

Recovery of Copper and Cobalt Contained in a Residue of a Zinc Electrolytic Refinery, and the Synthesis of Semiconductor Nanoparticles

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In the hydrometallurgical process for the recovery of zinc, by-products containing elements of interest and economic value are obtained. They are used for further metal recovery, or confined in tailing ponds. In the Zinc Electrolytic Plant in San Luis Potosí, in the various stages of purification, secondary products rich in copper, cobalt and zinc are generated. Particularly the copper cement, by now sold to a copper refining plant, contains mainly copper, but also cobalt in small quantity. In this work, the feasibility of a leach/solvent extraction process for recovery of copper and cobalt from the cement was considered. After stripping, nanoparticles were obtained and characterized.

1. Introduction

More than 80% of the world's zinc production is obtained from zinc sulphide concentrates by the Roasting-Leaching-Purification-Electrolysis process. This process is the main base of operation of the Zinc Electrolytic Plant of Grupo México, S.A. de C.V., in San Luis Potosí, Mexico, which processes more than 200,000 tons of sphalerite (ZnS), with a total zinc recovery of approximately 94.5% [1]. Metal-rich solutions and solids such as jarosite, lead-silver residues, cadmium and copper cements are obtained as by-products. In the stage where the copper cement is obtained, arsenic trioxide and zinc powder are added for precipitation of the prevailing copper and cobalt.

In order to recover metals from residues and by-products, the first step is usually the chemical and mineralogical characterization of the solid, to find out if a washing step with hot water could aid the solubilisation of the desired ions. Otherwise, for dissolving more material, a leaching step using acid solutions at low concentration can be carried out. After that, one of the easiest and more efficient ways to perform the separation and purification of valuable species is the solvent extraction process.

Aldoximes are characterized by their high Cu^{2+} loading capacity, with low affinity for Fe^{3+} . A line of products widely used for copper extraction is Acorga® (Cytec Co.), among them Acorga®M5774 is a well-known reagent for extraction of copper ions [2,3]. On the other hand, the extractant bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex®272), has a high affinity for Co^{2+} . It has been used for Co^{2+} and Ni^{2+} separation, and was previously used by some of us for the separation of zinc and cadmium [4]. Cobalt extraction takes place at $\text{pH}\approx 4$, but in solutions containing other metal

ions also susceptible to extraction with Cyanex®272, such as zinc, copper, manganese, cadmium, nickel or magnesium, the extraction is carried out at pH greater than or equal to 6 [5-8].

A nanoparticle is a fundamental component in the manufacture of advanced materials, and its size ranges from 1 to 100 nm. Nanoparticles have different physical and chemical properties compared to the bulk material. The synthesis and modular assembly of nanoparticles allows to exploit their unique properties, leading to new applications in catalysis, electronics, photonics, magnetism, as well as chemical and biological sensors [9-11]. Copper sulphides (Cu_xS_y) nanoparticles are used in the solar cell industry, as superionic conductors, photodetectors, electroconductive electrodes, photothermal conversion devices, gas sensors, etc. They have two different colours, depending on the chemical composition: emerald green in the case of CuS, and reddish brown for Cu_2S [12-14]. The cobalt sulphides family comprises CoS, CoS_2 , Co_3S_4 , and $\text{Co}_{1-x}\text{S}_x$ (synthetic material). Cobalt sulphides are used as catalysts in hydrodesulphurization, as part of the cathode in rechargeable lithium batteries, and have been used in electrodes in solar cells, photodetectors and biological labelling [15-18].

In this work, the recovery of cobalt from the copper cement by solubilizing the metal in a washing step is reported, as well as the separation of copper by acid leaching. Both metals were recovered from the aqueous solution using solvent extraction and acid stripping, and the strip solutions were used to synthesize metal sulphide nanoparticles.

2. Experimental

2.1 Reagents

Acorga®M5774 and Cyanex®272 were kindly provided by Cytec Solvay Group. The diluent, Exxsol™ D60, was supplied by Exxon Mobil Co. The copper cement was obtained from the Zinc Electrolytic Plant in San Luis Potosí. Other reagents were analytical-grade reagents.

2.2 Characterization and treatment of the copper cement

The copper cement was analysed by X-ray diffraction (XRD, X-ray Diffractometer Bruker D8) and inductively coupled plasma optical emission spectrometry (ICP- OES Varian 730-ES at IPICYT).

Washing and leaching steps: A mixture of cement (30 g) and deionized water (100 mL) was heated under stirring at 50 °C, for 10 min. The soluble fraction was transferred into solution (solution **S1**). To recover the copper present in the industrial solid, 30 g copper cement was contacted with 1 M H_2SO_4 (100 mL), heated to 65 °C under stirring for 10 min, and filtered (solution **S2**).

2.3 Extraction of cobalt and copper ions

Cobalt extraction was carried out using the **S1** solution and Cyanex®272 (20% in Exxsol™ D60, equilibrium pH values from 1 to 7), and the copper extraction (pH=2) was carried out using the **S2** solution and Acorga®M5774 (20% in Exxsol™ D60). The O/A ratio was 1:1. Counter current experiments with four stages were performed for cobalt in a system of mixers-settlers with size of 3.8×23.3×6.5 cm, stirring section of 3.8×3.8×6.5 cm (equilibrium pH 5.5). To control flows, pumps and valves were used. The metals contained in the organic phases were recovered by contacting with an equal volume of 1 M H_2SO_4 .

2.4 Synthesis and characterization of the nanoparticles

For the synthesis of Co_xS and CuS nanoparticles, an aliquot of 3 mL of the stripping solutions

were added dropwise to 2 M ammonium sulphide solution, containing 2% polyvinylpyrrolidone (PVP) as a stabilizer, all of these in a volume ratio 1:1 and under sonication. The powders were washed with water and acetone and characterized using XRD and scanning electron microscopy (SEM FIB Helios Nanolab at IPICyT, San Luis Potosí).

3. Results and Discussion

3.1 Characterization and treatment of copper cement

The residue, according to the X-ray diffraction, contains metallic copper, identified by the card 01-070-3038, cuprite (Cu_2O , 00-005-0667), anglesite (PbSO_4 , 00-001-0867), as well as arsenolamprite (As°), identified using the card 00-029-0142. The Rietveld structure refinement was performed using the TOPAS software, the cuprite content was found to be 57.4%, Cu° 38.3%, anglesite 2.3% and arsenolamprite 1.97% (Figure 1). Due to the low content, the technique was not able to identify cobalt. During the quantification performed by acid digestion and using ICP-OES, copper was found to be 51.6% of the total mass, cobalt 0.76%, arsenic 4.4%, and zinc 3.0%.

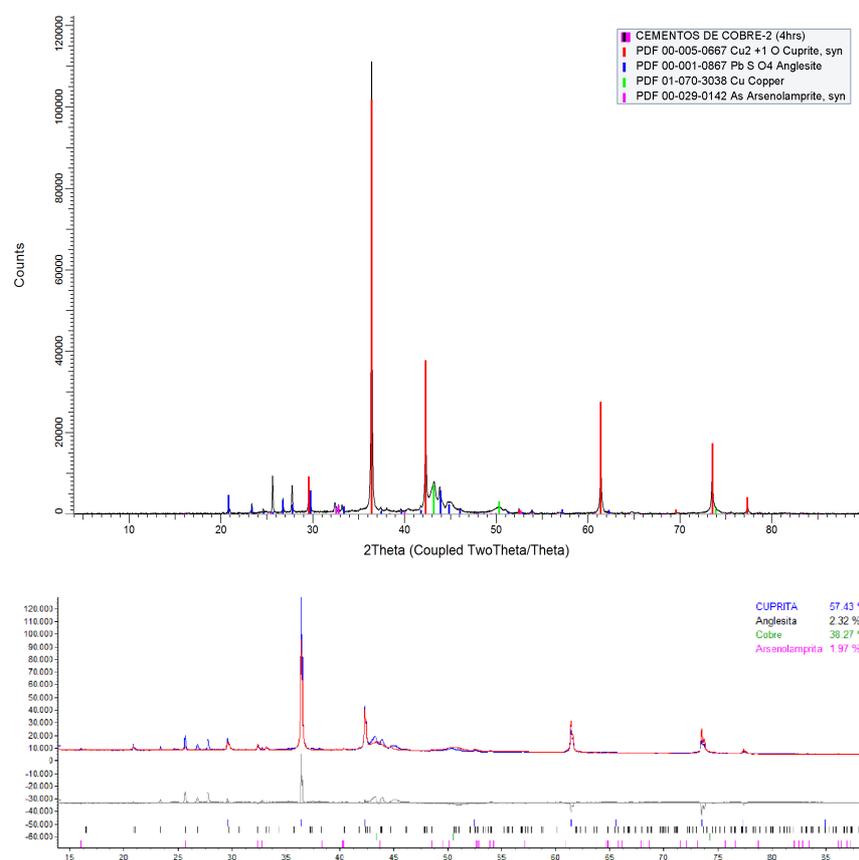


Figure 1. X-ray diffraction and Rietveld refinement of copper cement

3.2 Extraction of cobalt and copper ions

Extraction tests at several pH values (from pH 1 to 7) were carried out using **S1** and Cyanex®272. The highest extraction values for cobalt were reached at $\text{pH} > 6$, where the metal is extracted almost completely (98.6 %). Experiments were carried out in order to obtain the extraction

After a wash step with hot water, the chemical analysis of the solution **S1** ($\text{pH}=3.4$), showed that it contains mainly cobalt (1034.4 mg/L) and copper (2078 mg/L), as well as small amounts of cadmium, zinc and arsenic (98.8, 35.80 and 1.6 mg/L, respectively). By acid leaching of the cement, solution **S2** was obtained. The metal content was: cobalt (1187.2 mg/L), copper (31.67 g/L), cadmium (108.6 mg/L), zinc (136.3 mg/L) and arsenic (87.4 mg/L).

isotherm (Figure 2), and to calculate the O/A ratio for the countercurrent extraction tests (equilibrium pH 5.5), which turned out to be 1.3. For the system, a volume of 50 mL was considered, and therefore, the calculated flow for the organic phase was 8.7 mL/s, and for the aqueous phase 11.3 mL/s. The efficiency of the countercurrent cobalt extraction was calculated performing a mass balance by analyzing the amount of cobalt present in the charged organic and the raffinate. The stripping was performed using a concentrated solution of H_2SO_4 , and the cobalt concentration was determined. According to the isotherm, the theoretical extraction of cobalt should be 99.9%, but the experimental one in the countercurrent experiments was 92.6%, and the zinc extraction 10.44 %.

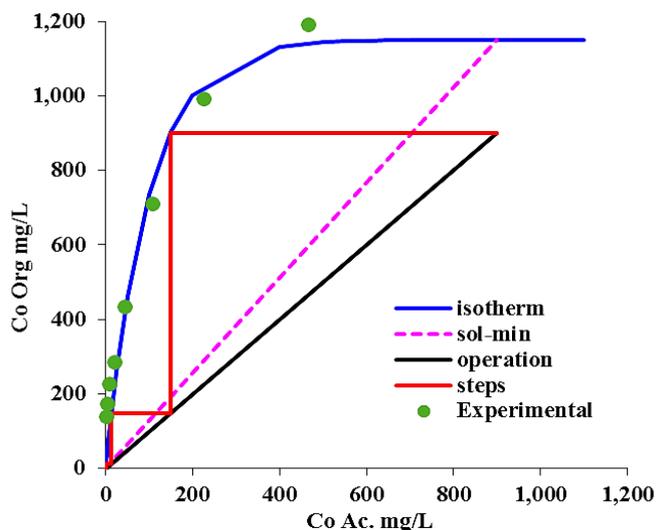


Figure 2: McCabe-Thiele diagram for cobalt extraction from solution S1 with Cyanex®272 (20% in Exxsol™ D60, equilibrium pH 5.5, 300 s)

As the copper concentration in liquor S2 was high, copper extraction in a single step was performed (A/O ratio 1:3.5). In this way 99.9% of the copper was extracted, and an organic phase with a concentration of 9048.8 mg/L Cu^{2+} was obtained. The metal was recovered from the organic phase using sulfuric acid, and the both strip solutions were used for the preparation of nanoparticles.

3.3 Synthesis and characterization of the nanoparticles

After precipitation of the sparingly soluble metal sulfides from the stripping solutions, the nanoparticles were characterized using FESEM and XRD (Figure 3). Cobalt sulfide particles are well dispersed and had a size distribution varying from 2 to 20 nm in diameter, with 70% of the particles in the range of 4-10 nm. Characterization using XRD was uncertain because of the amorphous nature of the precipitate, but a possibility is the presence of cattierite (CoS_2 , card 01-089-1493), and silica (a compound which can be extracted by the organic phase if present in the feed liquor in the form of colloidal particles) identified with the card 00-001-0357. Even though the presence of silica or other colloidal materials could represent a problem in liquid-liquid extraction since the formation of sludge occurs, the system did not show the formation of emulsions or cruds.

The size range of the copper sulfide nanoparticles varied from 2 to 14 nm, the 70% of the nanoparticles was between 4-9 nm in size. The particles seemed to be agglomerated, but this probably happened during the drying of the sample holder. The diffractogram of the copper sulfide particles showed a crystalline phase identified as copper sulfide ($Cu_{1.8}S$, card 01-089-2073), and covellite (CuS , card 00-001-1281). There is a slight displacement of the peaks because the texture of the sample and also an important peak broadening due to the small size of the crystallites.

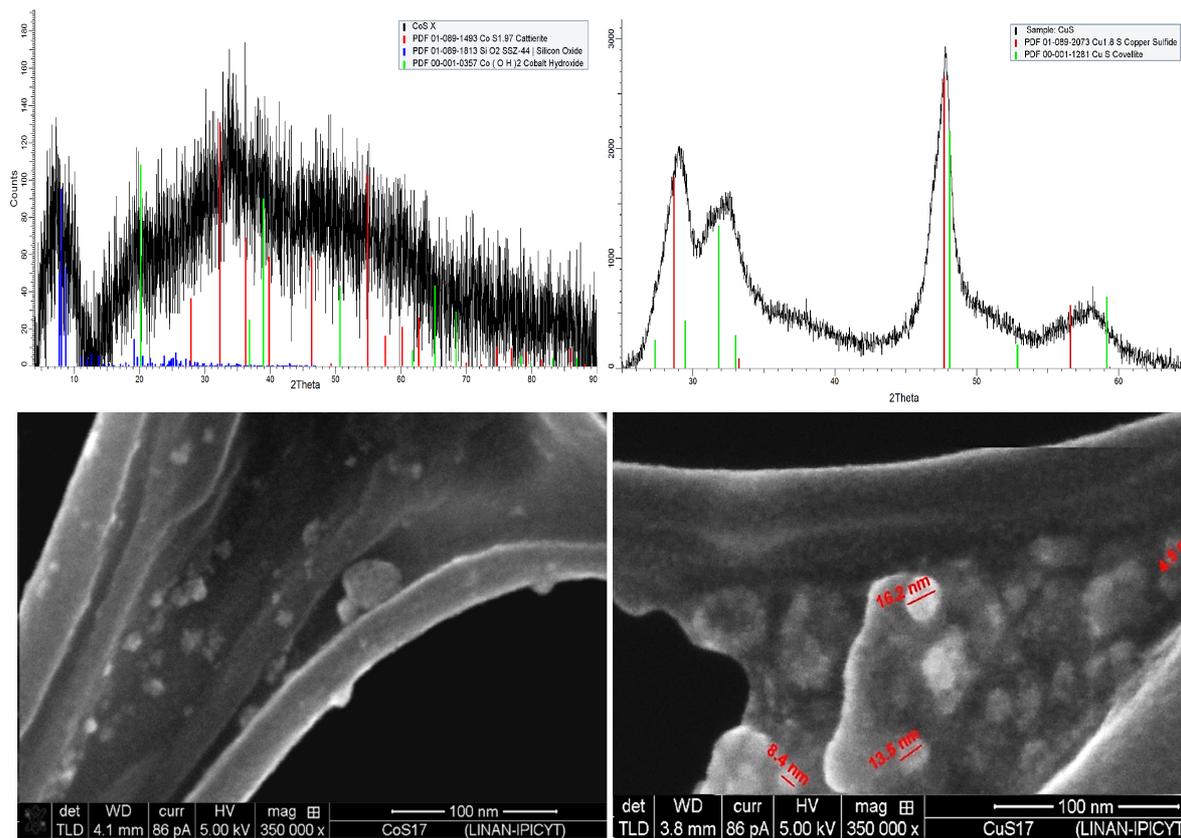


Figure 3: Diffractogram and image of: left, CoS nanoparticles, and right, Cu_xS nanoparticles

4. Conclusion

In this work, most of the cobalt present in the copper cement was obtained by a wash step with water at 50°C, and the charged liquor entered directly to the solvent extraction process, performed at pH=5.5. The efficiency of the counter current extraction was 92.6%. Copper was recovered by acid leaching and the metal was extracted using an organic to aqueous volume ratio of 3.5 to 1 in a single step, with an efficiency of 99.9%. Acidic stripping and a precipitation process allowed the preparation of dispersed nanoparticles of cobalt sulfide (4-10 nm), and copper sulfide (2-14 nm).

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