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Metals recovery from galvanic sludge by sulfate roasting and thiosulfate leaching

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ABSTRACT

The purpose of this work is the selective recovery of Au, Ag, Cu, and Zn from two types of galvanic sludge using a mixed process of sulfate roasting and sodium thiosulfate leaching. In the experiments, the sludge was mixed with a sulfate promoter (sulfur, iron sulfate, or pyrite) and treated by pyrometallurgical processes at temperatures up to 750 °C. At this stage, this agent is thermally oxidized, turning the furnace atmosphere into a reducing one and the metallic oxides into water-soluble sulfates. Afterward, the sulfates can be treated by leaching with water for recovery of Ag, Cu, and Zn. The gold does not form sulfates in this reaction and was recovered through a second leaching stage using sodium thiosulfate, an effective reagent and less harmful to the environment than cyanide. Different parameters such as the sulfate promoter that achieves the highest recovery of metals, the proportion of galvanic sludge to sulfating agent, the temperature, the heating time in the oven, and the leaching time were evaluated. Additionally, a comparison of gold recovery using cyanide versus sodium thiosulfate was performed. The configuration that showed the best metal recovery included a 1:0.4 ratio of sludge to sulfur, an oven temperature of 550 °C, a roasting time of 90 min, and a water leaching time of 15 min. Using these parameters, recovery rates of 80% of the silver, 63% of the copper, and 73% of the Zn were obtained. The sodium thiosulfate leaching resulted in a recovery of 77% of the Au, close to the values obtained using cyanide.

1. Introduction

One of the industries in which environmental issues are the highest is the surface treatment of metal objects (e.g. electroplating, galvanizing). Companies skilled in the production of plated jewelry generate a galvanic sludge (GS) that contains metals with high market value such as gold, silver, copper, and nickel, which can be recovered, thus avoiding large financial losses and environmental problems to manage this waste.

Galvanizing wastes consist primarily of solutions containing high concentrations of a metal or a mixture of metals. These solutions are usually treated using conventional physicochemical processes that generate the galvanic sludge. Compounds are present in the sludge in different forms such as hydroxides, hydrated oxides, and salts of metals from various electroplating processes. Carbonates, sulfates, and calcium phosphates tend to be present when the neutralization is done using CaO. The sludge may also contain inert materials from the alkali silicate bath used for cleaning, contaminations associated to the hydrated calcium oxide used for neutralization, and general impurities. Metal complexes with cyanide can also be present because insoluble metal compounds and nonoxidizable ones such as zinc ferrocyanide can be formed during the oxidation of cyanide with chlorinated compounds (Sharma et al., 2008).

In the last three decades, the economic conditions and the increasingly stringent environmental legislation worldwide have led the electroplating industry to adopt a variety of technologies for the treatment of the waste generated (Li et al., 2010). Methods such as vitrification had been evaluated, but they are focused on the stabilization or solidification of the metals in a matrix and not on recovering metals (Chou et al., 2012; Bassegio et al., 2008). Three routes can be used for the treatment of galvanic sludge aiming at metal recovery: hydrometallurgical processes, pyrometallurgical processes, or both associated (Bernardes et al., 1996).

The galvanic sludge hydration and leaching characteristics cause the hydrometallurgical processes to become an effective choice to recover metals from this waste (Chen et al., 2011). Alkaline sulfate, ammonium hydroxide, and various complexes such as pyrocatechol, phenanthroline, ethylenediamine tetraacetic acid (EDTA), nitrilotrimethylenephosphonic acid (NPT), and di (2-ethylhexyl) phosphoric acid (DEHPA) are used for the selective recovery

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of valuable metals (Park, 2001; Veglio et al., 2003; El-Nadi and El-Hefny, 2010; Buzaeva et al., 2011; Adams et al., 2011).

A process that uses the association of pyrometallurgical and hydrometallurgical methods is the sulfate roasting. This method is used for the treatment of galvanic sludge with high percentage of metals such as copper, cobalt, and nickel. The dry sludge is introduced with a sulfate promoter (SP) in an oven with an oxidizing atmosphere in order to oxidize it. When it releases sulfur in the form of sulfur dioxide, the atmosphere in the furnace is transformed from oxidize to reductive. The oxides and hydroxides of the metals present in the sludge react with the sulfur, turning it into metal sulfide. This reaction can be performed due to the affinity of iron with oxygen, which is much higher than, for example, with copper and nickel that, in turn, have a higher affinity for sulfur. At temperatures below 1000 °C and above 500 °C, the reaction with the iron sulfide may lead to the formation of metal sulfates, which are highly soluble in water (Van Andersale, 1953; Sulka et al., 1986; Tumen and Bailey, 1990; Althudogan and Tumen, 1997). Pyrite, sulfur, and sulfuric acid are the sulfate promoters normally used to produce the reductive atmosphere (Arslan and Arslan, 2002; Sulka et al., 1986; Yali et al., 2011; Wang and Wang, 2010; Rossini and Bernardes, 2006).

In sludges from the electroplating industry containing precious metals, however, the sulfate roasting process cannot recover gold from the sludge because there is no formation of gold sulfate, thus rendering ineffective any leaching with water. It is then necessary to use other more effective leaching agents such as cyanide, thiosulfate, and thiourea. The use of cyanide to extract gold from galvanic sludge yields recovery rates reaching values greater than 90%, leading to the widespread use of cyanide. However, cyanide produces a high volume of effluent and poses great environmental risks. As an alternative to the use of cyanide, thiosulfate has low toxicity and is able to recover large amounts of gold from various types of ores (Hu and Gong, 1991; Wensveen and Nicol, 2005; Zhang, 2008; Feng and Van Deventen, 2007; Xia and Yen, 2005).

Several authors (Hiskey and Altury, 1988; Jiang et al., 1993; Abbruzzese et al., 1995) describe the reactions of dissolution of gold on ammonia thiosulfate. Initially the gold is oxidized and complexed with ammonia to form the complex Au^{+} $[NH_3]^{2+}$ (reactions (1) and (2)). After that the complex reacts with $S_2O_3^{2-}$ in the solution to form the more stable complex $Au[S_2O_3]_2^{3-}$ (reaction (3)), which is more stable at pH 8 to 9.5. On the cathodic surface (reactions (4) and (5)) is the reduction of copper (II) to copper (I), both complexed with ammonia. After entering the solution, the dissolved oxygen acts directly on the cuprous complex, reoxidizing it to the cupric form and maintaining the continuity of the process.

Anodic reactions:

$$Au \rightarrow Au^{+} + e^{-} \tag{1}$$

$$Au^{+} + 2NH_3 \rightarrow Au[NH_3]_2^{+} \tag{2}$$

$$Au[NH_3]_2^{+} + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + 2NH_3 \tag{3}$$

Cathodic reaction:

$$Cu[NH_3]_4^{2+} + e^{-} \rightarrow Cu[NH_3]_2^{+} + 2NH_3 \tag{4}$$

$$Cu[NH_3]_2^{+} + 0.25O_2 + 0.5H_2O + 2NH_3 \rightarrow Cu[NH_3]_4^{2+} + OH^{-} \tag{5}$$

This work proposes the use of sulfate roasting with sulfur, pyrite, and ferrous sulfate as promoters of sulfate in the pyrometallurgical step of the process. The parameters used in both hydrometallurgical and pyrometallurgical steps are based on the research of Rossini and Bernardes (2006). Because gold cannot be extracted using the sulfate roasting process, sodium thiosulfate was used along with parameters successfully tested by Zhang (2008) on different types of ores. This leaching was performed on the solid residue produced during the sulfate roasting process.

2. Materials and methods

The experimental procedures used in this study are presented in Fig. 1 from the characterization of the materials to the processes of recovering the metals.

2.1. Preparation and characterization of samples

Galvanic sludge samples were obtained from the industrial jewelry facilities in the Guaporé region, state of Rio Grande do Sul, Brazil. Galvanic sludges from these facilities contain large amounts of heavy metals and precious metals such as gold and silver. To perform the characterization of the galvanic sludge, two different samples were dried at 110 °C for 24 h and grinded manually to a homogeneous particle size (below 0.25 mm). The samples were characterized by X-ray diffraction (XRD) and atomic absorption analysis. The EPA digestion method 3052 (EPA 3052) was used to dissolve all the metals in the solution to the atomic absorption analysis. This method is applicable to the microwave assisted acid digestion when a total decomposition analysis is required. The following matrices can be digested: ashes, biological tissues, oils, oil contaminated soils, sediments, sludges, and soils. A representative sample up to 0.5 g is digested in 9 mL of concentrated nitric acid and 3 mL of hydrofluoric acid for 15 min using microwave heating. This process was performed in an Anton Paar Microwave digester sample preparation system.

2.2. Pyrometallurgical tests

All pyrometallurgical experiments in this study were performed in a muffle type oven (Sanchis Electric Ovens) with total inner volume of 5.4 L. Mixtures of the galvanic sludge and the sulfate promoters were placed in the oven in not covered crucibles with inner capacity of 50 and 200 mL. The samples were placed in the oven only after the temperature was stable, and measurements of residence time in the oven began at this moment. This system is not open to air flow to reduce the entrance of new oxygen.

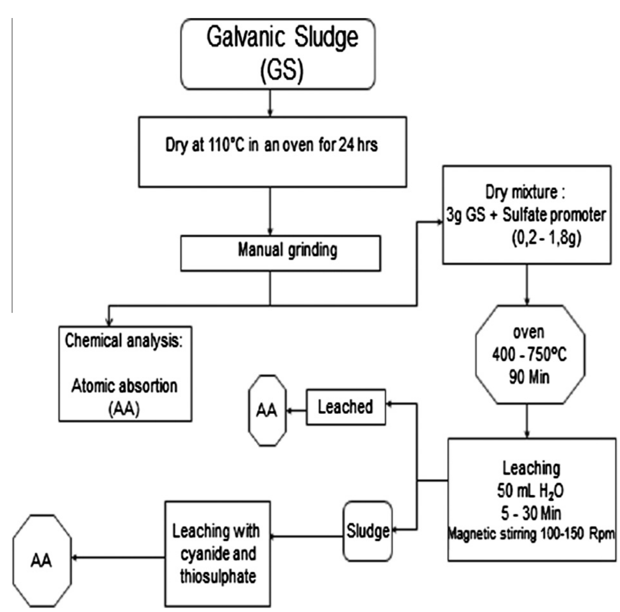

Fig. 1. Flowchart showing the procedures performed in this study.