Separation Science and Technology
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To cite this Article Yavuz, Ömer and Ziyadanoğullari, Recep(2000) 'Recovery of Gold and Silver from Copper Anode Slime', Separation Science and Technology, 35: 1, 133 — 141

To link to this Article: DOI: 10.1081/SS-100100147

URL: http://dx.doi.org/10.1081/SS-100100147

SEPARATION SCIENCE AND TECHNOLOGY, **35**(1), pp.133–141, 2000

Recovery of Gold and Silver from Copper Anode Slime

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ABSTRACT

This study has shown that gold and silver can be recovered from a complex anode slime containing copper, selenium, and tellurium, but a carefully planned leaching procedure is required. To extract the gold with thiourea, it is necessary to first remove the copper, selenium, tellurium, and most of the silver from the mixture. Once these elements are removed, the gold and most of the remaining silver can be extracted in high yields by leaching with thiourea solutions. It is possible to collect the gold and silver (as well as copper, selenium, and tellurium) in separate phases where they can be purified more easily. No additional step is necessary to separate the silver and gold from each other.

INTRODUCTION

Gold and silver that occur in elemental form can be recovered from ores by density concentration, amalgation, flotation, and pyrometallurgical, hydrometallurgical, or biochemical methods (1). Since 1880, recovery of gold and silver from ores and concentrates has been carried out hydrometallurgically by a cyanide-based method. The major problem with that approach is the high toxicity of the cyanide. Gold and silver in refractory ores such as sulfides, pyrite, arsenopyrite, and carbonaceous materials can be extracted with only

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low yields using these conventional methods. To apply the cyanide process to these ores, it is necessary to treat them first with a bioleaching, leaching under pressure, oxidizing acidic leach, or roasting step. The pretreatment makes recovery uneconomical.

Thiourea is a nontoxic reagent that dissolves gold and silver at rates that are actually higher than cyanide leaching rates. Thus, thiourea leaching of various gold- and silver-containing ores and concentrates such as anode slimes has been studied widely (2–8). However, thiourea leaching is sensitive to the presence of such basic metals as copper, lead, zinc, arsenic, and antimony, as well as other impurities. This paper describes an approach to avoid the interference of the other metals in treating a particular anode slime.

MATERIALS AND METHODS

The two different anode slimes used in this study were provided by Bras Factory in Kirikkale, Turkey. One slime had been roasted at 400°C; the other slime had not been roasted but had been dried at 100°C. Roasting converted the selenium in the anode slime to selenite; selenium in the unroasted slime was selenide. The analyses for key elements in the two anode slimes are given in Table 1.

Analyses for tellurium and selenium were carried out gravimetrically (9) while those for copper, gold, and silver were made with an Atomic Absorption Spectrophotometer (Varian Tectron 1200 Model). Copper concentrations were also determined iodometrically (10). Free thiourea concentrations were determined by titration with 0.05 M $Hg(NO_3)_2$, using a diphenylcarbazide indicator (11).

Copper leaching was carried out under pressure in an autoclave with 1.8 L internal volume and temperature controlled with a thermostat (NEL-TS 1351) using a Ni-Cr-Ni thermocouple. Thiourea leaching experiments were carried out in a jacketed reactor with 250 mL internal volume and monitored with a pH meter (NEL-890). Constant temperature operations were maintained with a thermostat (Frigomix 1495).

TABLE 1
Analysis Results of Anodes Slimes

	Composition, %(w)				
Samples	Cu	Se	Te	Ag	Au
Crude anode slime	28.0	15.0	2.1	7.9	0.37
Roasted anode slime	47.0	13.5	0.8	3.5	0.24

RESULTS AND DISCUSSION

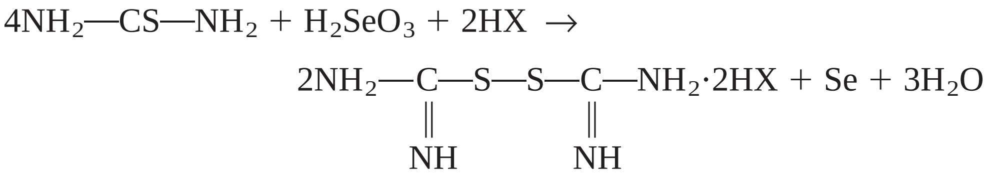
Removal of Copper, Silver, and Gold

The first step in this approach was to remove the copper from the anode slime [a mixture of roasted ($CuSeO_3$) and unroasted (CuSe) slimes] by dissolution with sulfuric acid according to (12):

$$\mathrm{Cu_2Se + CuSeO_3 + 3H_2SO_4 \rightarrow 3CuSO_4 + 2Se + 3H_2O} \qquad (1)$$

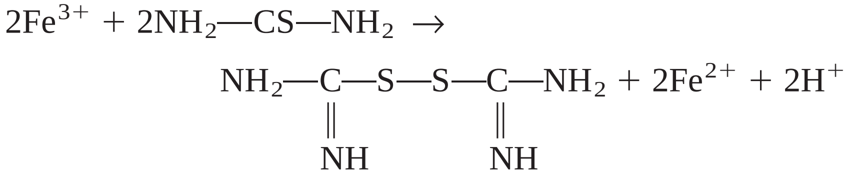
The dissolution was carried out for 1 hour under 6 atm N_2 pressure at 350°C. At the end of the experiment the dissolved copper was removed and the residue (decopperized anode slime) was washed with deionized water. This removed 99% of the copper; silver and selenium were not dissolved. Decopperized anode slime was then dried at 110°C and ground to sizes less than 100 mesh.

The decopperized anode slime was leached with a thiourea solution accompanied with an oxidant; several oxidants were tested. For instance, SeO_2 was accompanied with an oxidant; several oxidants were tested. SeO_2 oxidizes by the reaction



$$\mathrm{4NH_2{-}CS{-}NH_2 + H_2SeO_3 + 2HX \rightarrow 2NH_2{-}\underset{\underset{NH}{\|}}{C}{-}S{-}S{-}\underset{\underset{NH}{\|}}{C}{-}NH_2\cdot 2HX + Se + 3H_2O} \qquad (2)$$

but only 4% of the gold and 8% of the silver was extracted, and the extraction of silver actually decreased as the amount of SeO_2 increased. Fe^{3+} was also tested as the oxidant using solutions with 5 and 10 g/L of iron. The 5 g/L solutions leached 48% of the gold and 15% of the silver, but when the solution with 10 g/L of iron was used, only 2% of silver and none of the gold were leached. The decrease in gold and silver leaching with the higher iron concentration was caused by oxidation of the formamidine disulfide by the reaction



$$\mathrm{2Fe^{3+} + 2NH_2{-}CS{-}NH_2 \rightarrow NH_2{-}\underset{\underset{NH}{\|}}{C}{-}S{-}S{-}\underset{\underset{NH}{\|}}{C}{-}NH_2 + 2Fe^{2+} + 2H^+} \qquad (3)$$

The oxidation product is not stable in dilute acid solutions but decomposes to form sulfur, cyanamide, and thiourea (TU) (8):

$$\mathrm{2TU \underset{+2e}{\overset{-2e}{\longleftrightarrow}} + T_2H_2^{2+} \rightarrow TU + sulfinic\ compounds \rightarrow cyanamide} \qquad (4)$$

The first oxidation product of thiourea is formamidine disulfide (T_2 or $T_2H_2^{2+}$) in acid solutions by a reversible reaction. In an irreversible step, $T_2H_2^{2+}$ disproportions to yield thiourea and an unidentified sulfinic compound which, in turn, decomposes irreversibly to cyanamide and elemental sulfur (13). The elemental sulfur decreases the gold leaching rate by passivating the gold surface and decreases the silver leaching rate by the formation of insoluble Ag_2S (14):

$$2Ag^+ + 2NH_2\text{—}CS\text{—}NH_2 \rightarrow Ag_2S + NH_2\text{—}CN + 2H^+ \qquad (5)$$

Thus, these results show that the extraction of gold and silver could not be completed by oxidation alone. Instead, the selenium and tellurium should be extracted first using Na_2SO_3 and Na_2S solutions. This removes 80% of the selenium and 97% of the tellurium (15).

The residual selenium was only that assciated with silver in the form of Ag_2Se, and silver was either in the form of Ag_2Se or Ag_2S. The residue was then roasted for 4 hours at 700°C to remove the remaining selenium and sulfide (16). When the roasted sample was leached immediately with thiourea, only 35% of the gold and 10% of the silver were extracted.

But if the roasted samples were leached first with concentrated sulfuric acid in an autoclave at 350°C under 8 atm oxygen pressure, and then with 0.1 M sulfuric acid and 3 M NH_3, most of the silver was dissolved. This is shown in Table 2.

After drying at 110°C, the desilverized samples contained 3.08% Au, 0.9% Ag, 0.2% Se, and 0.1% Te. Leaching this material with thiourea (with and without Fe^{3+} oxidant) produced up to 60.4 and 75.0% dissolution of gold and silver, respectively (Fig. 1). The amount of gold and silver leached without Fe^{3+} oxidant is illustrated in Fig. 2. The higher extraction yields were obtained with the Fe^{3+} oxidant (Figs. 2–4). However, the oxidant also degraded

TABLE 2
The Reaction of the Sample with H_2SO_4 at Autoclave Conditions

Amount of H_2SO_4		Amount of silver passed into solution (%)		
Equivalent amount	Volume (mL)	0.1 M H_2SO_4	3 M NH_3	Concentrated HNO_3
1.0	0.25	82.1	17.7	0.2
1.5	0.375	75.2	24.7	0.1
2.0	0.50	70.4	29.3	0.3
2.5	0.625	65.0	34.8	0.2
3.0	0.75	60.8	39.1	0.1
4.0	1.00	57.2	42.6	0.2
5.0	1.25	60.2	39.6	0.2

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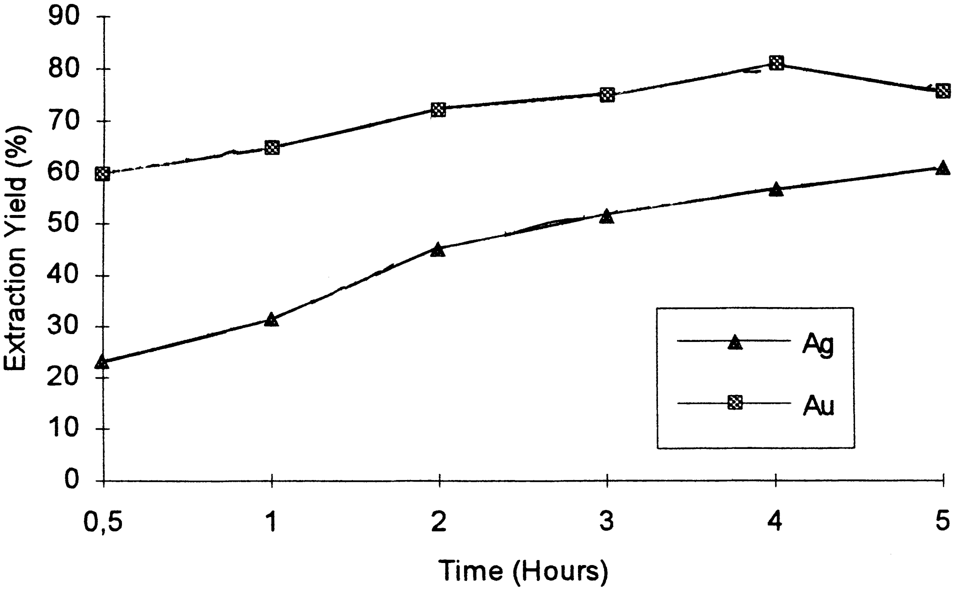

FIG. 1 Leaching of desilverized sample with thiourea solution. Experimental conditions: amount of sample, 1.4373 g; volume of extraction solution, 250 mL; concentration of thiourea solution, 10 g/L; pH, 1.0; temperature, 30°C.

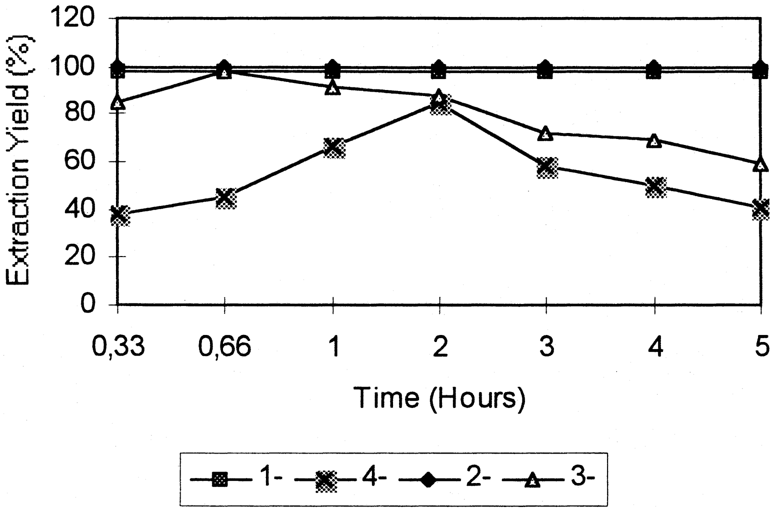

FIG. 2 Effect of temperature on leaching of gold and silver extraction. Experimental conditions: amount of sample, 1.4708 g; volume of extraction solution, 250 mL; concentration of thiourea solution, 10 g/L; amount of Fe^{3+}, 2.5 g/L; pH, 1; temperature, 30°C and 40°C. 1: 30°C Au; 2: 40°C Au; 3: 40°C Ag; 4 :30°C Ag.

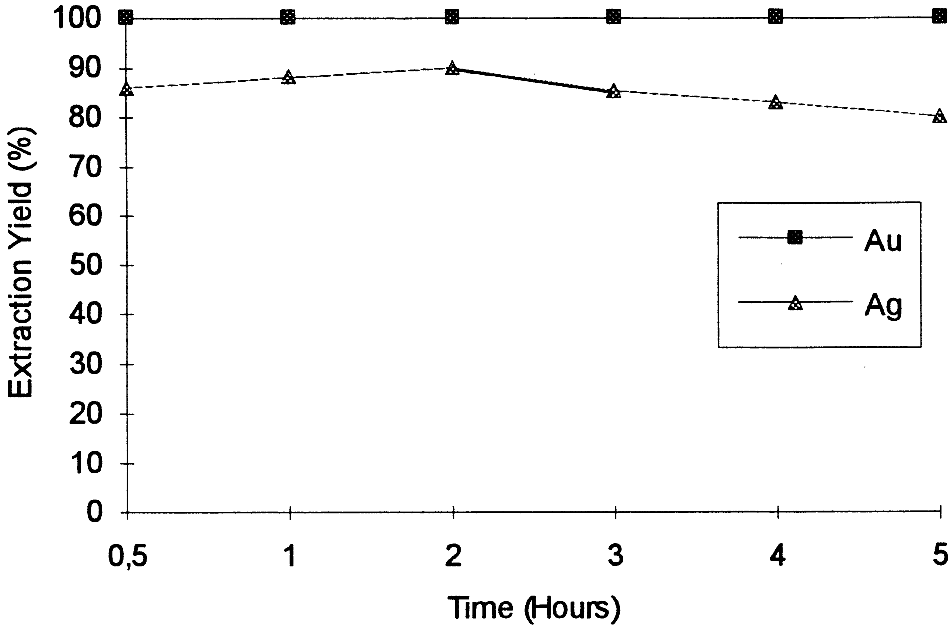

FIG. 3 Leaching of desilverized sample with thiourea solution. Experimental conditions: amount of sample, 1.5993 g; volume of extraction solution, 250 mL; concentration of thiourea solution, 10 g/L; amount of Fe^{3+}, 5 g/L; pH, 1.0; temperature, 30°C.

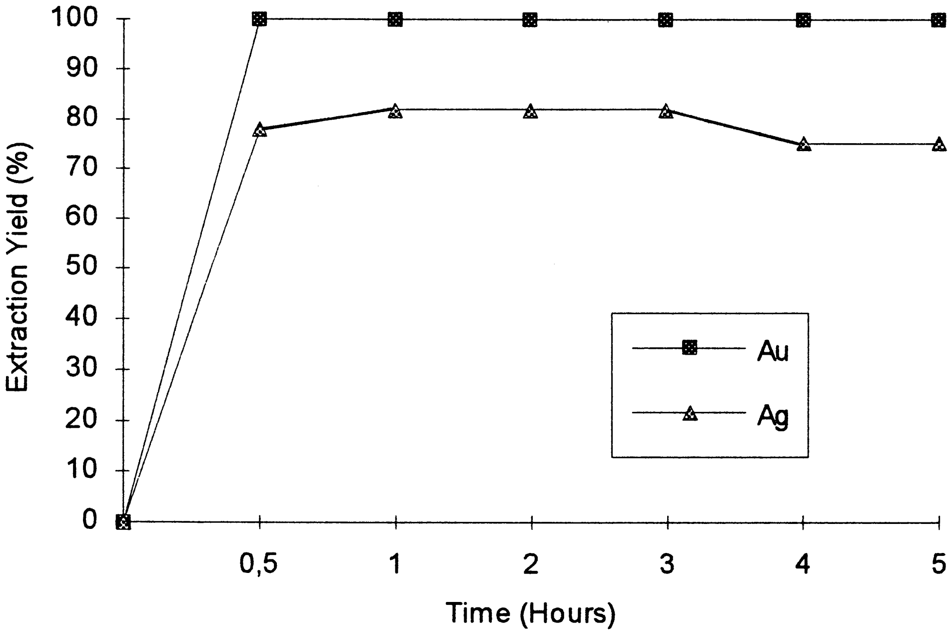

FIG. 4 Leaching of desilverized sample with thiourea solution. Experimental conditions: amount of sample, 1.4084 g; volume of extraction solution, 250 mL; concentration of thiourea solution, 10 g/L; amount of Fe^{3+}, 7.5 g/L; pH, 1.0; temperature, 30°C.

TABLE 3
Influence of Fe^{3+} Concentration on Extraction of Gold and Silver

Concentration of Fe^{3+} (g/L)	Extraction yield, %		Degraded thiourea (%)
	Au	Ag	
0.00	41.5	72.9	0.1
1.25	97.8	88.2	14.4
2.50	99.9	90.2	21.3
5.00	99.9	85.6	63.4
7.50	99.9	83.0	97.8

the thiourea, and the degree of degradation is shown in Table 3 and Fig. 5. As the concentration of the oxidant is increased, the degradation also increases and reduces the silver leaching slightly at Fe^{3+} concentrations above 2.5 g/L. Leaching of gold is not affected significantly by the oxidant concentration over this concentration range (Fig. 5).

The effects of temperature on leaching are also illustrated in Fig. 2. Gold leaching is very high for both temperatures tested, but silver leaching is notably better at 40°C than at 30°C. The variation of the leaching efficiency for the remaining silver with time can be attributed to degradation of the thiourea and the subsequent formation of insoluble Ag_2S. The effect of the solid/liquid

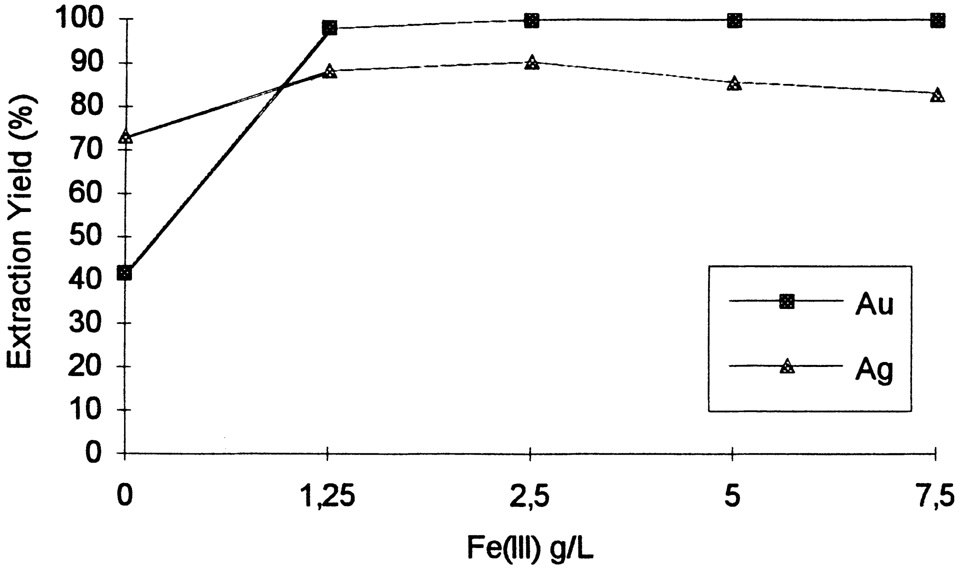

FIG. 5 Influence of Fe^{3+} on the extraction of gold and silver. Experimental conditions: amount of sample, 1.5000 g: volume of extraction solution, 250 mL; concentration of thiourea solution, 10 g/L; pH, 1, extraction time, 2 hours; temperature, 30°C.

TABLE 4
Effect of Solid/Liquid Ratio on Extraction
Yields of Gold and Silver

	Extraction yield (%)	
Solid/liquid ratio	Au	Ag
1:10	62.9	40.9
1:20	94.5	49.0
1:30	99.6	57.2
1:40	99.6	62.3
1:50	99.6	76.6
1:60	99.6	80.3

ratio on leaching efficiency is shown in Table 4. The leaching efficiency increases with decreasing solid/liquid ratio over the entire range tested.

DISCUSSION

In this study the recovery of copper, selenium, tellurium, silver, and gold in anode slime takes place in separate steps. For extractability of gold with thiourea, it is necessary first to remove copper, selenium, tellurium, and silver from the anode slime. Following removal of these elements, the gold (and the remaining silver residue) can be extracted in high yields by leaching with thiourea solutions. With this method it may be possible to collect copper, selenium, tellurium, silver, and gold in separate phases and purify them more easily. No other process is needed to separate gold and silver from each other after thiourea extraction because the gold and most of the silver are recovered in different steps.

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Received by editor December 20, 1995
First revision received March 2, 1997
Second revision received February 1999

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