Mineral Processing & Extractive Metall. Rev., 33: 363–373, 2012
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ISSN: 0882-7508 print/1547-7401 online
DOI: 10.1080/08827508.2011.601483

RECOVERY OF SILVER AND GOLD FROM CYANIDE SOLUTION BY MAGNETIC SPECIES FORMED IN THE ELECTROCOAGULATION PROCESS

J. R. Parga[1], M. Rodríguez[1], V. Vázquez[1], J. L. Valenzuela[2], and H. Moreno[3]
[1]*Department of Metallurgy and Materials Science, Saltillo Institute of Technology, Saltillo, Coahuila, Mexico*
[2]*Department of Chemical Engineering and Metallurgy, University of Sonora, Hermosillo, Sonora, Mexico*
[3]*Department of Chemical Engineering, La Laguna Institute of Technology, Torreón, Coahuila, Mexico*

Cyanidation is the predominant process by which gold and silver are recovered from their ores in metallurgical operations, and it is recognized that the Carbon in Pulp, the Merrill–Crowe, the Ion Exchange, and Solvent Extraction processes are used for concentration and purification of gold and silver from cyanide solutions. Among other available options for recovery of precious metals from cyanide solutions, Electrocoagulation (EC) is a very promising water and wastewater electrochemical technique that does not require high concentrations of silver and gold in cyanide solutions to yield excellent results. In this work, an introduction to the fundamentals of the EC process is given, followed by the conditions and results of the EC test run for removal of precious metals from cyanide solutions, and finally the characterization of the solid products formed during the EC process with X-ray Diffraction, SEM, and Transmission Mossbauer Spectroscopy. Results suggest that magnetite particles and amorphous iron oxyhydroxides are present (Lepidocrocite and Gohetite). With the EC process, the achieved removal efficiency of silver and gold from cyanide solutions, within 5 min, exceeded 99%.

Keywords: electrocoagulation, gohetite, green rust, lepidocrocite

INTRODUCTION

Cyanidation processes are especially suitable for treating gold/silver-bearing sulfidic materials. Modern hydrometallurgy technology of precious metals is based on the application of cyanide leaching for the dissolution of gold and silver. Gold cyanidation are reported to involve the chemical reactions shown in Eqs. (1) and (2). Silver follows a similar process.

$$2Au + 4NaCN + O_2 + 2H_2O \rightarrow 2Na\left[Au(CN)_2\right] + 2NaOH + H_2O_2 \qquad (1)$$

Address correspondence to J. R. Parga, Department of Metallurgy and Materials Science, Saltillo Institute of Technology, V. Carranza 2400, 25000, Saltillo, Coahuila, Mexico. E-mail: jrparga@its.mx

$$2\mathrm{Au} + 4\mathrm{NaCN} + \mathrm{H_2O_2} \rightarrow 2\mathrm{Na}\left[\mathrm{Au(CN)_2}\right] + 2\mathrm{NaOH} \tag{2}$$

The equation 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 mol of cyanide are needed for each mole of oxygen present in solution. At room temperature and standard atmospheric pressure, approximately 8.2 mg of oxygen are present in 1 L 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 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, Valenzuela, and Cepeda 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 O_2 to the gold surface. Lime or sodium hydroxide (caustic) is added to keep the system at an alkaline pH beteween 10 and 11. This protective alkalinity is required to counteract the generation of acid during cyanidation, to prevent cyanide degradation, and the formation of the deadly HCN gas.

The two conventional processes for gold and silver recovery from cyanide leach solution are: The Carbon Adsorption Process and the Merrill–Crowe zinc dust cementation process. In the Carbon Adsorption Process, the precious metals are absorbed onto granules of activated carbon. After loading, they are then stripped of the loaded gold by a hot caustic-cyanide solution. This solution is then fed to electrowinning cells where gold and silver are electrolytically deposited onto steel wool cathodes. In the Merrill–Crowe process, the product is filtered zinc dust precipitate. The cathodes from the carbon adsorption process or the precipitates from the Merrill–Crowe process (metal displacements) are then melted in crucible furnaces along with fluxing materials such as borax, niter, and silica. The resultant product from smelting is Dore bullion of precious metals typically analyzed with more than 97% of precious metals.

Each recovery method has advantages and disadvantages. Process selection depends on the specific conditions for a particular operation and the facilities already available. Traditionally, The Merrill–Crowe method was the preferred process for many years. In just the past 40 years, the carbon adsorption process has become popular for recovering gold from large volumes of low grade pregnant leach solutions that contain mainly gold.

The Ion Exchange Resins and Solvent Extraction process has recently been reviewed as an alternative for gold and silver recovery from alkaline cyanide solutions (Valenzuela et al. 2003; Aguayo et al. 2007). Another method that has been tried for the recovery of gold and silver uses adsorption on a chemically modified chitosan with magnetic properties (Donia, Atia, and Elwakeel 2007).

The alternative processes are compared in Table 1 along with those of the EC (Parga et al. 2005; Moreno et al. 2009). The EC process is seen to be a very promising technique for the recovery of precious metals such as silver and gold: EC needs no chemical reagents, and does not generate toxic materials requiring special disposal making it an ecologically viable technique. Literature review shows the potential of EC as an alternative to traditional treatment recovery of precious metals (silver and gold cyanide) yet to be exploited.

Table 1 Advantages and disadvantages of methods for recovery of gold and silver (Mollah et al. 2004; Parga, Valenzuela, and Cepeda 2007; Emamjomeh and Sivakumar 2009)

Method	Advantages	Disadvantages
Merrill–Crowe	• 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.	• The pregnant solution needs clarification and deoxygenating. • Low concentrations of metals increases amount of zinc. • Depends on the pH and concentration of the free cyanide. • The precipitate contains cyanides like copper and arsenic.
Adsorption with Activated Carbon	• Does not require pretreatment of pregnant solution. • Not dependent on the concentration of metals. • Large specific surface. • The pulp needs no clarification.	• 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	• Does not need: washing, revitalization, or heat treatment. • High abrasion resistance in tanks of adsorption. • High selectivity.	• High cost of the process. • Lower loading capacity. • Royalty payments. • The resin must be regenerated in acid medium.
Solvent Extraction	• High selectivity. • Does not need: washing, revitalization, or heat treatment.	• High cost of the process. • New technology. • Stripping Difficult.
Electrocoagulation	• Low residence time (minutes). • Does not use chemicals. • Handles solutions containing lower or high silver and gold contents. • Energy costs per m^3 of pregnant solution are lower than conventional treatment systems.	• Sacrificial anode must be replaced periodically. • Precise initial pH control. • New technology. • The product is high in iron.

ELECTROCOAGULATION CHARACTERISTICS

Electrocoagulation (EC) has been known as an electrochemical phenomenon for more than 70 years. EC has been employed previously to treat many types of wastewater with varying degrees of success (Mollah et al. 2004; Parga et al. 2005; Emamjomeh and Sivakumar 2009).

The EC process can be considered as an accelerated corrosion process where green rust (GR) is an intermediate product responsible for the removal of contaminants (suspended and dissolved solids, metals, organic compounds, etc). EC mechanisms may involve oxidation, reduction, decomposition, deposition, coagulation, absorption, adsorption, precipitation, and flotation. EC operates on the principle that hidrolized cations produced electrolytically from iron and/or aluminum anodes enhance the coagulation of contaminants from an aqueous medium. The sacrificial metal anodes are used to continuously produce polyvalent metal cations in the vicinity of the anode. These cations facilitate coagulation by neutralizing the negatively charged particles that are carried toward the anodes by electrophoretic motion.

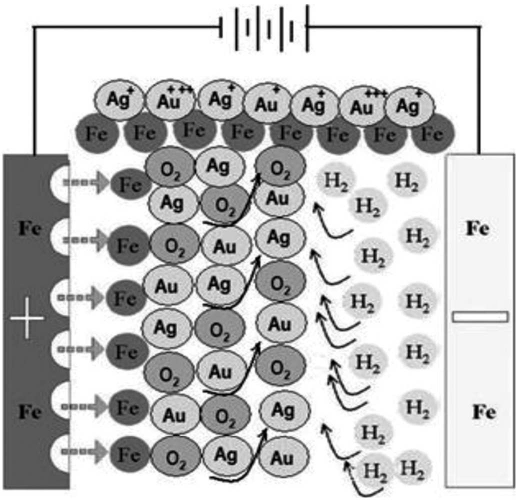

Figure 1 An illustration of the EC mechanism to remove gold and silver (arrows indicate the migration of electrolysis gases O_2 and H_2).

Bipolar electrodes are generally used in the EC process (Mollah et al. 2004; Emamjomeh and Sivakumar 2009; Zhao et al. 2010). It is reported that cells with bipolar electrodes connected in series operating at relatively low current densities produced iron or aluminum coagulant more effectively. In the EC technique, the production of polyvalent cations from the oxidation of the sacrificial anodes (Al or Fe) and the production of electrolysis gases (O_2 and/or H_2) are directly proportional to the amount of current applied (Faraday's law). The electrolysis gases enhance the flotation of the coagulant material. A schematic representation of the EC process, using iron electrodes, is shown in Figure 1. Aforementioned, the gas bubbles produced by electrolysis carry the gold and silver along with the sludge to the top of the solution where it is collected and removed.

It is the reactions of the metal ions that enhance the formation of the coagulant. The metal cations are hydrolyzed, releasing hydrogen ions that result in hydrogen evolution at the cathode. This process yields both soluble and insoluble hydroxides which react with or adsorb gold and silver from the cyanide solution and contribute to coagulation by neutralizing the negatively charged colloidal particles if present in a neutral or alkaline pH. This enables the particles to closely approach and agglomerate under the influence of Van der Waals attractive forces. The EC mechanism and chemical reactions (Moreno et al. 2009) when using iron electrodes are:

$$Fe \leftrightarrow Fe^{+3} + 3e^- \tag{3}$$

$$Fe(OH)^{+2} + H_2O \rightarrow Fe(OH)_2^{+1} + H^+ \tag{4}$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \uparrow \tag{5}$$

$$Fe(OH)_2^{+1} + e^- \rightarrow Fe(OH)_{2(aq)} \tag{6}$$

$$Fe(OH)_{2(aq)} + H_2O \rightarrow Fe(OH)_3^{-1} + H^+ \tag{7}$$

$$Fe(OH)_3^{-1} \rightarrow Fe(OH)_{3(aq)} + e^- \tag{8}$$

Overall reaction

$$6Fe + (12 + x)H_2O \rightarrow 1/2(12 - x)H_{2(g)} \uparrow \ + xFe(OH)_3 * (6 - X)Fe(OH)_{2(s)} \tag{9}$$

The pH of the medium usually rises as a result of this electrochemical process and the GR formed [$xFe(OH)_3{}^*$ (6 – X) $Fe(OH)_{2\ (s)}$] remains in the aqueous stream as a gelatinous suspension, which can remove the gold and silver from pregnant cyanide rich solutions, either by complexation or by electrostatic attraction followed by coagulation and flotation.

Formation of rust (dehydrated hydroxides) occurs after the following processes:

$$2Fe(OH)_3 \leftrightarrow Fe_2O_3 + 3H_2O \text{ (hematite, maghemite)} \tag{10}$$

$$Fe(OH)_2 \leftrightarrow FeO + H_2O \tag{11}$$

$$2Fe(OH)_3 + Fe(OH)_2 \leftrightarrow Fe_3O_4 + 4H_2O \text{ (magnetite)} \tag{12}$$

$$Fe(OH)_3 \leftrightarrow FeO(OH) + H_2O \text{ (goethite, lepidocrocite)} \tag{13}$$

Due to the high voltage in the EC cell, a very strongly oxidizing environment is produced around the anode suitable for destroying strong cyanide solutions (greater than 1000 ppm) (Parga et al. 2009). This represents 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, Wang, and Wan 1987). The reactions are as follows:

In strong alkaline solution (pH = 12)

$$CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e \tag{14}$$

$$CNO^- + 2OH^- \rightarrow CO_2 + 1/2N_2 + H_2O + 3e \tag{15}$$

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

$$2CN \rightarrow C_2N_2 \tag{16}$$

$$C_2N_2 + 2OH^- \rightarrow CNO^- + CN^- + H_2O \tag{17}$$

$$CNO^- + 2H_2O \rightarrow NH_4^+ + CO_3^{2-} \tag{18}$$

In weak acidic solution (pH = 5.2–6.8)

$$C_2N_2 + 4H_2O \rightarrow C_2O_4^{2-} + 2NH_4^+ \tag{19}$$

Tamura et al. (1974) determined that the anodic oxidation of cyanide is proportional to the alkalinity of the electrolyte consistent with the following mechanism:

$$CN^- + 2OH \rightarrow CNO^- + H_2O + 2e^- \tag{20}$$

$$2CNO^- + 4OH^- \rightarrow 2CO_2 + N_2 + 2H_2O + 6e^- \tag{21}$$

$$CNO^- + 2H_2O \rightarrow NH_4 + CO_3^- \tag{22}$$

EXPERIMENTAL DETAILS

EC experiments were performed with a Fisher magnetic stirrer and a 400 mL beaker size reactor equipped with two carbon steel electrodes (6 × 3 cm) 5 mm apart. The electrodes were properly scrubbed and rinsed prior to each experiment trial run to ensure a clean surface free of passive oxide layers. A universal AC/DC adaptor was used as a source of current and voltage. The pH was measured with a VWR scientific 8005 pH meter. 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 Au, 1357 mg/L Ag, 200 mg/L free $CN^-$and 1400 mg/L total $CN^-$and pH of 8). Analyses were performed with ICP/Atomic Emission Spectrometry (Perkin Elmer 3100). The conductivity of pregnant solutions was adjusted by adding 1 g 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) and Scanning Electron Microscope (SEM/EDX, FEI Quanta 2000, Oxford Instruments) were used.

Analyses of Au and Ag were conducted with the Bacis solution by AES. EC was run at 15 V (DC) and the corresponding current was of 0.1 A.

EC was performed on five replicates for 5 min each with a sample taken every minute in order to determinate the removal efficiency for Au and Ag. Solutions and solids (shown in Figure 2) 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 resulting sludge of iron hydroxide gel precipitate with Au/Ag is filtered. 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 is leached into solution with gold and silver remaining in the residue. The resultant residue from the filtration step is gold, silver, and some iron (10% Au, 80% Ag, and 5% Fe) suitable for further refining by conventional commercial method.

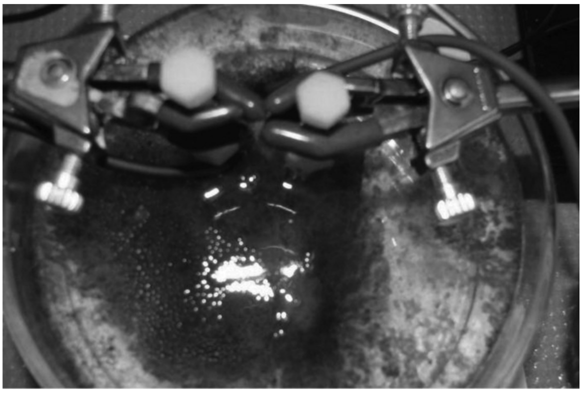

Figure 2 Picture of the EC process for the removal of Au and Ag, showing GR.

RESULTS AND DISCUSSION

The EC process, gave the results shown in Table 2, values of concentration come from the arithmetic average of five replications. As shown in Figure 3, the maximum values for gold and silver recovery achieved within 5 min of treatment are of 99.24% for Au and of 99.93% for Ag with a standard deviation of 0.26 for gold and 0.06 for silver. This study showed very good recovery values within 2–3 min for gold and 1–2 min for silver. These results occur with pH ranging from 9 to 11, which coincides with the production of magnetite (Fe_3O_4). Magnetite's magnetic properties accelerate the process of metal adsorption. The adsorption rate is physically determined by the magnetic forces of the magnetite into gold and silver without altering their chemical composition. The high voltage in the EC cell around the anode destroys some of the cyanide. It is likely that the EC cell oxidize Au and Ag cyanide complexes, thus converting them to a less soluble form that might be captured by the iron hydroxide gel.

Figure 4 graphically displays the evolution of pH during the operation time. There is an increase in pH of the bulk solution, which is attributed to the hydrogen evolution at the cathode that accompanied the generation of hydroxyl ions during EC.

Figure 4 also shows cyanide concentration vs. time. In the EC cell, with iron electrodes, cyanides decompose in the gold and silver pregnant solution, and the concentration changes from the original cyanide content of 1400 to 210 mg/L.

Table 2 Recovery of gold and silver by EC

EC residence time (min)	Au (mg/L)	Recovery (%)	Ag (mg/L)	Recovery (%)	pH	Cyanide (mg/L)	Cyanide removal
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

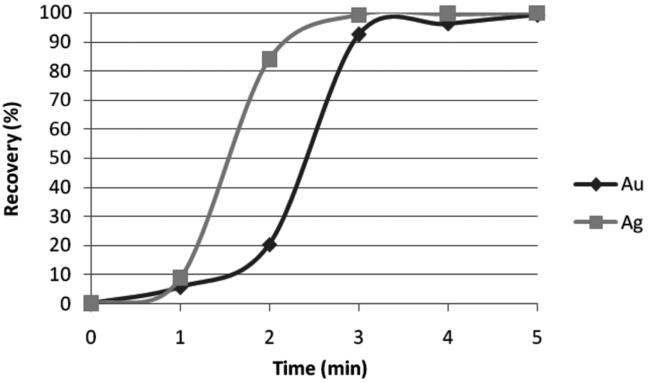

Figure 3 Gold and silver recoveries from Bacis cyanide solutions.

PRODUCT CHARACTERIZATION

X-Ray Diffraction Analysis

Diffraction patterns of experimentally collected flocs with gold and silver (samples 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 2θ analysis range of 10°–70°. The X-ray source is a copper anode, whose radiation is filtered with a graphite monochromator ($\lambda = 1.541838\ \text{Å}$) with scan rate of 0.02° and a duration of 10 s per count. The X-Ray Diffractometer is controlled using a Gateway 2000 computer by PC-APD 2.0 with software for Windows.

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

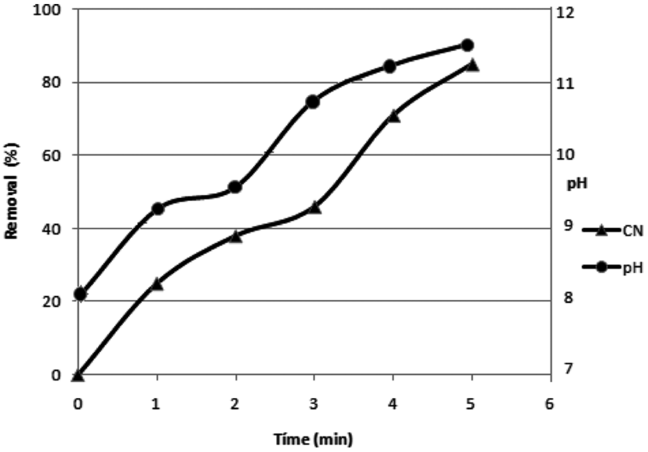

Figure 4 pH vs. EC residence time and Cyanide removal vs. time.

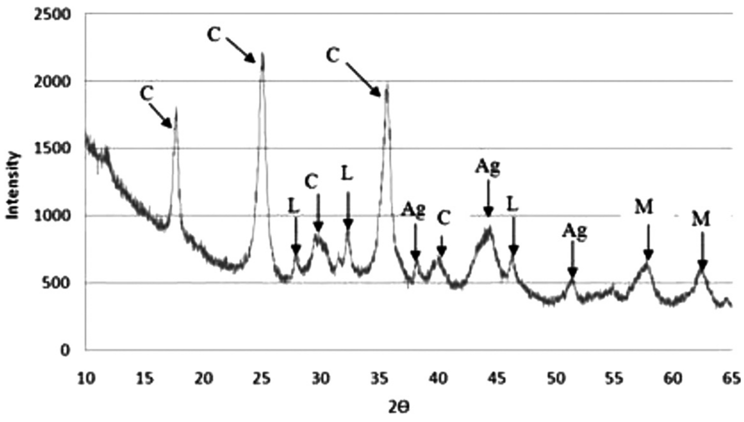

Figure 5 X-ray diffractogram of solids obtained in the recovery of gold and silver C: $Cu_2Fe(CN)_6 2H_2O$ A: Silver, M: Magnetite, and L: Lepidocrocite.

Scanning Electron Microscopy (SEM/EDAX)

Figure 6 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. Given the low concentration of gold, it was impossible to locate any nanoparticle of it.

Transmission Mössbauer Spectroscopy

Figure 7 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

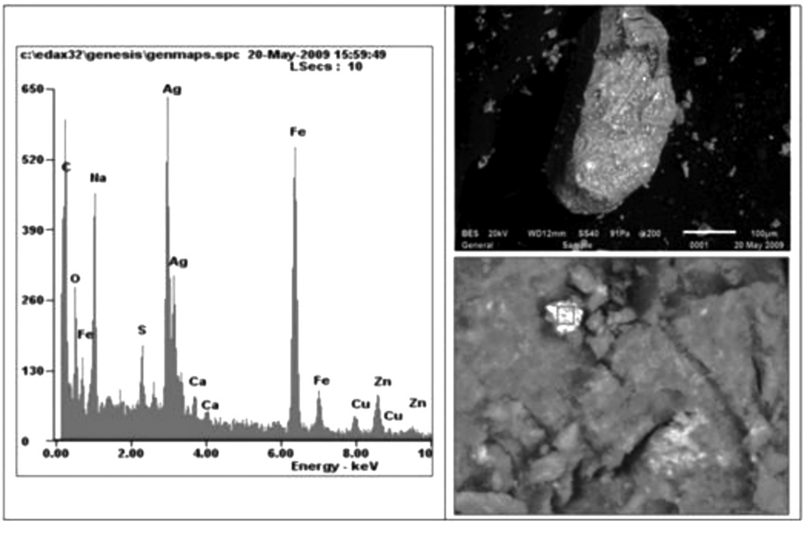

Figure 6 Chemical composition of solid product as determined by EDX, which shows the presence of silver in the particle of iron.

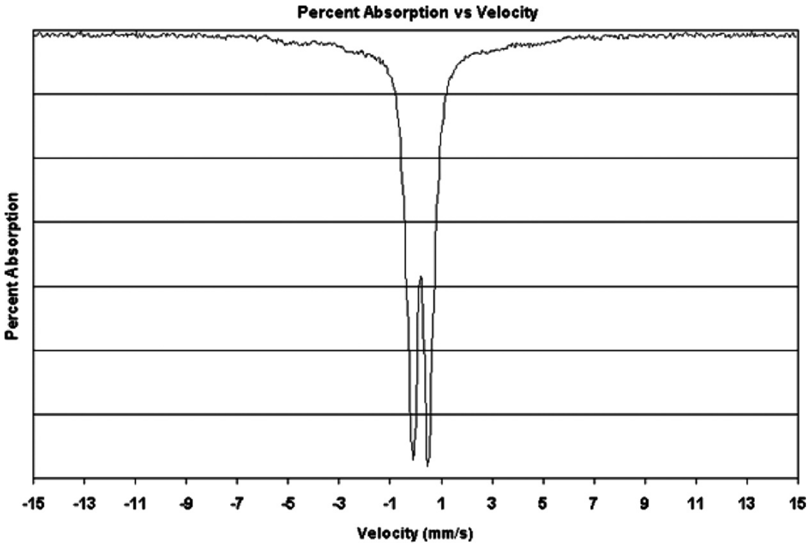

Figure 7 Mössbauer spectrum with silver and gold at pH = 10.5, indicating the presence of magnetite species.

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 (nonstoichiometric 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: nonstoichiometric magnetite, goethite, and iron hydroxide oxide.

CONCLUSIONS

The results of this study indicate that silver and gold can be successfully adsorbed on iron species produced by the EC process. EC may be a viable method to recover gold and silver from cyanide solutions.

The X-Ray Diffraction, Scanning Electronic Microscopy, and Transmission Mössbauer Spectroscopy techniques demonstrate that the formed species are magnetic (e.g., lepidocrocite and magnetite and amorphous iron oxyhydroxide), which adsorb the silver and gold particles on the surface by electrostatic attraction.

Yields of 99.93% gold and 99.24% silver were efficiently removed in the experimental EC reactor within 5 min and a current efficiency of 99.7%.

Aditionally, the high voltage in the EC cell around the anode destroys some of the cyanide.

ACKNOWLEDGMENTS

The authors wish to acknowledge support of this project to the National Council of Science and Technology (CONACYT) and to Dirección General de Educación Superior Tecnológica (DGEST) from Mexico.

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