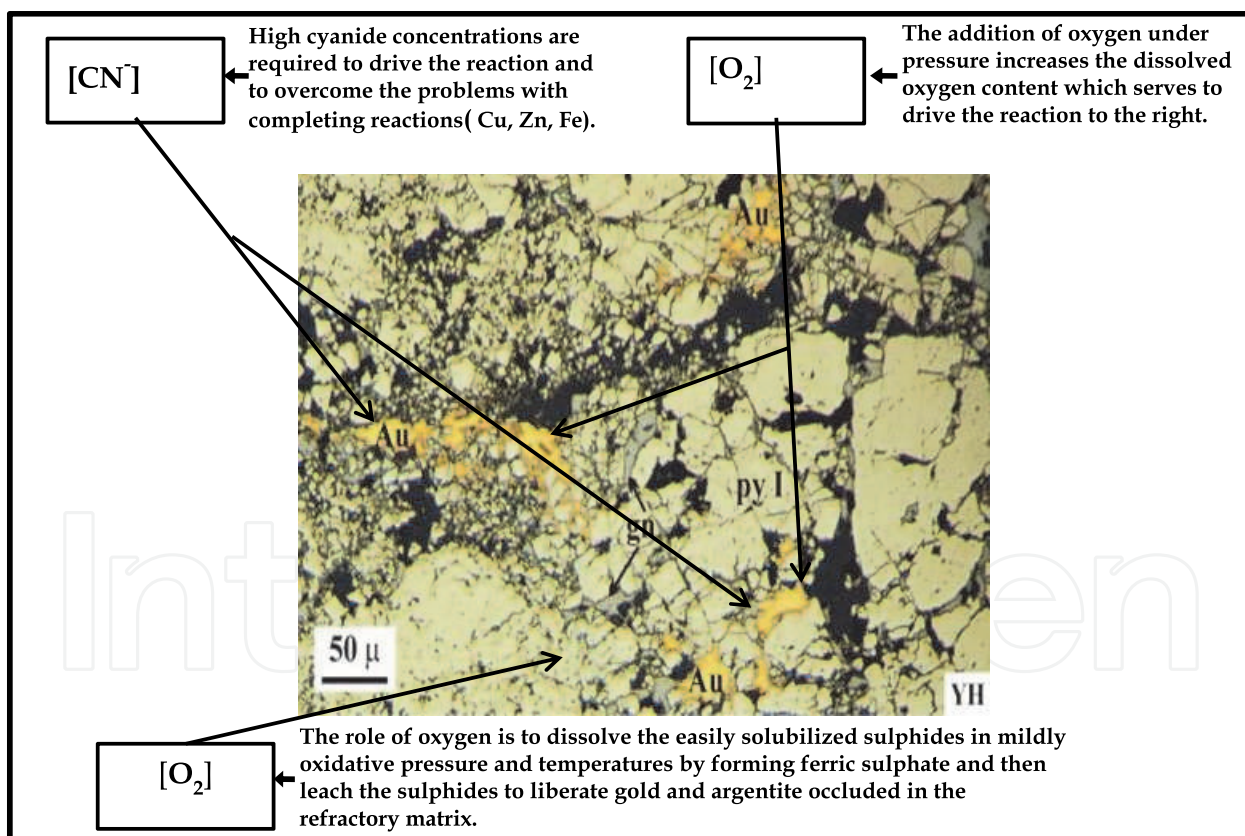
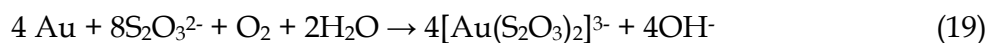


Fig. 1. Schematic mechanism of gold and silver leaching.

Better extractions of gold with thiosulphate are achieved when elevated temperatures (e.g. 65 °C) are used (Wan et al.,1993). The proposed leaching reaction mechanism for gold and

silver dissolution in relatively mildly operating conditions of 70 °C and 60 psi oxygen pressure is described in Figure 1. The role of oxygen gas is to dissolve the easily solubilized sulphides in mildly oxidative pressure and temperature by forming sulphate and metals (e.g. Fe²⁺ to Fe³⁺) to liberate gold occluded in the refractory matrix.

2.2 Experimental details

Mineralogical analysis indicates that the sulfide minerals for the Bacís Mining Co. concentrate include pyrite, argentopyrite, pyrrhotite, arsenopyrite, chalcopyrite, covellite, hematite and magnetite. The non-opaque minerals were quartz, calcite, apatite, gypsum, fluorite and barite. Also, several photomicrographs indicate occlusion and/or dissemination of micron-size gold, silver, electrum particles in the sulfide minerals such as argentopyrite, pyrite, sphalerite, arsenopyrite and quartz (Figure 2). The compositions are listed in Table 3.

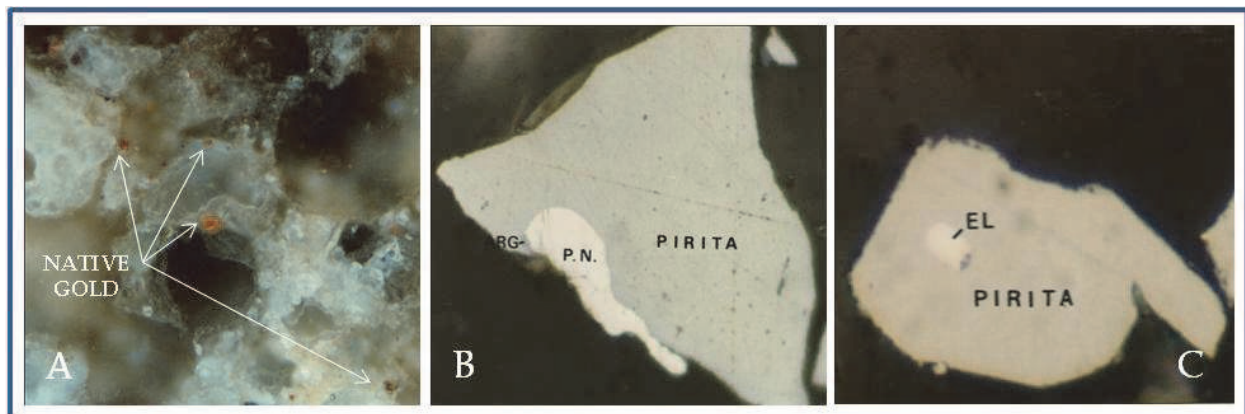


Fig. 2. Photomicrograph, Native gold, size 5 µm, Argentite (ARG) occluded in pyrite, size 60 µm, Electrum (EL) occluded in pyrite, size 10 µm.

	gr./ton		%					
	Au	Ag	Pb	Zn	Cu	Fe	As	S
Concentrate	87.09	12320	2.6	3.8	0.5	29.2	0.15	32
Ore	4.12	289	0.5	0.4	0.04	3.67	0.1	3.7

Table 3. Analytical data for the composite samples.

2.2.1 Leaching experiments

Experiments were carried out in a four-liter Parr autoclave assembled with impeller, thermowell, pressure gauge, gas inlet and outlet pipes were used for simultaneous oxidation and cyanidation in the same autoclave. Samples were ground to 84% minus 40 µm or finer, pulped with fresh tap water. Depending on test requirements, variables such as NaCN, reaction time, temperature, particle size, pH and pulp density were set and the leaching experiments were undertaken.

2.3 Results and discussion

2.3.1 Ambient condition

Preliminary batch testing had indicated that at ambient conditions (25°C, 1atm.) direct cyanide leaching of the concentrate with air gave poor silver and gold recoveries. The results obtained are shown in Figures 3 and 4.

2.3.2 Effect of the autoclave retention time

Figure 5 shows that there is an optimum leach time to achieve both maximum gold and silver extractions. The optimum leach time appears to lie close to 60 minutes at 80°C.

Increase in time beyond this value leads to chemical degradation of gold and silver cyanocomplexes, due to the hydrogen ions produced by the sulfide oxidation. Also for prolonged leaching time there is significant loss in cyanide, since the oxygen present oxidizes the cyanide to cyanate and ultimately to ammonia and carbon dioxide.

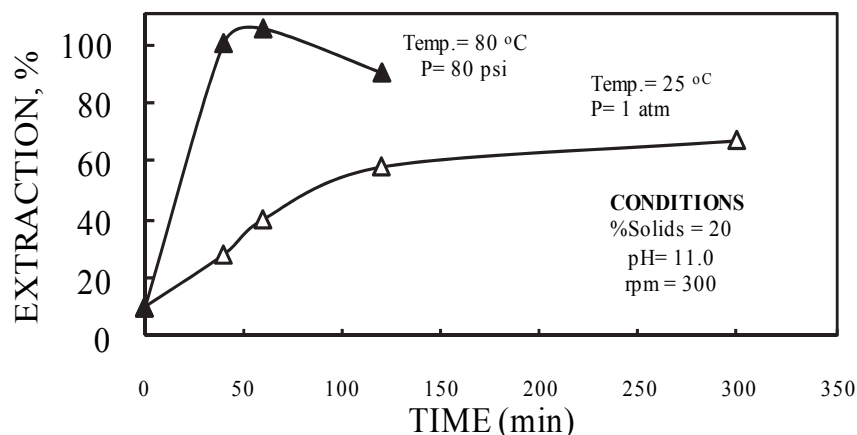


Fig. 3. Comparison of silver extraction at ambient conditions and high pressure.

2.3.3 Effect of cyanide concentration

Concentrations of 0.6 - 1.1 wt. % sodium cyanide were used to leach the concentrate in the autoclave. When the concentration of sodium cyanide was less than 0.6%, gold and silver extraction could not be completed optimally in a single stage of autoclave leaching. Increasing the cyanide concentration resulted in an increase in the gold and silver extraction. The results obtained are shown in Figure 6.

2.3.4 Effect of temperature

The concentrate was leached as 20-wt.% solids slurry with 1 wt.% of NaCN for 60 minutes. Temperature was varied from 60 to 200°C. As the temperature was increased, the gold and silver extractions decreased, since at temperatures higher than 80°C, the oxidation of cyanide ions is too rapid resulting in the formation of CO₂ gas and ammonium ion. Cyanide is then not available for complexation with the gold and silver. See Figure 7.



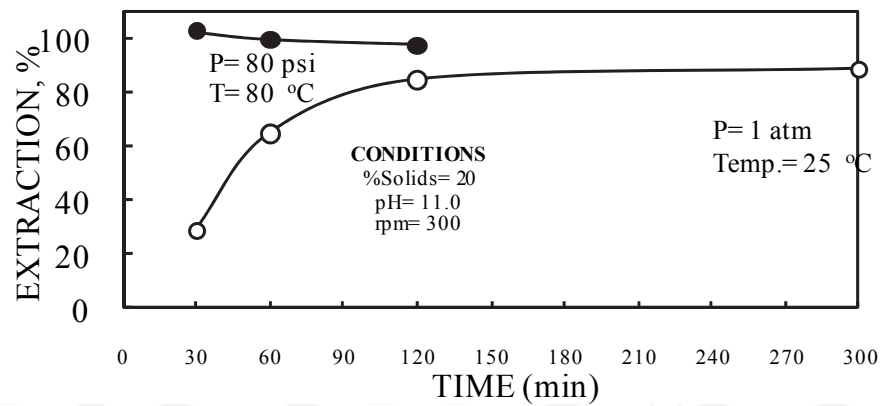


Fig. 4. Comparison of gold extraction at ambient conditions and high pressure.

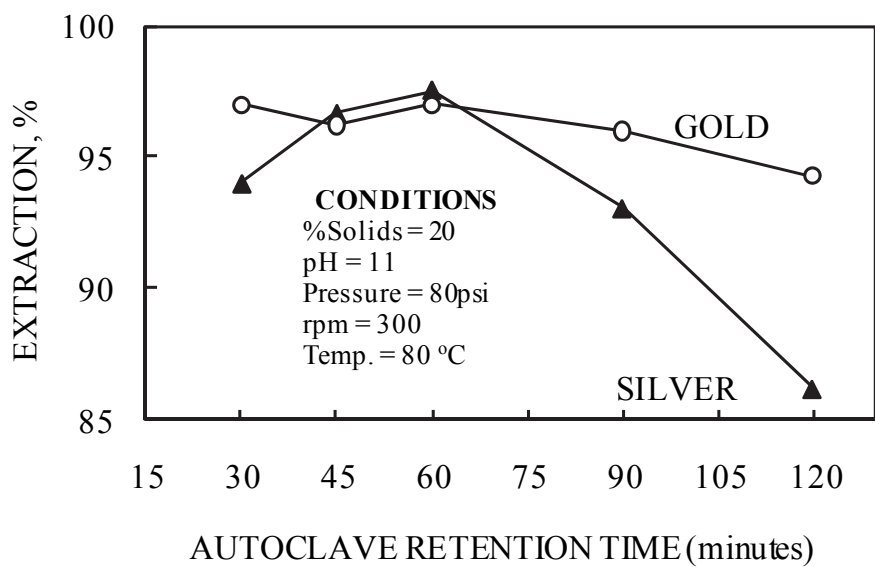


Fig. 5. Effect of autoclave retention time on gold and silver extraction.

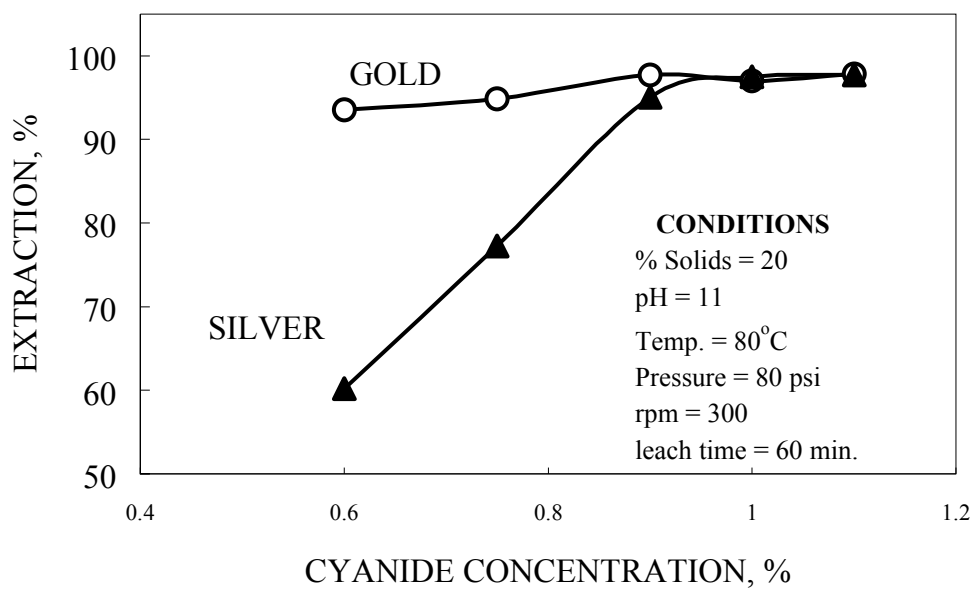


Fig. 6. Effect of the cyanide concentration on gold and silver extraction

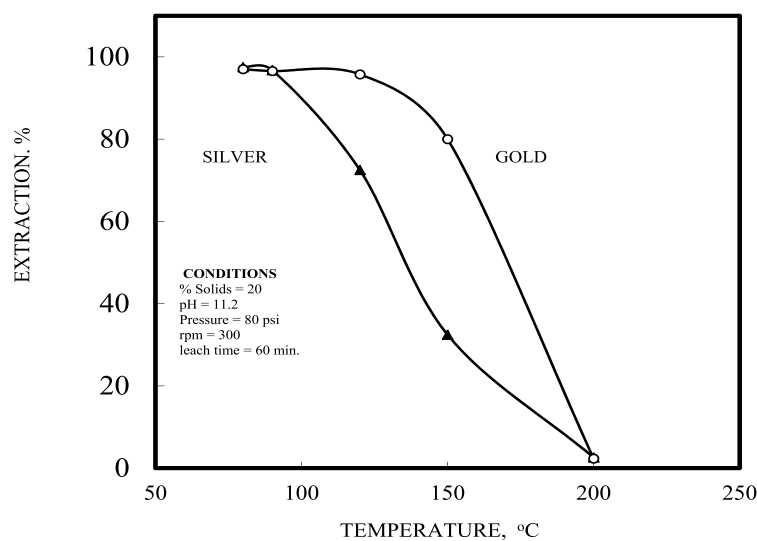
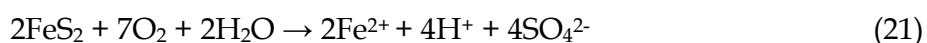


Fig. 7. Effect of temperature on gold and silver extraction.

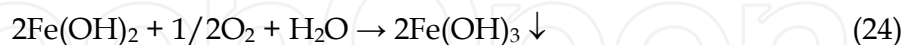
2.3.5 Effect of pH

A pH range of 10.5-13, was examined for the extraction of gold and silver. In Figure 8, it can be seen that at a pH of 11.5 or above, optimum extractions could not be maintained.

This behavior is because in alkaline-oxidizing medium the pyrite and pyrrhotite in the concentrate competes with gold and silver for consumption of oxygen, and this mechanism may be responsible for the decrease in extraction.



Eventually the ferrous sulfate formed is converted to the stable, insoluble ferric hydroxide.



The decrease in the extraction of gold and silver with increasing pH may also be due to a decrease in the formation of ferric sulfate which is the reagent that contributes to the oxidation of sulfide minerals which occlude gold and silver. Also Deitz (Deitz and Halpern, 1953) found that at high pH values between 12 to 13, the silver surface was coated with a whitish film of CaO_2 and thus the leaching process was retarded.

2.3.6 Effect of pulp density

The effect of varying the pulp density in the range of 15-30% solids is shown in Figure 9.

Gold and silver extractions gradually decreased as the pulp density increased apparently due to the increased apparent viscosity of the slurry which impedes good oxygen dispersion in the system, and also for the excessive acid generation.

2.3.7 Plant operation

The optimum conditions as delineated in the laboratory study (Table 4) were used to study the extraction of gold and silver during a continuous one-month plant campaign. A total of 600 tons of concentrate was processed. Recoveries for both gold and silver averaged approximately 96%. These plant data are shown in Figure 10.

On the basis of the results described above the plant tests were in good agreement with the results obtained in the laboratory autoclave and relative to any comparable process, low temperature, low pressure and with these conditions cheaper autoclaves can be used. Thomas shows (Thomas et al., 1992) that a 1400 t/d acid pressure oxidation circuit might cost C\$30 million while the corresponding non-acid circuit might cost only C\$15 million.

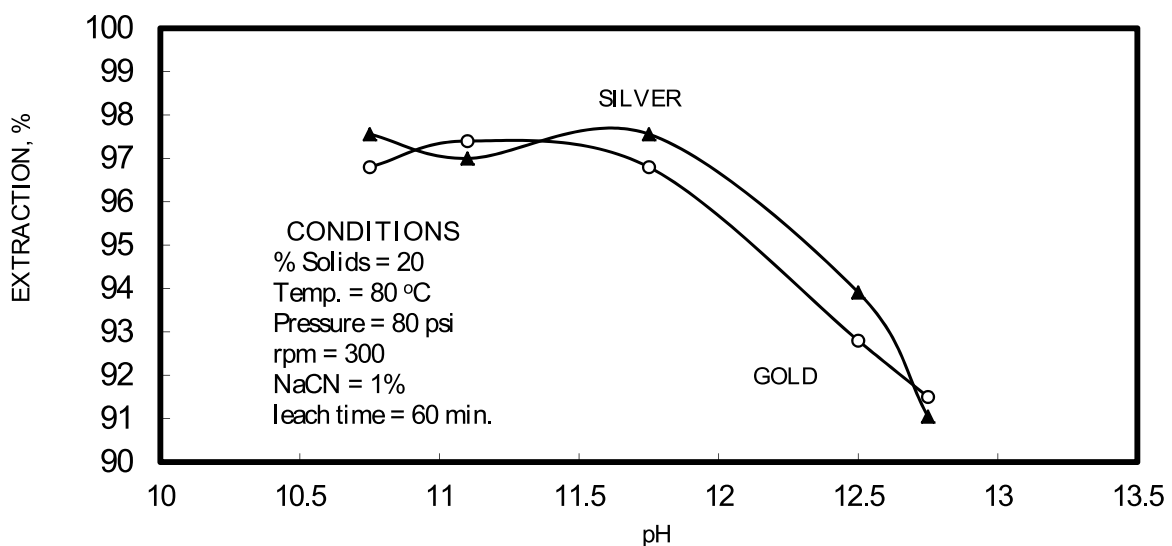


Fig. 8. Effect of pH on gold and silver extraction.

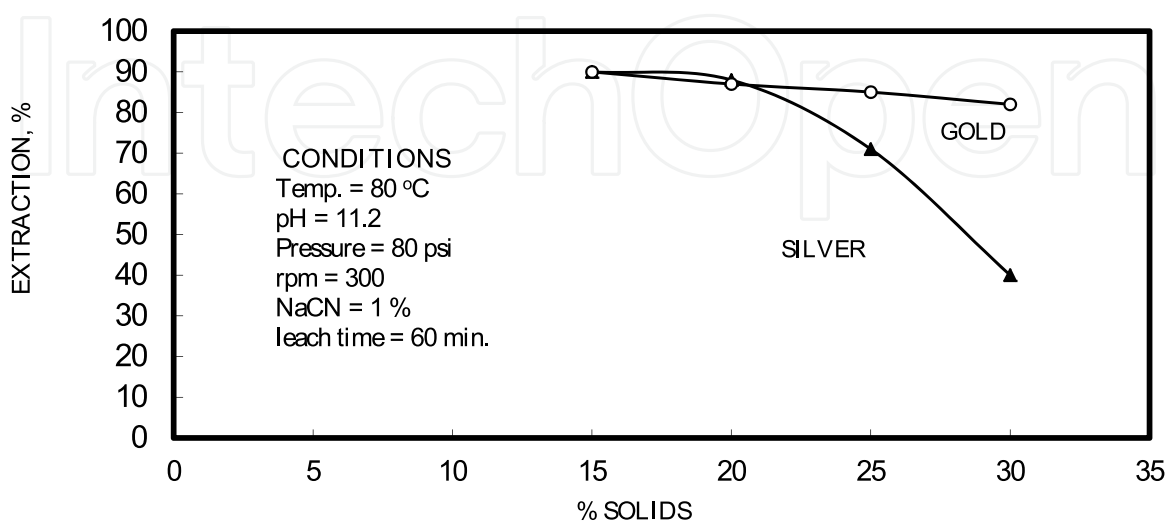


Fig. 9. Effect of percent solids in the extraction of gold and silver.

Solid % = 20	Cyanidation time = 60 min.
Temperature = 80°C	NaCN = 1%
Pressure = 5.6 kg./cm ² (psi)	pH = 10.7
rpm = 300	PbO = 100gr./ton

Table 4. Optimum parameters for the autoclave

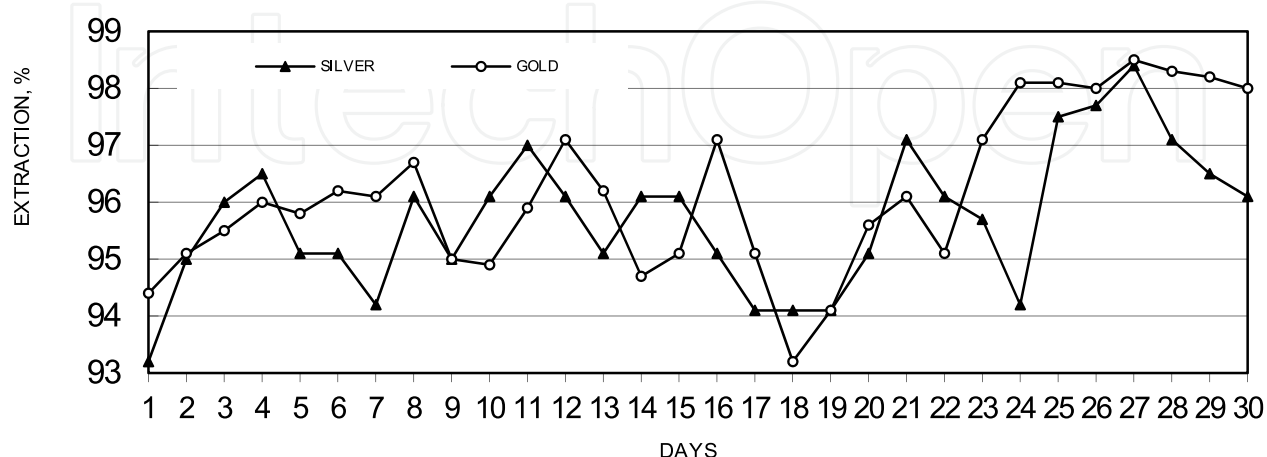


Fig. 10. Result from continuous plant operation.

3. Electrocoagulation process alternative for silver and gold recovery

After the extraction of gold and silver from the argentopyrite/argentite ore, the next step is the recovery of the precious metals from the cyanidation process by which gold and silver are recovered from their ores, and it is recognized that the Carbon in Pulp, the Merrill-Crowe (Metal displacements), the Ion Exchange and Electrowinning processes are used for concentration and purification of gold and silver from cyanide solutions. Each recovery method has advantages and disadvantages. Process selection depends on the specific conditions for a particular operation and the facilities already available. The Merrill-Crowe method had been the preferred process for many years for recovery silver and gold from high reach solutions. Only recently, in the past years, has the carbon adsorption process become popular for recovering gold from large volumes of low grade pregnant leach solutions that contain mainly gold. Other processes, Ion-Exchange Resins and Solvent Extraction, have recently been reviewed as an alternative for gold and silver recovery from alkaline cyanide solutions, (Aguayo et al., 2007). Commercially available resins were unable to compete with activated carbon due to poor selectivity, mechanical breakdown of the beads and the requirement for complex elution, generation of HCN and regeneration process.

Among several available options for recovery of precious metals from cyanide solutions, Electrocoagulation (EC) is a very promising electrochemical technique that does not require high concentrations of silver and gold in cyanide solutions in order to recovery them. Also, literature review showed that the potential of EC as an alternative to traditional treatment recovery of precious metals (silver and gold cyanide) has not yet been exploited. Advantages and disadvantages for the different processes are presented in Table 5, along with those of the EC (Mollah et al., 2004; Parga et al., 2005). EC has been proposed since before the turn of the 20th century. A plant was built in London in 1889

Method	Advantages	Disadvantages
Merrill-Crowe	<ul style="list-style-type: none"> • Lower capital and operating costs. • Handles solutions containing high silver and gold content. • It is highly efficient (99.5%). • Also can treat high-grade solutions produced by carbon elution. • Alternative to Electrowinning. Well known technology. 	<ul style="list-style-type: none"> • The pregnant solution need clarification and deoxygenating. • Low concentrations of metals, increases amount of zinc • Depends on the pH and concentration of the free cyanide. • The precipitate contain cyanides like copper and arsenic. • The precipitate spend one week in the filter press.
Adsorption with Activated Carbon	<ul style="list-style-type: none"> • Does not require pre-treatment of pregnant solution. • Not dependent on the concentration of metals. • Large specific surface. • The pulp needs no clarification. 	<ul style="list-style-type: none"> • Fouled carbon needs to be regenerated by heating. • Large carbon inventory. • The pregnant solution has to go through 5 or 6 columns. • High operating costs.
Ion Exchange Resins	<ul style="list-style-type: none"> • Does not need: washing, revitalization or heat treatment. • High abrasion resistance in tanks of adsorption. • High selectivity. 	<ul style="list-style-type: none"> • High cost of the process. • Lower loading capacity. • Royalty payments. • The resin must be regenerated in acid medium.
Electrocoagulation	<ul style="list-style-type: none"> • Low residence time (minutes). • Does not use chemicals. • Handles solutions containing lower or high silver and gold contents. • Energy costs per m³ of pregnant solution are lower than conventional treatment systems. 	<ul style="list-style-type: none"> • Sacrificial anode must be placed periodically. • Precise initial pH control. • New technology. • The product is high in iron. • The sludge need to be leaching with sulfuric acid.

Table 5. Advantages and disadvantages of methods for recovery of gold and silver (Emamjomeh et al. 2004; Mollah et al., 2009; Parga et al., 2007).

for the treatment of sewage mixing it with seawater and electrolyzing it. In 1906, EC was first patented (Parga et al., 2005) and used to treat bilge water from ships. In 1909, in the United States J.T. Harries received a patent for wastewater treatment by electrolysis using sacrificial aluminum and iron anodes (Vik et al., 1984). Matteson (Matteson et al., 1995), described a device of the 1940's, the "electronic coagulator" which electrochemically dissolved aluminum (from the anode) into solution, reacting this with the hydroxyl ion (from the cathode) to form aluminum hydroxide. The hydroxide flocculates and coagulates

the suspended solids and thereby purifies water. A similar process was used in Britain in 1956 in which iron electrodes were used to treat river water (Holt et al., 2005).

3.1 Electrocoagulation fundamentals

The electrochemical phenomenon of Electrocoagulation has been employed previously for treating many types of wastewater with varying degrees of success. This electrochemical method of contaminant removal requires smaller quantities of salt addition to increase the conductivity of the solution (typically, an aqueous electrolyte), and the maintenance and operation of the EC cells are relatively simple. Electrocoagulation processes offer significant potential for removing ionic species from solution, particularly heavy metals (Mollah et al., 2004; Parga et al., 2007). Operating conditions are highly dependent on the chemical composition and properties of the aqueous medium, specifically, conductivity and pH. Other important process variables, such as particle size, type of electrodes and retention time between electrodes, electrode spacing and chemical-constituent concentrations influence the operating process-parameters (Parga et al., 2007). The fundamental operating-principle is that cations produced electrolytically from iron and/or aluminum anodes (by oxidation) provide for the coagulation of contaminants contained in the aqueous electrolyte. Thus, the (sacrificial) metal-anodes provide a continuous supply of polyvalent metal cations in the vicinity of the anode. These cations participate in the coagulation process by neutralizing the negatively-charged ions (anions) that are transported toward the anode by electrophoresis. In a continuous-flow EC system, the production of polyvalent cations from the oxidation of the sacrificial anodes (Fe and/or Al) and the evolution of electrolysis gases (H_2 at the cathode and O_2 at the anode) are directly proportional to the current (charge) supplied according to Faraday's Law of Electrolysis. The evolved gases enhance the flocculation of the coagulant species.

A schematic of the electrocoagulation process for recovery gold and silver is shown in Figure 11. The gas bubbles produced by electrolysis convey the gold and silver species to the top (free-surface) of the electrolyte where it is concentrated, collected and removed. The removal mechanisms in EC may involve oxidation, reduction, decomposition, deposition, coagulation, absorption, adsorption, precipitation and flotation.

However, it is the reaction involving the metal ions that enhance the formation of the coagulant. The metal cations react with the OH^- ions produced at the cathode during the evolution of hydrogen, to yield both soluble and insoluble hydroxides that will react with or adsorb pollutants, respectively, from the solution and also contribute to coagulation by neutralizing the negatively charged colloidal particles that may be present at neutral or alkaline pH. This enables the particles to approach closely and agglomerate under the influence of Van der Waals attractive forces. Depending on the pH range, the electrode reactions that have been proposed to describe EC mechanisms for the production of $H_{2(g)}$, OH^- (cathode) and H^+ and $O_{2(g)}$ (anode) are (Moreno et al., 2009):

i. $pH < 4$

Anode:



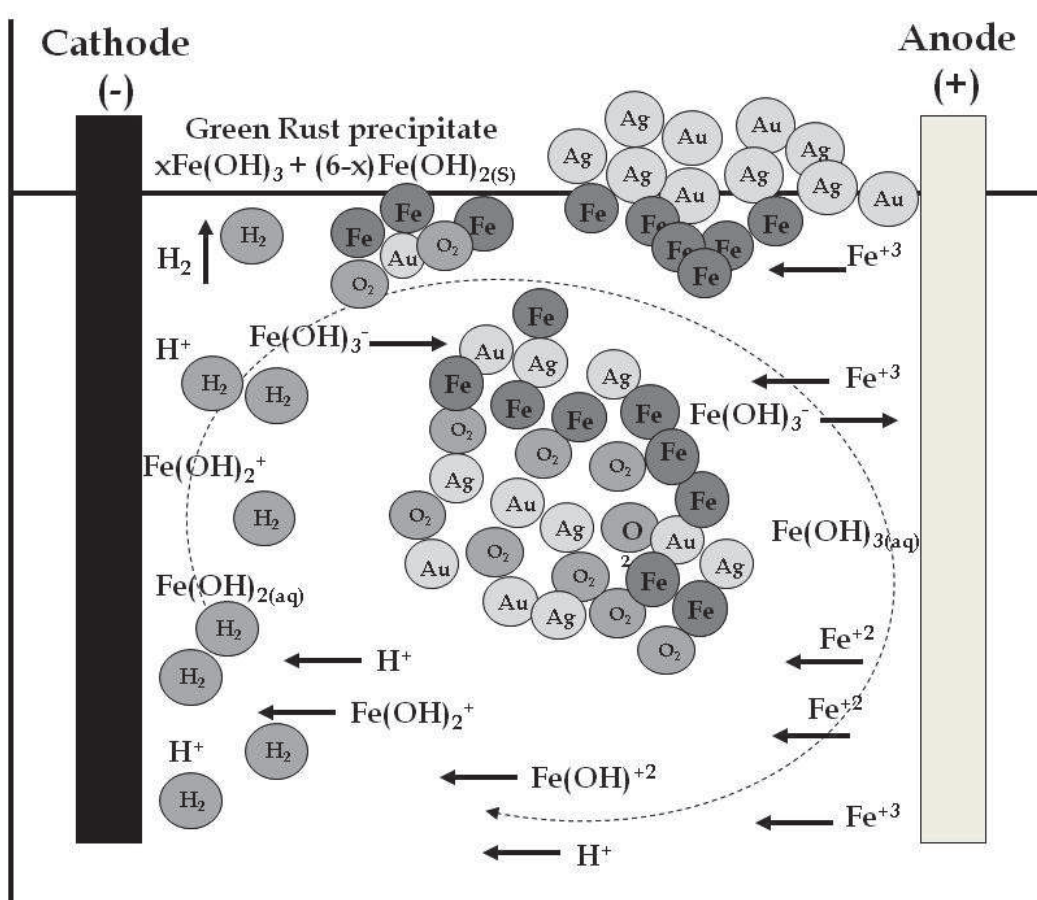


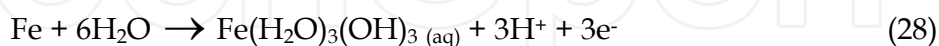
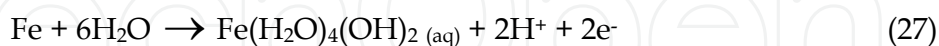
Fig. 11. An illustration of the EC mechanism (arrow indicate the migration of ions, the H₂ evolution and the formation of green rust).

Cathode:

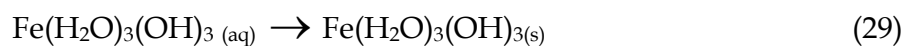


ii. pH 4 < pH < 7:

Anode: as before, reactions (25) and (26). Furthermore, iron also undergoes hydrolysis:



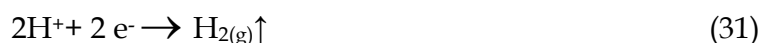
Fe(III) hydroxide begins to precipitate as a floc with yellowish color.



“Rust” can also be formed.



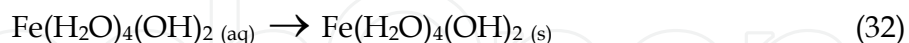
Cathode:



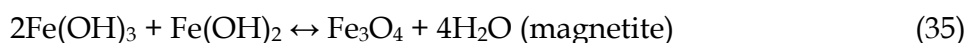
Additional hydrogen evolution takes place, but $[H^+]$ now comes from iron hydrolysis.

iii. $pH\ 6 < pH < 9$:

Anode: reactions (25) and (26). Precipitation of Fe(III) hydroxide occurs according to Reaction (30) simultaneous with Fe(II) hydroxide precipitation whereby a dark-green floc is produced.



The minimum solubility of iron hydroxides, $Fe_x(OH)_y$, occurs in the pH range of 7–8. EC flocs are formed due to the polymerization of iron oxyhydroxides. Formation of rust (dehydrated hydroxides) occurs according to the following:

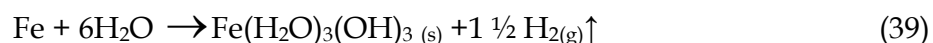
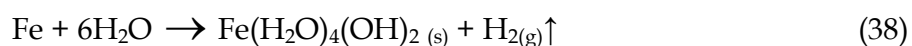


The species hematite, maghemite, rust magnetite, lepidocrocite and goethite have been identified as EC products by (Parga et al. 2005).

Cathode:



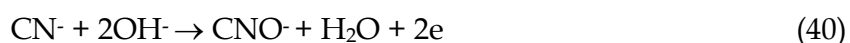
Overall reactions are:

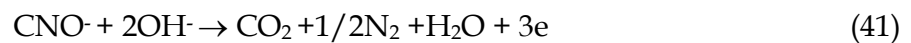


The concentrations of the various species within the cell are not uniform; in addition the concentration of species such as iron and hydronium ion are also time dependent. Typically, the EC process employs bipolar electrodes (Parga et. al. 2005). It has been demonstrated that with this configuration where the electrodes are connected in series, and consequently low current-densities are present, iron (or aluminum) coagulant is produced more effectively, at higher rates and more economically compared to chemical coagulation (Parga et. al. 2005).

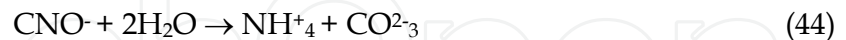
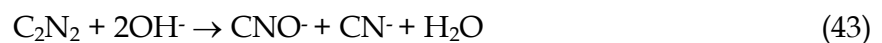
Also, in the electrocoagulation cell for the high voltage we produce a very strongly oxidizing environment around the anode and this is suitable for destroying strong cyanide solutions (greater than 1000 ppm) and is a direct oxidation of the cyanide ion at the anode to cyanate ion which is further decomposed to carbon dioxide and nitrogen, ammonium, and carbonate or oxalate ions according to the pH (Hwang et. al., 1987). The reactions are as follows:

In strong alkaline solution (pH=12):

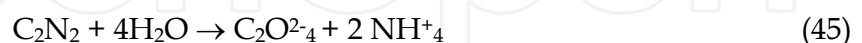




In neutral and weak alkaline solution (pH = 7.0-11.7):



In weak acidic solution (pH = 5.2-6.8):



3.2 Experimental details

The EC experiments were performed with a Fisher magnetic stirrer and a 400ml beaker size reactor equipped with two carbon steel electrodes (6 cm x 3 cm) that were 5 mm apart. As a source of current and voltage a universal AC/DC adaptor was used. pH was measured with a VWR scientific 8005 pH meter and electrodes were properly scrubbed and rinsed prior to each experiments to ensure a clean surface free from passive oxide layers. Gold and silver adsorption onto iron hydroxide species was investigated with pregnant cyanide solutions provided by Bacis S.A. de C.V mining group (13.25 mg L⁻¹ Au, 1357 mg L⁻¹ Ag, 200 mg L⁻¹ free CN⁻ and 1400 mg L⁻¹ total CN⁻ and pH of 8). Analysis were performed by ICP/Atomic Emission Spectrometry (Perkin Elmer 3100). The conductivity of pregnant solutions was adjusted by adding one gram of NaCl per liter (Fisher, 99.8% A.C.S. Certified, lot #995007). To identify and characterize the iron species in the solid products, formed during the EC process for the removal of gold and silver using iron electrodes, X-ray diffraction (XRD) (Phillips model X-PERT), FT-IR analysis were carried out by Thermo Nicolet FTIR spectrometer and Scanning Electron Microscope (SEM / EDX) (FEI Quanta 2000, Oxford Instruments) were used.

Analysis of Au and Ag were conducted to the Bacis solution, by AES. EC was run at 15 Volts (DC) and the corresponding current was of 0.1 A. EC was run for five minutes, and a sample was taken every minute in order to determinate the removal efficiency for Au and Ag. Solutions and solids from the EC process were separated by filtration through cellulose filter paper. The sludge from the EC was dried either in an oven or under vacuum at room temperature and characterized. The experimental set-up is presented in Figure 12. The current and voltage during the EC process were measured and recorded, using Cen-Tech multimeters. The pH values of the solution before and after EC were measured with a VWR scientific 8005 pH meter.

The resulting sludge of iron hydroxide gel precipitate with Au/Ag is filtered. Then, this rich sludge is treated in an acid leach step with sulfuric acid under oxidizing conditions caused by the addition of air. The conditions of this acid leach are such that the major portion of iron and copper are leached into solution with gold and silver remaining in the residue. The resultant residue from the filtration step is gold and silver, as well as little iron (10 % Au, 80 % Ag and 5 % Fe) suitable for further refining by conventional commercial method.

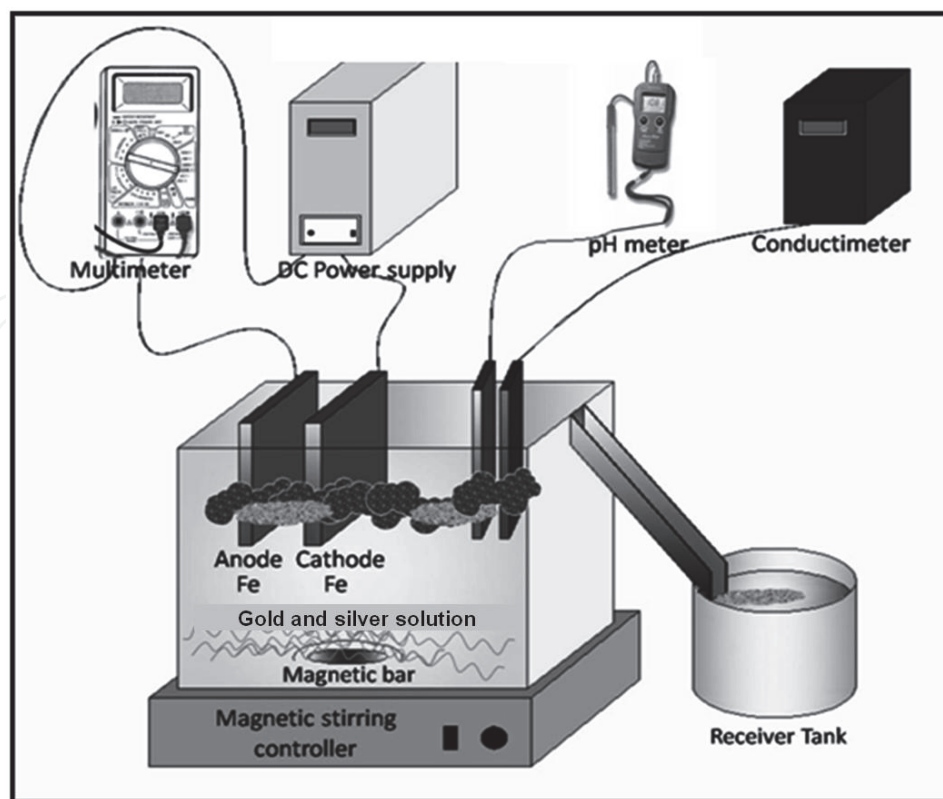


Fig. 12. Experimental set-up of the EC process for the removal of Ag and Au.

3.3 Results and discussion

With the optimal parameters for cell work of EC, they were tested for removal efficiency of gold and silver, the table 6 shows the results when making treatment of the solution containing gold and silver and also the removal efficiency of cyanide, as shown in Figure 13. A maximum in gold and silver recovery were achieved at 5 minutes of treatment and as the arithmetic average of five replications; achieved an efficiency of 99.24% Au to 99.93% Ag for both, with a standard deviation of 0.26 in gold and 0.06 in silver. Also, this studies shown a very efficient recovery in the range of 2 to 3 minutes for gold and 1 to 2 for silver, this occurs in the pH range from 9 to 11 approximately, which coincides with the production of the magnetic iron, Fe_3O_4 , which has magnetic properties that accelerates the process of adsorption of metals, the adsorption rate is then physically, because it is caused by the magnetic forces of the magnetite into gold and silver these forces without altering their chemical composition. Also, it is likely that the electrocoagulation cell is oxidizing the Au and Ag cyanide complexes and converting them to a less-soluble form that is captured by the iron hydroxide gel. The high voltage in the EC cell around the anode destroys some of the cyanide.

About the same studies, Figure 14 shows graphically the evolution of pH during the operation time, there was an increase in pH of the solution which is attributed to the evolution of hydrogen at the cathode which is accompanied by alkalization of the aqueous solution. The final effect is the oxidation suffered by the water coupled with the generation of hydroxyl ions generated during EC.

EC residence time (min)	Au (mg L ⁻¹)	Recovery (%)	Ag (mg L ⁻¹)	Recovery (%)	pH	Removal of Cyanide (mg L ⁻¹)	Removal of Cyanide (%)
0	13.25	0	1357.0	0	8.0	1400	0
1	12.50	5.66	1240.0	8.62	9.2	1050	25
2	10.50	20.37	219.5	83.82	9.5	870	38
3	1.00	92.45	9.0	99.33	10.7	750	46
4	0.50	96.22	7.0	99.48	11.2	400	71
5	0.10	99.24	0.9	99.93	11.5	210	85

Table 6. Recovery of gold and silver by EC.

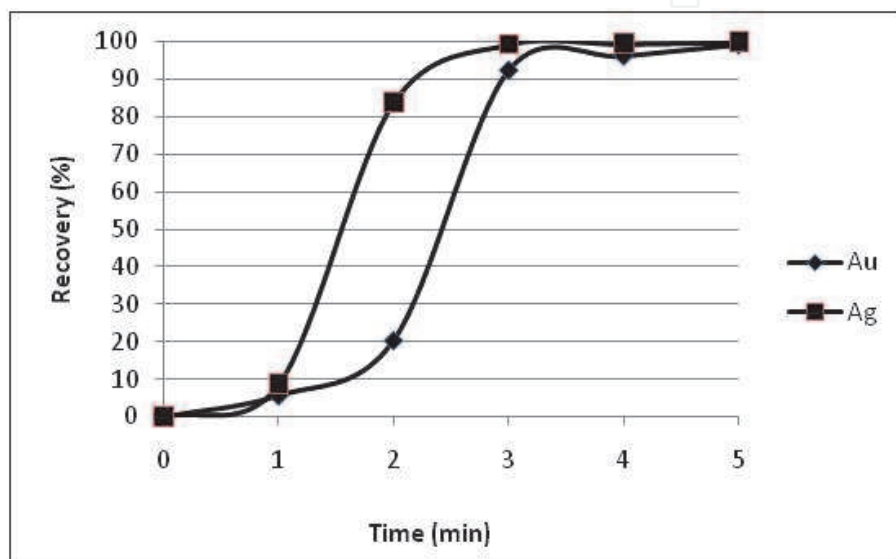


Fig. 13. Gold and silver recoveries from Bacis cyanide solutions.

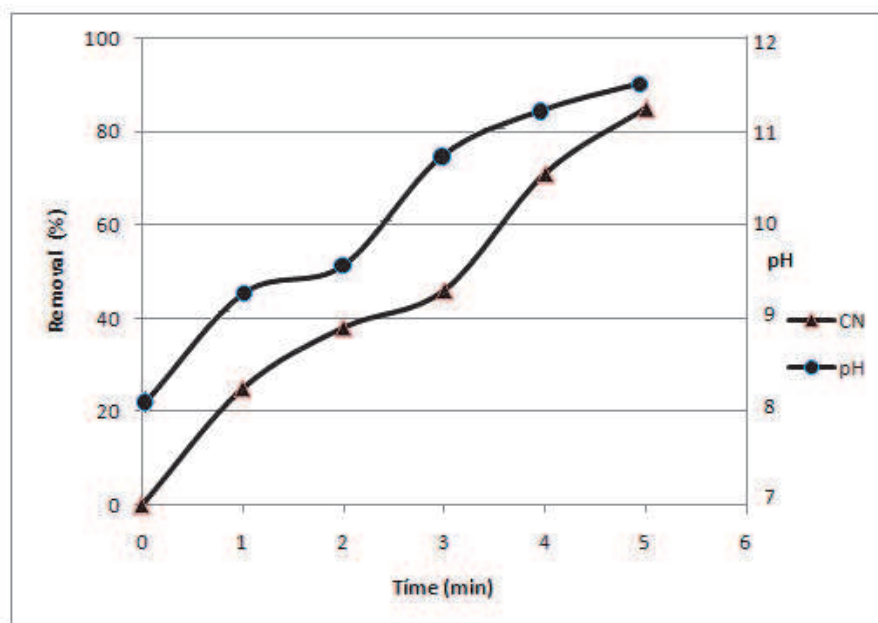
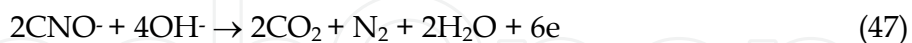
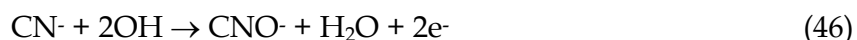


Fig. 14. Variation of pH vs. EC residence time and Cyanide removal vs time.

This results shown that in the EC cell with the iron electrodes decompose the content of cyanide in the pregnant reach solution of gold and silver from initial cyanide content of 1400 to 210 mg L⁻¹. It was found that (Tamura et al., 1974) the anodic oxidation of cyanide is proportional to the alkalinity of the electrolyte and consistent with the following mechanism:



3.3.1 Product characterization

X-ray Diffraction Analysis. Diffraction patterns of flocs collected from the experiment with gold and silver, (the sample were ground to a fine powder and loaded into a sample holder) were obtained with a diffracted X-PERT Phillips meters equipped with a vertical goniometer, with a range of analysis 2θ 10 ° to 70 °. The source of X-rays has a copper anode, whose radiation is filtered with a graphite monochromator (λ = 1.541838Å) with scan rate of 0.02 ° and a duration of 10 seconds per count. The X-Ray Diffractometer is controlled by a Gateway 2000 computer, by PC-APD 2.0 with software for Windows.

Figure 15 shows the ray diffraction pattern of the flocs recovered from the sample of gold and silver, respectively 13.25 mg/L and 1357 mg/L, initial pH 8, 5 minutes of treatment, 0.1 amperes and 15 volts. The species identified were magnetite, lepidocrocite, goehtite, silver and copper hexacyanoferrate.

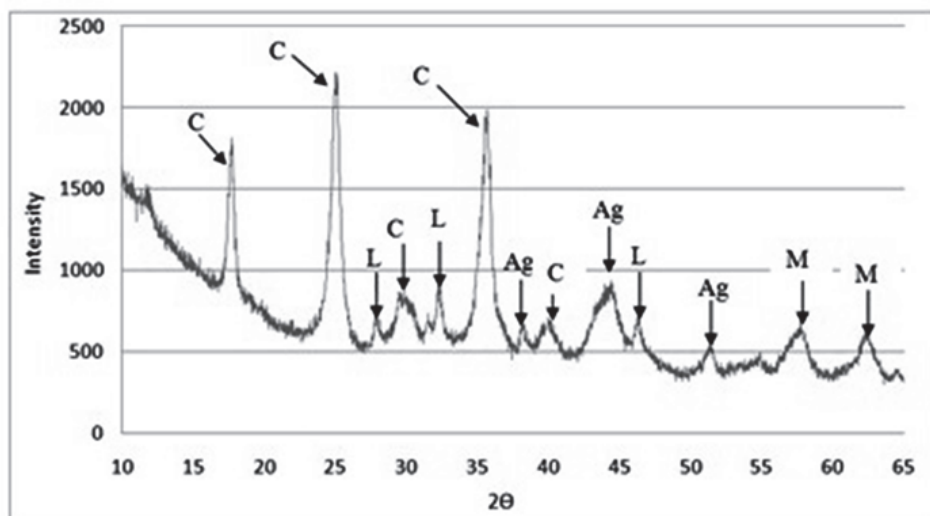


Fig. 15. X-ray diffractogram of solids obtained in the recovery of gold and silver. C: Cu₂Fe (CN)₆H₂O A: Silver, M: Magnetite and L: Lepidocrocite.

Fourier Transform Infrared Spectroscopy. FT-IR analysis were carried out by Thermo Nicolet FTIR spectrometer and OMNIC software using potassium bromide pellets (sample: KBr =1: 50). The spectra were usually recorded in the range of 4000-400 cm⁻¹ with 2 cm⁻¹ resolution. 64 scans were collected for each specimen. Figure 16 shows the FT-IR spectrum of the by-product. Infrared analysis of iron electrode by-product showed OH

stretching at 3738 and 3447 cm^{-1} , hydroxyl bending and γ (OH) water bending vibration or overtones of hydroxyl bending around 1637 cm^{-1} . Bands for lepidocrocite phase showed up at 1120, 1023, and 745 cm^{-1} . Magnetite (Fe_3O_4 or $\text{Fe}_{3-x}\text{O}_4$) band at 575 cm^{-1} and Fe-O vibration band is seen at 469 cm^{-1} . For details of FT-IR analysis see Table 7.

XRD analyses also confirmed the presence of these species detected by FT-IR.

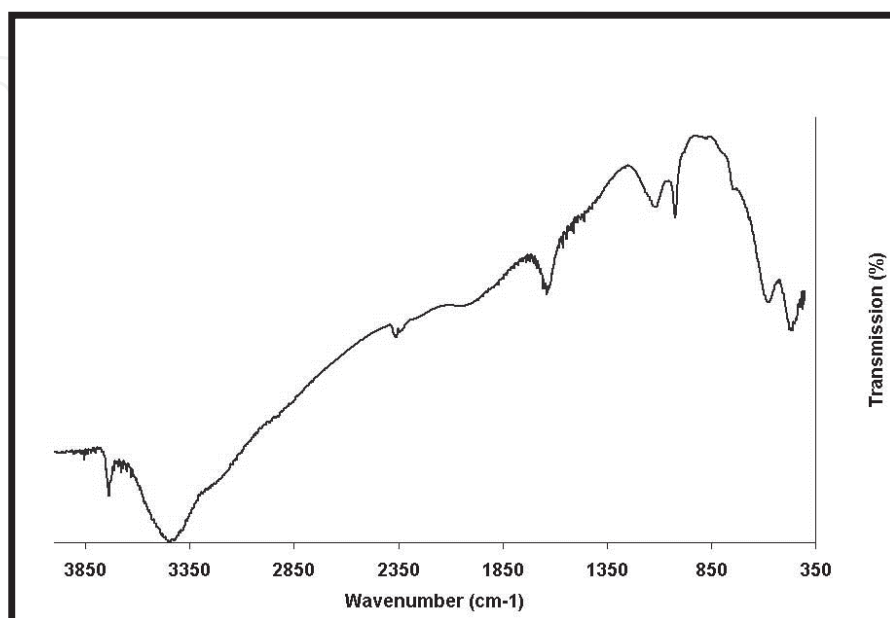


Fig. 16. FT-IR spectrum of iron electrode by-product.

Electrode Material	Type of Vibrations	Vibration wavenumbers (cm^{-1})	Vibration Range (cm^{-1})
Iron	OH stretching	3738	3689-3787
		3447	3550-3000
	Hydroxyl bending	1637	1572-1813
	γ (OH) water bending	1637	1572-1813
	Overtone of hydroxyl bending	1637	1572-1813
	Magnetite (Fe_3O_4 or $\text{Fe}_{3-x}\text{O}_4$)	575	526-840
	Fe-O	469	416-510
	Lepidocrocite	1120	1090-1245
		1023	923-1057
745		730-790	

Table 7. FT-IR vibrations and their corresponding wave numbers and region for the bands observed for the EC-byproduct

Scanning Electron Microscopy (SEM/EDAX). Figure 17 shows SEM images and EDAX of silver adsorbed on iron species. These SEM and EDAX results show that the surfaces of these iron oxide/oxyhydroxide particles were coated with a layer of silver. It is worth clarifying that, given the low concentration of gold it was impossible to locate any nanoparticle of it.

Transmission Mössbauer Spectroscopy. Figure 18 shows the spectrum obtained from the EC silver, gold and iron solid product from 1350 mg/L of silver and 13 mg/L of gold cyanide solutions at pH = 11.0, Mössbauer Spectra for each sample was obtained on a ± 15 mm/s velocity scale, which allows observation of wide magnetic hyperfine spectra expected from iron oxide compounds. The spectrum consists of a doublet magnetic spectrum, which is probably due to fine particles of iron oxides (non-stoichiometric magnetite) or iron hydroxides (Lepidocrocite, Goethite, etc.). From the analysis of these techniques the in-situ generated small fine particles of iron- oxide/oxyhydroxides in the EC process are: non-stoichiometric magnetite, goethite and iron hydroxide oxide.

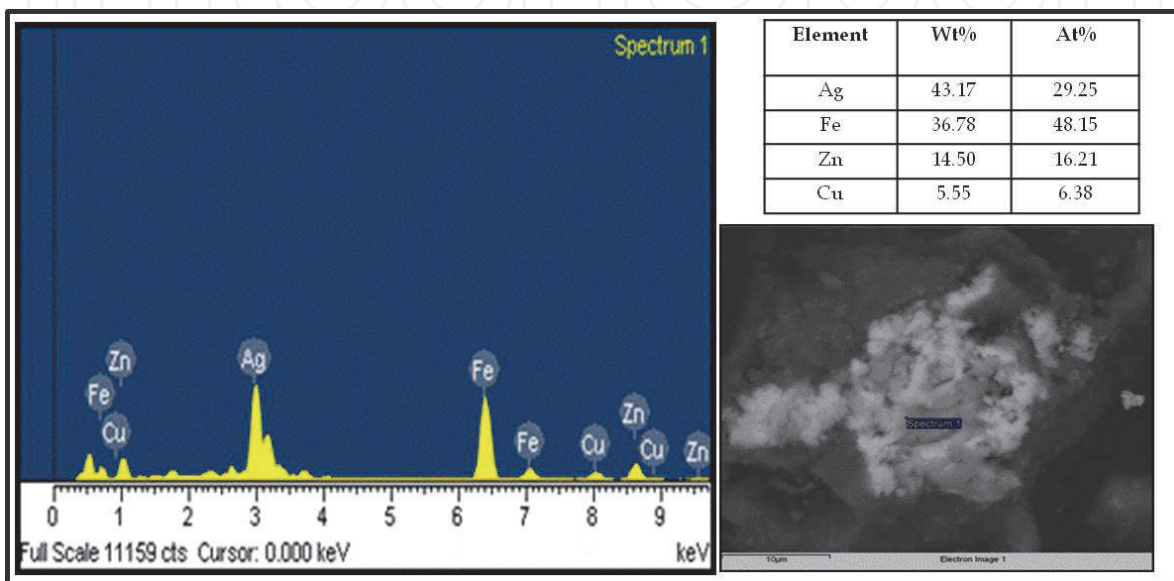


Fig. 17. Chemical composition of solid product as determined by EDX, which shows the presence of silver in the particle of iron.

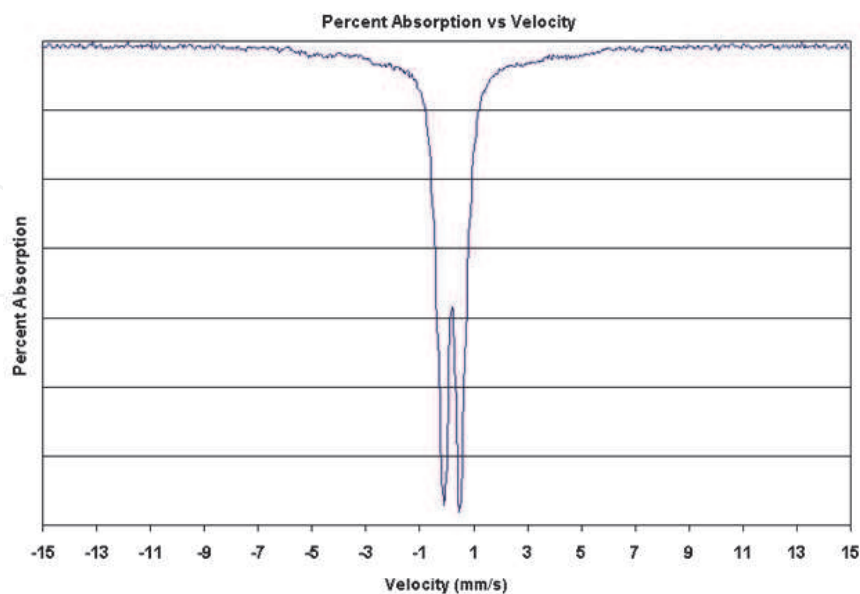


Fig. 18. Mössbauer spectrum with silver and gold at pH=10.5, indicating the presence of magnetite species.

4. Conclusions

This study has been very valuable in identifying that, gold and silver values are associated with argentopyrite, pyrite, sphalerite and chalcopyrite in the Bacís concentrate. The kinetics of the direct pressure oxidation/cyanidation was found to be strongly dependent on particle size, concentration of sodium cyanide, oxygen pressure, temperature and pH. Single stage direct pressure oxidation/cyanidation, has proven to be effective in treating argentopyrite refractory gold and silver concentrates from the Bacís mining and processing operations, for both gold and silver it was found that the precious metals recovery exceeded 95%.

Also in this process, because of the short leaching time the inventory of gold and silver is reduced. The relatively mild operating conditions of 80 °C and 80 psi oxygen pressure offer distinct advantages. For example, low cost materials of construction can be utilized for the autoclave. Finally the pressure oxidation cyanidation process is flexible and can accommodate gold and silver ore of different mineralogical composition and origin.

In addition it has been shown that Electrocoagulation is an interesting process for the recovery of gold and silver from the cyanide leach solution that is yet to be fully realized. EC comprises complex chemical and physical processes involving many surface and interfacial phenomena. Also, the results of this study suggest that EC produces magnetic particles of magnetite and amorphous iron oxyhydroxides, and that this process can be used to remove gold and silver cyanide ions. The results of this study indicate that silver and gold can be successfully adsorbed on iron species produced by the Electrocoagulation process. So EC may be used to recover gold and silver from cyanide solutions.

The X-Ray Diffraction, FT-IR analysis and Scanning Electronic Microscopy techniques demonstrate that the formed species are of magnetic type, like lepidocrocite and magnetite, and amorphous iron oxyhydroxide which adsorbed the silver and gold particles on his surface due to the electrostatic attraction between both metals.

The 99.5% of gold and silver were removed in the experimental EC reactor, and it was achieved in 5 minutes or less with a current efficiency of 99.7%. Finally, the high voltage in the EC cell around the anode destroys some of the cyanide and this process can be accelerated in the presence of copper ions.

5. Acknowledgment

The author thanks the management of Bacís Mining Co., Williams Mining Co., CONACYT and DEGEST for the support and permission to publish this chapter and appreciation is extended to Professor Jan D. Miller of University of Utah and Gerard P. Martins of Colorado School of Mines for their interest in this research.

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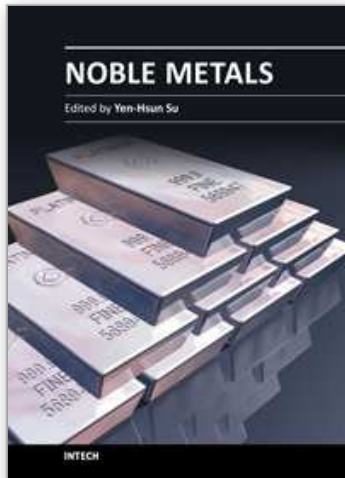
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Edited by Dr. Yen-Hsun Su

ISBN 978-953-307-898-4

Hard cover, 426 pages

Publisher InTech

Published online 01, February, 2012

Published in print edition February, 2012

This book provides a broad spectrum of insights into the optical principle, resource, fabrication, nanoscience, and nanotechnology of noble metal. It also looks at the advanced implementation of noble metal in the field of nanoscale materials, catalysts and biosystem. This book is ideal not only for scientific researchers but also as a reference for professionals in material science, engineering, nonascience and plasmonics.

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