Electrochemical stripping of gold from Au–Ni–Cu electronic connector scrap in an aqueous solution of thiourea

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The electrochemical behaviour of a gold-plated connector from electronic scrap in aqueous thiourea solution has been investigated. An attempt was made to recover gold from scrap in a nontoxic thiourea medium by an electrochemical method rather than the traditional cyanide process. Linear sweep voltammetry indicated that thiourea extraction of gold is more efficient in acidic solution than in neutral and alkaline. Hydrochloric acid is preferable to control the pH of the solutions; the optimum concentration of thiourea is 2.5% (0.33 M). Analysis of voltammetric data yielded a critical potential (0.40 V vs SCE), which is the upper limit for significant extraction of gold from scrap. Higher potentials should be avoided in practice to prevent decomposition of thiourea and its passivation of the scrap. Electrolysis at constant potential indicated that gold was extracted selectively in the range 0.20–0.30 V vs SCE. Electrolysis at potentials either less than 0.15 V vs SCE or greater than 0.40 V vs SCE is not recommended, because of slow dissolution in the former and severe passivation in the latter.

1. Introduction

Although a cyanide process has long been used to extract gold from both primary and secondary resources, it is uneconomical to treat directly refractory ores because of poor extraction of gold and high consumption of reagents. The cyanide materials constitute a severe pollution problem [1].

Acidic leaching of gold by thiourea is evolving as an alternative to leaching by cyanide. Dissolution of gold in thiourea solution was reported first in 1941 by Plaskin and Kozhukhova [2] and continued in 1960 [3]. Other researchers have since investigated the dissolution of gold from metallic discs [4, 5] and ores [6, 7]. Electrochemical experiments on gold electrodes have been conducted [8, 9]. The advantages of acidic thiourea solution in the presence of an oxidant over cyanide leaching are small toxicity, greater rate of dissolution, high selectivity and smaller consumption by complexation reactions with interfering ions [10, 11]. This process seems a prospective substitute that may reach commercial application before other nonconventional lixiviants [12]. The hydrolysis or degradation of thiourea by oxidation remains a critical limitation.

Both natural ores and secondary resources are main sources of gold production. Many ores are successfully extracted in thiourea solution [1, 5–7, 10, 12]. Secondary resources such as electronic scrap and electrical parts are commonly leached to recover gold in aqua regia and cyanide solutions rather than in thiourea [13, 14]. The objective of this work was to examine electrochemical dissolution of Au–Ni–Cu connector scrap in thiourea solutions, to try to discover optimum conditions for selective stripping of gold from scrap.

2. Experimental details

A gold-plated connector from electronic scrap was taken as raw material for this work. After dissolution in aqua regia and analysis by atomic absorption spectrophotometry (Perkin Elmer 5100PC), the composition was calculated in wt % to be Au 0.55, Ni 0.36, and the balance in Cu. Examination by SEM and EPMA (Fig. 1(a), (b) and (c)) showed the connector to have a thin layer (~10 μm) of gold on the surface, beneath which was a thin film of nickel (~5 μm) deposited on the copper substrate. Interdiffusion was evident between these elements, especially between gold and nickel. The specimen was cleaned ultrasonically in acetone and coated with epoxy resin to produce an exposed area of 60 mm² for linear-sweep voltammetry. Thiourea solutions at various concentrations were prepared by dissolving recrystallized thiourea into doubly distilled water at 0.1, 0.5, 2.5 and 4.0 wt %, (0.08, 0.40, 1.9 and 3.0 M, respectively). The solution pH was adjusted with NaOH and mineral acids (HCl, H₂SO₄ and HNO₃). The freshly prepared solutions were used as electrolytes for anodic stripping using a beaker (500 ml) and magnetic stirring.
A graphite plate (40 mm x 30 mm x 2 mm) was used as cathode. Electrolysis was conducted at controlled constant potentials 0.100, 0.200, 0.300, 0.400, and 0.500 V vs SCE, respectively. During electrolysis the current was recorded and the concentrations of gold, nickel and copper in the solution were analysed by atomic absorption spectrophotometry (Perkin–Elmer 5100PC) with respect to reaction duration. The morphology of the specimen was examined by optical microscopy and SEM.

3. Results and discussion

3.1. Effect of pH on the stripping of scrap in thiourea solution

3.1.1. Effect of pH on anodic current of the linear-sweep voltammogram. From the forward scan of anodic (cyclic voltammogram) curves the variation of anodic current with potential in thiourea solutions (2.5%) at various pH is shown in Fig. 2. The pH of a freshly prepared thiourea solution (2.5%) is 7.2; this was adjusted within the range 1.4–12.0 by addition of HCl or NaOH. The anodic current in acidic solutions of thiourea was much greater than that in either neutral or alkaline solutions (Fig. 2). Hence dissolution of gold is more significant in acidic thiourea solution in an optimal range of potential. This result is illustrated by the concept of electrochemical equilibrium between gold and thiourea as follows.

The redox potential of gold (I) thiourea complex in acidic thiourea solution is

\[
\text{Au}^+ + \text{CS(NH}_2\text{)}_2\text{S}^2_2 + e^- = \text{Au} + 2\text{CS(NH}_2\text{)}_2
\]

\[E^0 = 0.38 \text{ V vs NHE} \quad (1)\]

Accordingly, gold is thermodynamically dissolved in acidic thiourea solutions at potentials greater than 0.38 V vs NHE (0.14 V vs SCE), the threshold potential for dissolution of gold. The potential is set either by connecting the gold anode to an external d.c. rectifier or by adding oxidants to the solutions [1–10].

The bis(thiourea) gold (I) ion indicated in Equation 1 is a stable cationic complex of which the formation constant is governed by [15]

\[
\text{Au}^+ + 2\text{CS(NH}_2\text{)}_2 = \text{Au[CS(NH}_2\text{)}_2\text{]}^+ \quad pK = 21.3
\]

Due to its complexing ability, thiourea is an effective extractant for gold at a potential exceeding 0.14 V vs SCE. During dissolution of gold, thiourea may suffer oxidation in successive stages to several products that fail to dissolve gold [16, 17]. The stage, and thus the dominant product, is determined by the electrochemical potential. For instance, in a solution with potentials at 0.42 V vs NHE (0.18 V vs SCE), oxidation of thiourea terminates at the first stage and forms formamidine disulphide (\(\text{NH}_2\text{(NH)CSSC(NH)NH}_2\))...