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ANALYSIS OF THE ADSORPTION OF GOLD AND SILVER ON MAGNETIC SPECIES FORMED IN THE ELECTROCOAGULATION PROCESS

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Abstract

In metallurgical operations, cyanidations is the predominant process by which gold and silver are recovered from their ores and it is recognized that the Carbon in Pulp, Merrill-Crowe process or the Ion Exchange resins are used for the concentrations and purification of gold and silver from cyanide solutions. Among several options are available for recovery precious metals from cyanide solutions, Electrocoagulation (EC) is a very promising electrochemical treatment technique that does not require high concentrations of gold and silver in solutions.

First, this study will provide an introduction to the fundamental concepts of the EC method for recovery precious metals from cyanide solutions. In this research, X-ray Diffraction, SEM and Transmission Mossbauer Spectroscopy were used to characterize the solid products formed at iron electrodes during the EC process. The results suggest that magnetite particles and amorphous iron oxyhydroxides present in the EC products remove gold and silver in 5 minutes.

Introduction

Cyanidation processes are especially suitable for the treatment of gold/silver-bearing sulphidic materials. Modern hydrometallurgy technology of precious metals is based on the application of cyanide leaching for the dissolution of gold and silver. Gold cyanidation has been reported to involve the chemical reactions shown in Eqs. (1)–(2). The silver leach is accomplished in the same fashion.

$$2\ Au + 4\ NaCN + O_2 + 2\ H_2O = 2\ Na\ [Au\ (CN)_2] + NaOH + H_2O_2 \quad (1)$$

$$2\ Au + 4\ NaCN + H_2O_2 = 2\ Na\ [Au\ (CN)_2] + 2\ Na\ OH \quad (2)$$

Later work, however, showed that the first equation was the most important one during leaching. According to the stoichiometry of the process, 4 moles of cyanide are needed for each mole of oxygen present in solution. At room temperature and atmospheric pressure, 8.2 mg oxygen are present in one liter of water. This corresponds to 0.27 x 10^{-3} mole/l. Accordingly, the sodium cyanide concentration (molecular weigth of NaCN = 49) should equal to 4x 0.27 x 10^{-3} x 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 0.5 % -5 % [1]. Also, 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 a 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.

At this time, 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 first case, the precious metals are absorbed onto granules of activated carbon with, after loading, are then stripped of the loaded gold by a hot caustic-cyanide solution. This solution is in turn fed to electrowinning cells where the gold and silver are electrolytically deposited onto cathodes of steel wool. In the second case, the Merrill-Crowe product is a filtered zinc dust precipitate. The cathodes from the carbon adsorption process or the precipitates from the Merrill-Crowe process are then melted in crucible furnaces along with fluxing materials such as borax, niter, and silica. The resultant product from smelting is a dore bullion of precious metals typically analyzing more than 97 percent 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. The Merrill-Crowe method had been the preferred process for many past years; only recently in the past 40 years has the carbon adsorption process become popular for recovering gold from large volumes of low grade pregnant leach solutions that contain mainly gold.

Process alternatives for gold and silver recovery from alkaline cyanide solution, including Carbon in pulp, Merrill-Crowe process and The Ion-Exchange Resins , have recently been reviewed [2] and their advantages and disadvantages discussed in Table I, along the EC process [3-4]. In view of these considerations, the EC process is a very promising technique in the recovery of precious metals such as gold and silver, which needs no chemical reagents, does not generate toxic materials requiring disposal side and this makes it an ecologically viable technique. In reviewing the literature it is clear that the potential of EC as an alternative to traditional treatment recovery of precious metals (gold and silver) has not yet been exploited.

Electrocoagulation Characteristics

Electrocoagulation has been known as an electrochemical phenomenon since the last century. It has been employed previously for treating many types of wastewater with varying degrees of success [3,5].

Table I. Advantages and Disadvantages of Methods for Recovery of Gold and Silver [1,5]

Method	Advantage	Disadvantaged
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 need clarified and deoxygenating - Low concentrations of metals, increased amount of zinc - Depends on the pH and concentration of the free cyanide - The precipitate contain cyanicides
Adsorption with Activated Carbon	- Does not require pre-treatment of pregnant solution - Not dependent on the concentration of metals - Large specific surface	- Fouled carbon need be regenerate by heating - Larger carbon inventory - The pregnant solution has to go through 5 or 6 columns - High operating costs
Ion Exchange Resins	- Expensive reagent - No need: washing, revival or heat treatment - Royalty payments	- High cost of the process - Lower loading capacity - Low abrasion resistance in tanks of adsorption - The resin must be regenerated in acid medium
Electrocoagulation	- The residence times are minutes - Do 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 - New technology

The EC process operates on the principle that the 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. In the flowing EC techniques, the production of polyvalent cations from the oxidation of the sacrificial anodes (Fe and/or Al) and the production of electrolysis gases (H_2 and O_2) are directly proportional to the amount of current applied (Faraday's law). The electrolysis gases enhance the flocculation of the coagulant materials. Passage of an alternating current at an inert electrode, such as titanium, has also been observed to remove metal ions from solution and to initiate the coagulation of suspended solids. A schematic representation of the EC process is shown in Figure 1. As mentioned above, the gas bubbles produced by the electrolysis carry the pollutant to the top of the solution where it is concentrated, collected and removed. The removal mechanisms in EC may involve oxidation, reduction, decomposition, deposition, coagulation, absorption, adsorption, precipitation and flotation.

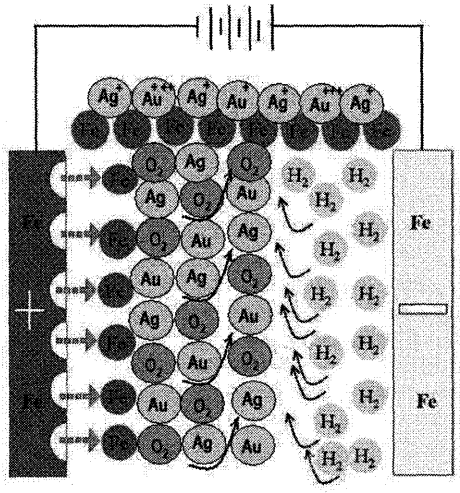

Figure 1. An illustration of the EC mechanism to remove gold and silver (arrows indicate the migration of electrolysis gases O_2 and H_2).

However, it is the reactions of the metal ions that enhance the formation of the coagulant. The metal cations react with the $OH^{\pm}$ ions produced at the cathode (see Equation 7) during the evolution of hydrogen, to yield both soluble and insoluble hydroxides that will react with or adsorb gold and silver, 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. The chemical reactions that have been proposed to describe EC mechanisms for the production of $H_{2(g)}$, $OH^{-}_{(aq)}$ (cathode) and $H^{+}_{(aq)}$ and $O_{2(g)}$ (anode) [4,5] are:

When $M_{(s)}$ = Fe metal electrode

$$Fe_{(s)} \rightarrow Fe^{2+} + 2e^{-} \tag{3}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \tag{4}$$

Anode:

$$aM_{(s)} \rightarrow aM^{n+} + an(e^{-}) \tag{5}$$

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-} \tag{6}$$

Cathode:

$$an(H_2O)+an(e^-)\rightarrow\frac{an}{2}H_2+an(OH^-) \quad (7)$$

$$4H^++4e^-\rightarrow 2H_2 \quad (8)$$

Overall:

$$aM_{(s)}+(2+an)H_2O\rightarrow(2+\frac{an}{2})H_2+O_2+an(OH^-)+aM^{n+} \quad (9)$$

Where constant a is a stoichiometric coefficient, and n is number of electrons. The pH of the medium rises as a result of this electrochemical process and the $Fe(OH)_{n(s)}$ formed 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. Generally in the EC process bipolar electrodes are used [5]. It has been reported that cells with bipolar electrodes, connected in series operating at relatively low current densities produced iron or aluminum coagulant more effectively, more rapidly and more economically when compared to chemical coagulation.

Experimental details

The adsorption experiments were performed in a 400ml glass beaker equipped with two carbon steel electrodes (6 cm x 3 cm) were 5 mm apart. There was used a source of current and voltage (universal AC/DC adaptor). The pH was measured with an electrode/pH meter - VWR scientific 8005. Gold and silver adsorption onto iron species was investigated with electrolytes prepared with gold and silver, (analytical reagent with a purity of 99.99 % supplied by Chemical Products, Monterrey) and deionized water with conductivity of 0.95 $\mu S\ cm^{-1}$ (Aldrich Chemical Co. 99.5 %). The concentrations prepared ranged from 1mg/L to 30 mg/L of gold and silver. Analysis was performed according to an analytical method for detection of metals and trace elements by ICP/Atomic Emission Spectrometry). The conductivity was adjusted by adding one gram of NaCl per liter of water (Fisher, 99.8% A.C.S. Certified, lot #995007). The solutions and solids were then separated by filtration through cellulose filter paper. The sludge from the EC was dried either in an oven or under vacuum at room temperature.

Optimization of parameters

In order to find the optimum parameters of the EC process, the recovery of gold and silver experiments were conducted by changing the pH of the solution, residence time in the EC cell, voltage and amperage. The initial pregnant cyanide solutions was provided by the mining group of Bacis S.A. de C.V. and the chemical assays and the optimal parameters are listed in Table II:

Table II. Chemical Assays and the Optimal Parameters

SAMPLE	CONCENTRATION (ppm)		TEMPERATURE (°C)	PH	CURRENT (AMPERE)	VOLTAGE (VOLT)	TIME (MIN)
	AU	AG					
PREGNANT SOLUTION	13.25	1357	25	8	10	15	5

Results

With this optimal parameters the EC process give the following results show in Table III and in figure 2 show efficiency recovery of gold and silver vs. Time and pH.

Table III. Recovery of gold and silver by EC

Elements	Time min	Au (ppm)	Ag (ppm)	pH Variation
Au/Ag	0	13.25	1357	8
Au/Ag	1	12.5	1240	9.2
Au/Ag	2	10.5	219.5	9.5
Au/Ag	3	1	9	10.7
Au/Ag	4	0.5	7	11.2
Au/Ag	5	0.1	0.9	11.5

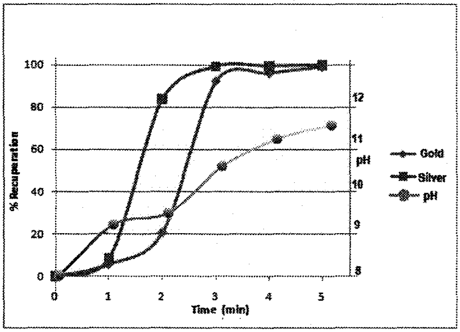

Figure 1. Electrocoagulation recoveries of gold and silver from cyanide solutions and variation of pH

From this results we can determine that, when the time increase from 1 to 3 minutes the recoveries of gold and silver increase to 99%, 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 in Figure 4, shows graphically the variation of pH during the increase of time, this increment in pH of the solution is attributed to the evolution of hydrogen at the cathode which is accompanied by alkalinization of the aqueous solution, likewise oxygen evolution occurs at the anode gas accompanied by an acidification of the solution. The final effect is the oxidation suffered by the water coupled with the generation of hydroxyl iron ions generated during EC process.

Product Characterization

To know the iron species present, was carried out X-ray diffraction (XRD) and Scanning Electron Microscope (SEM / EDX) to characterize the solid products formed during the EC process for recovery gold and silver which uses iron electrodes.

X-ray diffraction analysis

Diffraction patterns of flocs collected from the experiments with gold and silver, (the 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 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 computer Gatawey 2000, by PC-APD 2.0 software for Windows. Figure 5 shows the ray diffraction pattern of the flocs recovered from a sample of gold and silver, respectively 13.25 ppm and 1357 ppm, initial pH 8, 5 minutes of treatment, 10 amperes and 15 volts. The species identified were magnetite, lepidocrocite, silver and copper hexacyanoferrate.

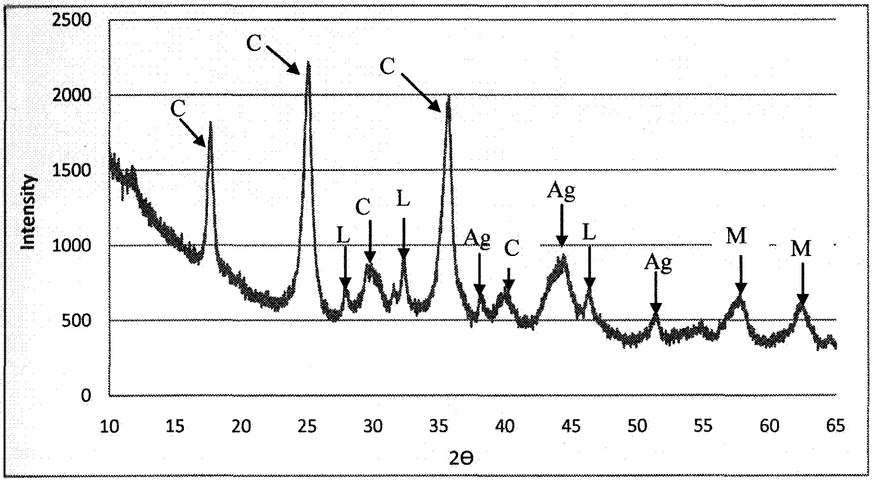

Figure 5. X-ray diffractogram of solids obtained in the recovery of gold and silver in water C: Cu2Fe (CN) 62H2O A: Silver, M: Magnetite and L: lepidocrocite

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 and gold. It is worth clarifying that, given the few *mg/L* of gold achievement not locate a particle of it because is too small the amount of these element.

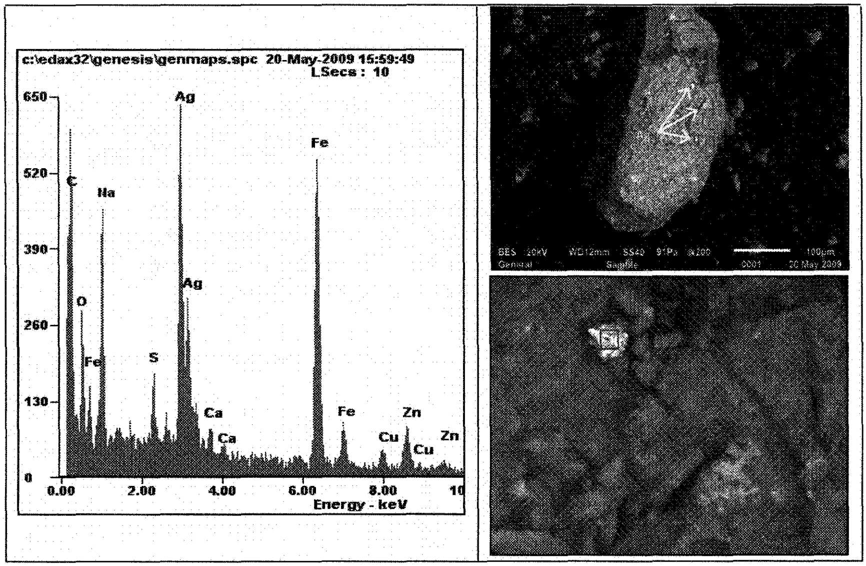

Figure 6. Chemical composition of solid product as determined by EDX, which shows the presence of silver in the particle of iron

Conclusions

The results of this study indicate that gold and silver can be succesfully adsorbed on iron species by electrocoagulation process.

Also, the results of this study suggest that EC produces magnetic particles of magnetite. lepidocrocita and amorphous iron oxyhydroxide species that can be used to recovery gold and silver. The X-ray diffraction, Scanning Electronic Microscopy, techniques demonstrate that the formed species are of magnetic type, like lepidocrocite and magnetite 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 removal in the experimental EC reactor is usually completed within 5 minutes or less for most experiments with current efficiency of 100%.

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