Hydrochemically separation of gold from Copper Anode Slime by means of Thiourea solution

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ABSTRACT

Although the conventional gold recovery process is cyanidation, due to the recent environmental laws, researchers are looking for alternative methods for the recovery of gold. Furthermore, the copper anode slime is one of the most important secondary sources of gold (about 1200 ppm). So, the main objective of the current work is gold separation from copper anode slime as a rich secondary source of gold by determining the mechanism of the reaction between thiourea (TU) and H_2O_2 in the thiourea leaching of gold. Thiourea can form cationic complex with gold in the gold extraction process from copper anode slime. Thiourea consumption levels were also examined during the leaching operations for different leaching parameters, i.e. solution volume, concentration ratio of thiourea/H_2O_2, pH, leaching time and agitation rate. Ammonia was added to the gold containing solution and, consequently, gold was precipitated in the metallic form. X-Ray pattern confirms the formation of metallic gold.

1-Introduction

Methods employed for recovery of precious metals from their sources include zinc–dust cementation [1], carbon adsorption [2], solvent extraction [3,4], and ion exchange [5]. Resin adsorption is another method used for recovery of gold and silver [6]. Another method is the absorbent process using activated carbon. Conventional precipitation and hydrometallurgy methods are also most often used to remove gold and heavy metals [7].

In the gold leaching process, cyanide leaching has some disadvantages such as low leaching rate, low selectivity since cyanide forms stable complexes containing almost every metal usually present in gold ores, and high toxicity which leads to the introduction of new methods.

Due to these problems, the study and development of an alternative process to leach gold from its ores and other sources are still of interest [7]. Another research work in gold hydrometallurgy has been developed as green technology to recover gold from non-metallic secondary sources. It is based upon heating the scrap material along with an "eco-friendly" or "green" reagent which is considered as the advantage of this process [8]. Among the reagents that have been pointed out as alternatives to cyanide in the leaching of gold, halogens, thiocyanate, and thiourea appear to be more interesting [9-12]. Processes that use thiourea (TU) as a leachant for gold have already some industrial applications, and research works on possible improvements in these processes

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still continue. The use of thiourea (NH_2CSNH_2) as a gold extraction agent has shown considerable promise. In acidic conditions, thiourea dissolves gold, forming a cationic complex; the reaction is rapid and gold extractions of up to 99% can be achieved [13]. At low concentrations, thiourea is used as an additive in the electrode position of metals such as copper from acid solutions, whereas at high concentrations, it is considered as a possible leachant in hydrometallurgy for the recovery of gold and silver from minerals and slimes. These applications are related to the special properties of thiourea for those metals. In fact, for gold, a number of complexes involving the $[Au(CS[NH_2]_2)_2]^+$ cation have been produced, isolated, and identified by X-ray diffractometry [12]. The anodic reaction is as follows [14]:

$$Au+2CS(NH_2)_2 = Au(CS[NH_2]_2)_2^+ + e^-$$
$$E^0 = 0.36v \qquad (1)$$

For a significant leaching rate in this reaction, an oxidant (ferric ion or hydrogen peroxide) at a high concentration is required [15,16].

In the current research work, a facile method is introduced, in which the gold is completely recovered from the Sarcheshmeh (Kerman, Iran) anode slime.

2-Experimental
2-1-Materials
The gold-containing copper anode slime was obtained from the National Sarcheshmeh Copper Company in Iran. All chemicals used in the present study were purchased from Merck Company (Germany). Atomic adsorption spectroscopy (AAS) was conducted using a Varian Spectra AA 220FS.

2-2-Preparation of gold solution with thiourea
The leaching of gold from copper anode slimes is affected by the presence of some elements such as silver, iron, and selenium. Thus, at first, the copper anode slime was washed with concentrated nitric acid.

High speed leaching experiments were performed in a 500-ml round bottom flask at room temperature and atmospheric pressure. For gold leaching with thiourea, thiourea powder, hydrogen peroxide (as the oxidizing agent), and sulfuric acid (for pH adjustment) were used.

2-3-Characterization of gold-containing thiourea solution
In order to maximize gold dissolution as well as to optimize the process, three significant parameters, i.e. the pulp density, the amount of hydrogen peroxide, and the effect of pH were studied in detail.

The first parameter studied was pulp density (solid mass/solution volume). A solution of 60 g/l thiourea and 30 g/l hydrogen proxide in 300 ml deionized water was prepared at a pH level of 1.3, and 5 g slime was subsequently dissolved in the solution. To change the pulp density and acquire solutions with greater concentration, the experiment was repeated by dissolving the slime in 150ml, 90ml, 60ml, 30ml and 15ml of thiourea solution. In fact, to obtain more concentrated gold solutions and decrease the consumption of thiourea and other materials, the solution volume was decreased.

By altering the amount of hydrogen peroxide in the solution, the potential was changed. As the gold-thiourea complex is stable at a specific potential and pH range, TU to hydrogen peroxide ratio affects the gold extraction percentage in the solution. In these experiments, TU to H_2O_2 volume ratios of 0.5, 1, 2, and 3 were considered. Thiourea concentration was constant at 60 g/l, and the solution volume was 60 ml. The pH value was also set at 1.3.

Finally, the effect of varying pH on the gold extraction was studied. The pH (as well as potential) is important for the stability of the complex, as shown in the Au-thiourea Pourbaix diagram [13]. The pH was changed to 0.75, 1, 1.25, 1.5, and 1.75, and its influence on gold extraction was studied. All the prepared solutions were stirred with a rate of 500 rpm for 24 hours and at room temperature.

After each process, the solutions were analyzed by AAS with MIBK (Methyl isobutyl ketone) solution to measure the concentration of the dissolved gold. Other elements were analyzed using XRF_Philips unique 2.

2-4-Recovery of metallic gold from thiourea solution
For recovery of metallic gold, ammonia was added to the gold-containing thiourea solution step by step to increase the pH over 8. As a result,

black sediment was deposited, and the color of the gold-thiourea solution changed from gold to colorless.

2-5-Reaction chemistry of thiourea and hydrogen peroxide

Reaction chemistry and kinetics of thiourea and ferric sulfate thiourea leaching is related to the formation of cationic gold complex in acid. Air and oxygen are not appropriate as oxidants; Fe(III), H_2O_2, and $Fe_2(SO_4)_3$ are the most suitable oxidants for thiourea leaching of gold ores [13]. Previous researches have shown that Ferric ion as an oxidant is as effective as hydrogen peroxide since gold extractions by both of these two elements are very similar. However, it appears to have two main disadvantages: it consumes an excessive amount of thiourea due to the formation of iron-sulphate-thiourea complex according to reaction (2), and it leads to an important buildup of impurities which would introduce much more expensive purification step. Also, the presence of iron in the final product (gold) is possible [9,17].

$$Fe^{+3} + SO_4^{2-} + CS(NH_2)_2 \leftrightarrow (FeSO_4(CS(NH_2)_2)^+ \tag{2}$$
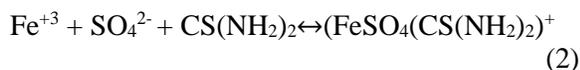
The oxidants used for the dissolution of gold in acidic solution of thiourea also oxidize thiourea, the first product being formamidinedisulphide:

$$2CS(NH_2)_2 \leftrightarrow NH_2(NH)CSSC(NH).NH_2 + 2H^+ + 2e^- \tag{3}$$

This oxidation is reversible, and the formation of formamidinedisulphide can be controlled by monitoring the solution potential with H_2O_2 concentration. Formamidinedisulphide oxidizes to produce cyanamide, hydrogen sulfide, and elemental sulfur.

$$NH_2(NH)CSSC(NH).NH_2 \leftrightarrow NH_2CSNH_2 + Sulfinic\ compound \tag{4}$$
$$Sulfinic\ compound \rightarrow CNNH_2 + S^0 \tag{5}$$
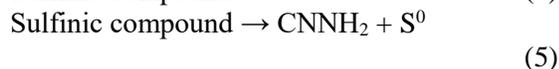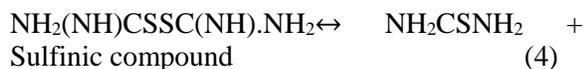
The dissolution of gold is dependent on the H_2O_2 concentration because if this value is too high, an irreversible decomposition of thiourea occurs according to the above reactions which have been pointed out as the main cause for the high thiourea consumption [18, 19].

3-Results and discussion

3-1-Anode slime characterization

Chemical composition of the delivered copper anodic slime from National Sarcheshmeh Copper Company is presented in Table 1 before and after the washing process using nitric acid obtained from XRF and AAS tests. As shown, gold and silver contents in the slime were 1200 ppm and 5 percent, respectively.

It can be inferred that most of the copper, selenium, and silver were eliminated by dissolving in nitric acid. These elements moved into the nitric solution in nitride form. The concentration of Au did not change clearly because of poor concentration.

3-2-The pulp density

In the first series of experiments, the solution volume decreased. The conditions for each experiment are summarized in Table 2. In fact, in this set of experiments, the pulp density (mass of slime to solvent volume fraction) changed.

The percentage of dissolved gold can be calculated using the following formula:

$\%Au = 100.[m_{gold(s)}/m_{gold(sl)}] = 100.[V_s.X/0.0012.m_{(sl)}]$

1200 ppm = 0.12%

$m_{gold(s)}$ = Mass of gold in gold-containing thiourea solution

$m_{gold(sl)}$ = Mass of gold in slime

X = Amount of gold in solution obtained from AAS (mg/l)

V_s = Solution volume (ml)

m_{sl} = Mass of slime used for preparing the solution(g)

Therefore, the experimental results can well be compared with the theoretical ones.

Table 1. Chemical analysis of the main elements in the delivered copper anode slime.

Elements	CuO	SeO2	Ag$_2$O	Sb$_2$O$_3$	BaO	PbO	SrO	Au
Before washing (Wt%)	5.4	10.2	4.8	2.58	34.1	3.81	0.98	0.12
After washing (Wt%)	0.128	0.42	0.2	3.72	64.7	3.81	1.82	0.12

Table 2. Pulp density variation test results.

Experiment no.	Solution volume (ml)	Dissolved gold concentration (mg/l)	Max theoretical gold Concentration (mg/l)	Dissolved gold %	Pulp Density
1	300	19.8	20	99	1/60
2	150	39.8	40	99.5	1/30
3	90	66	66.7	98.9	1/18
4	60	99.9	100	99.9	1/15
5	30	198	200	99	1/6
6	15	331	400	82	1/3
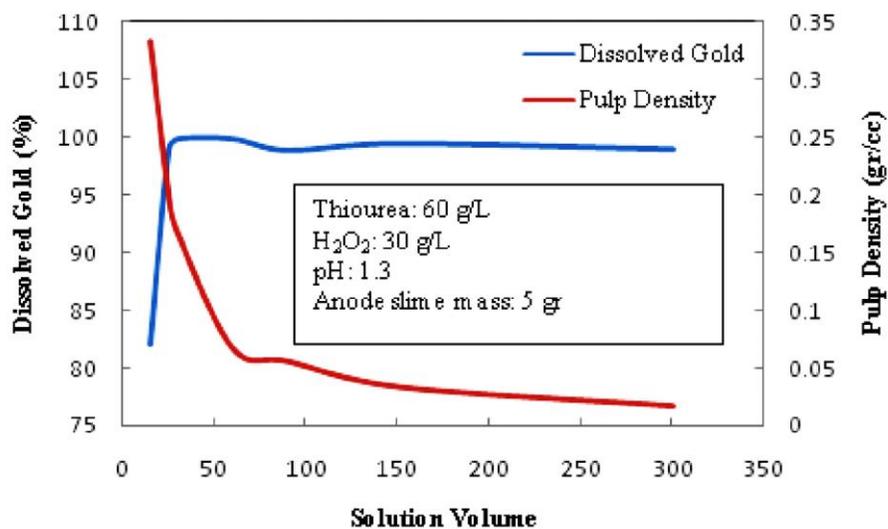
Figure 1. Effect of pulp density on dissolved gold%.

As demonstrated in Figure 1, thiourea consumption is proportional to solid-mass/solution-volume because the amount of materials per unit of volume was constant and, consequently, with a decrease in the solution volume, thiourea consumption decreased. It is also observed that the percentage of extraction remained nearly unchanged initially by increased the pulp density. A further decrease in the volume (increase in the pulp density) to less than 30 ml caused a significant decrease in the recovery percentage because in a volume of less than 30 ml, the slime in the thiourea solution was mud-like, and the dissolution process did not proceed correctly. Therefore, the critical value of solid-mass/solution-volume for minimum thiourea consumption and maximum extraction percentage is near 1/6.

3-3- TU/H_2O_2 variation
In the second series of experiments, the TU to H_2O_2 ratio was changed.
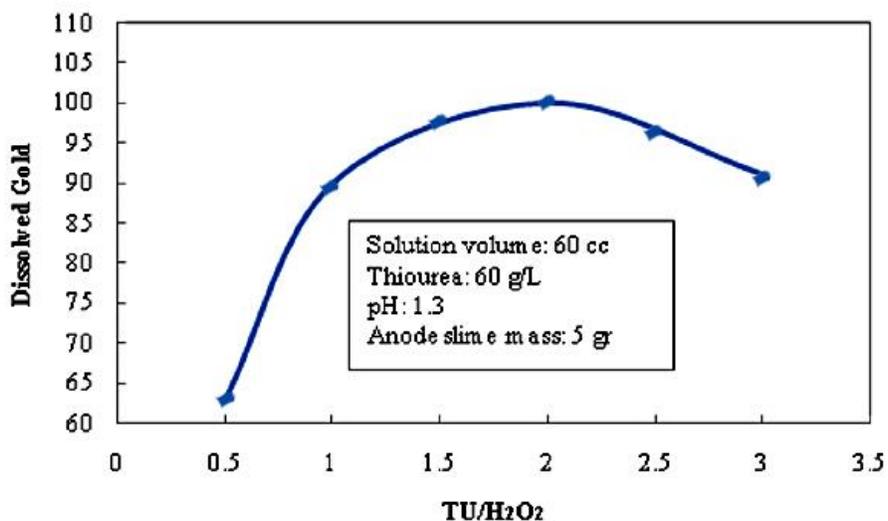
Figure 2. Variation of dissolved gold percentage vs. TU/H$_2$O$_2$.

Figure 2 shows that the amount of dissolved gold depends largely on the oxidant concentration. As it was mentioned in section 3.2 and equations 3-5, at excessive concentrations, irreversible thiourea decomposition to elemental sulfur and cyanamide occurred. This not only results in high consumption of thiourea but also the elemental sulfur forms a passive layer on gold particles, preventing them from reacting with thiourea for making the complex [20]. As a result, the optimum amount of TU/H$_2$O$_2$ is 2, which was also observed by Reza et al. [20].

3-4-pH variation

In this series, pH was changed within a range of 0.75 to 1.75. Au-TU complex is stable in acidic solutions. Many studies report pH 1-1.5 for higher extractions [17-20]. To find the exact and suitable pH, the pH value was varied and its influence on extraction percentage was investigated.
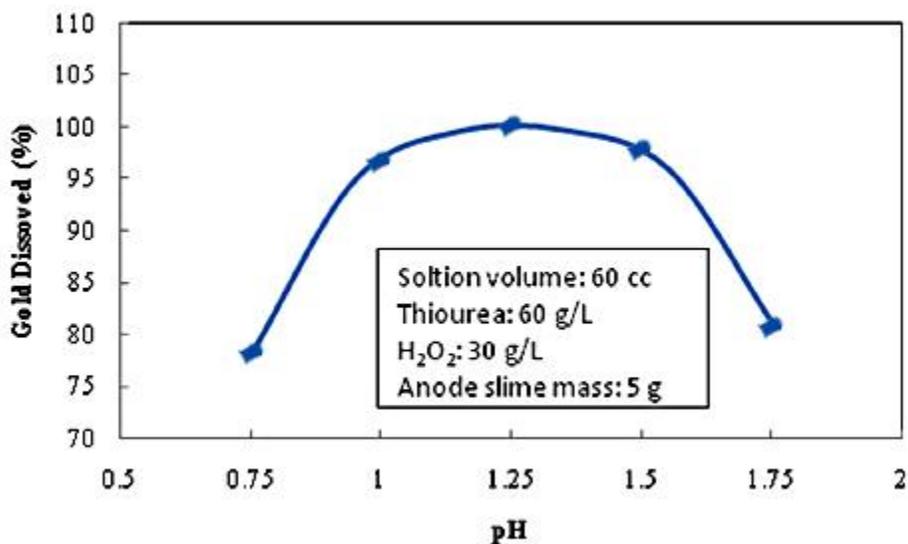
Figure 3. Variation of dissolved gold percentage with pH.

It illustrates that extraction percentage is completely sensitive to solution pH and solution redox potential which has an inverse relationship with oxidant concentration. pH also affects the Au-TU complex stability. In fact, as shown below, in the Au-TU Pourbaix diagram [13], it is observed that the complex is stable in a zone which has a combination of pH and potential range. It can be concluded by the conducted experiments that the optimum pH value in the mentioned leaching conditions was about 1.25. In such acidity, the gold can be completely extracted into the solution.
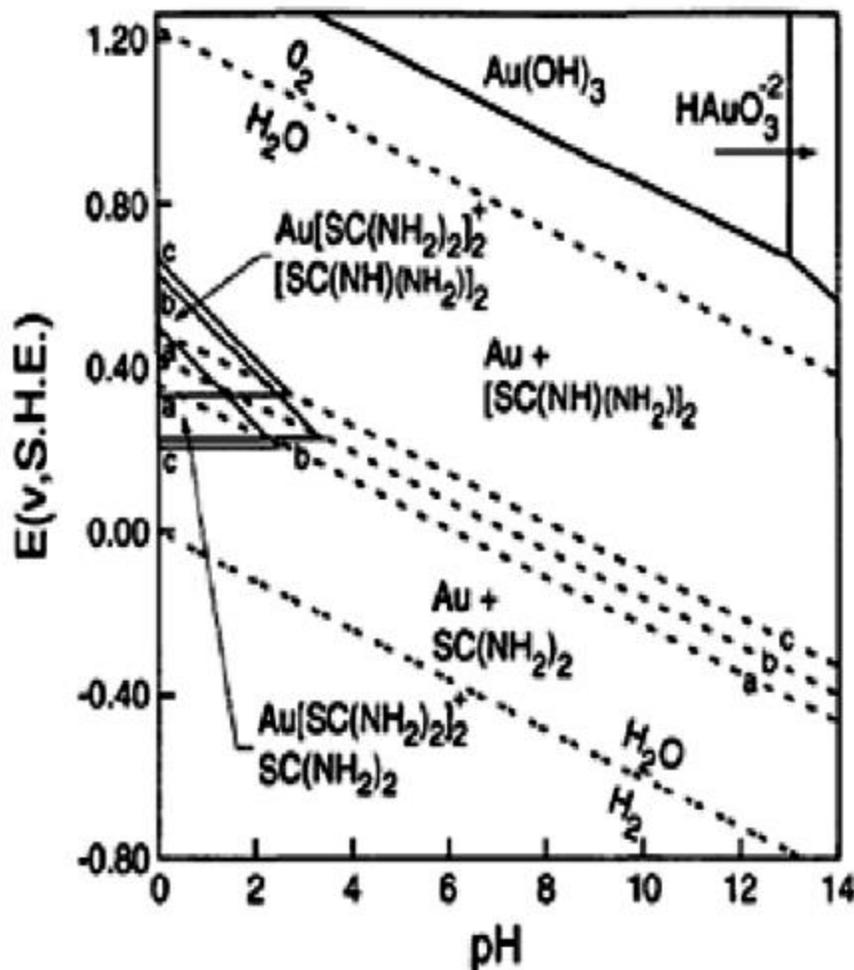
Figure 4. Pourbaix diagram for Au-TU-H_2O_2 system at 250˚C [13].

3-5-The leaching time
The effect of mixing time was investigated under the condition of TU/H_2O_2=2 and pH=1.25. The extraction increased with time at the beginning of the leaching process. After 24 h, it reached the highest value (99.9%) and then stayed at this value until 28h and then decreased [21, 22]. This shows that there was no dissolution after 24 h. After 24 h, the negative factors such as thiourea decomposition, sulfur passivation, or the adsorption of Au(TU)$_2^+$ complex became important and this decreased the gold extraction extent. Likewise, this result was observed by C.M. Juarez et al. [23].
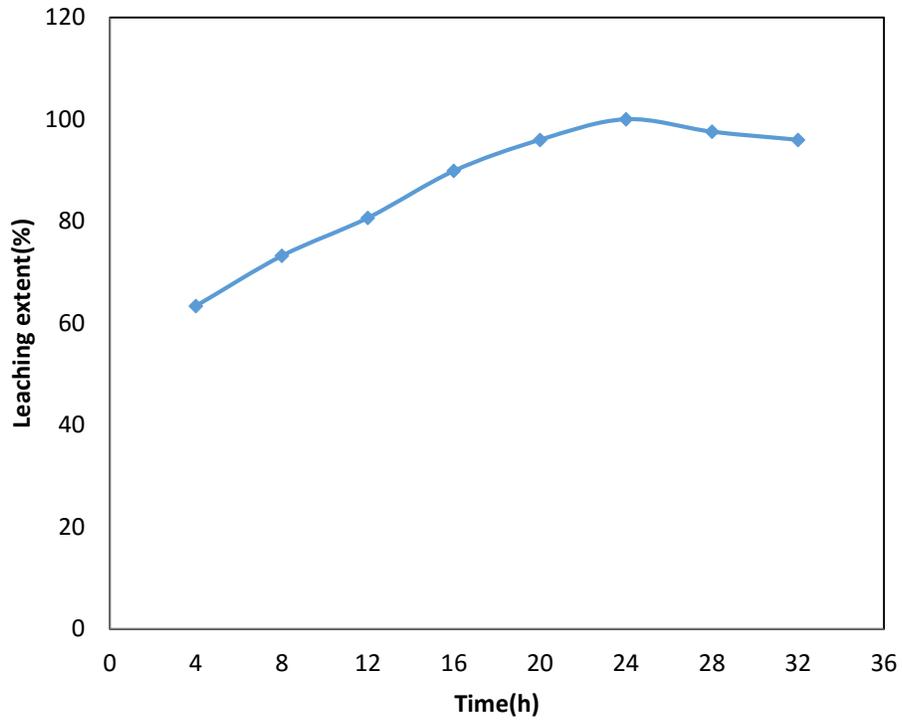
Figure 5. Diagram of leaching extent vs. time.
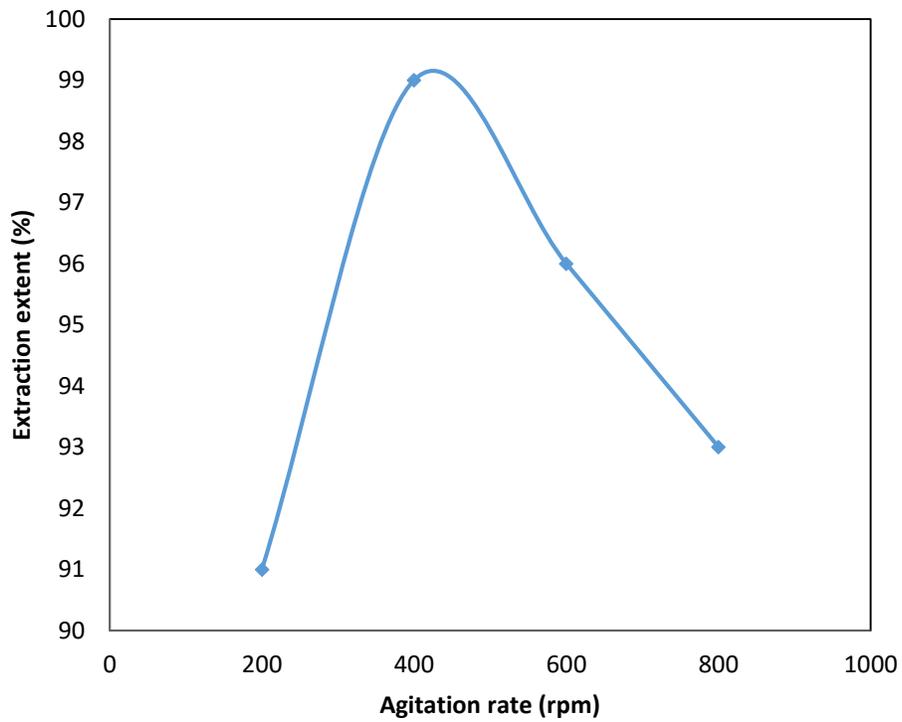
Figure 6. Diagram of extraction extent vs. agitation rate.

3-6-The agitation rate

The effect of agitation rate was investigated at the best amount of TU/H$_2$O$_2$ (about 2) and at pH=1.25. The extraction extent increased at a rate per minute (rpm) of about 400. Any increase in the agitation rate reduces the thickness of the diffusion layer to such an extent that the diffusion of the reagents becomes faster than the rate of the chemical reaction or than the inner diffusion [21]. The extraction extent decreased by the increase in rpm values from 400 rpm. Figure 6 shows the effect of agitation rate on the extraction extent. This shows that there is no time-to-extraction process at higher rpms such as 800 rpm. The best agitation rate is calculated at 400 rpm.

This result was observed in the research conducted by Harvanova et al. [24].

3-7-Gold recovery

AAS tests were conducted on the solution to determine the amount of remaining gold in thiourea solution after the addition of ammonia. The results showed that for all samples, all the gold present in thiourea solution precipitated, and the amount of gold remaining in thiourea solution was about zero.

The gold complex is stable in the pH range of 1-1.5. Thus, by adding ammonia to the solution, pH reaches over 8, and the complex dissociates according to the reaction mentioned in the introduction section.

The residue was characterized with XRD. The results are shown in Figure 7. In fact, metallic gold precipitated, and thiourea in ammonia (alkaline solution) reacted in several steps, and several carbon base products shown in Figure 7 were obtained. The obtained results and Figure 7 show that approximately all the gold content in thiourea solution precipitated in a metallic form and a trace amount of gold remained in the thiourea solution. Other impurities such as sulfur were omitted by heating and washing the residue. Finally, it was concluded that all the gold from copper anode slime was hydrochemically recovered using the thiourea solvent.
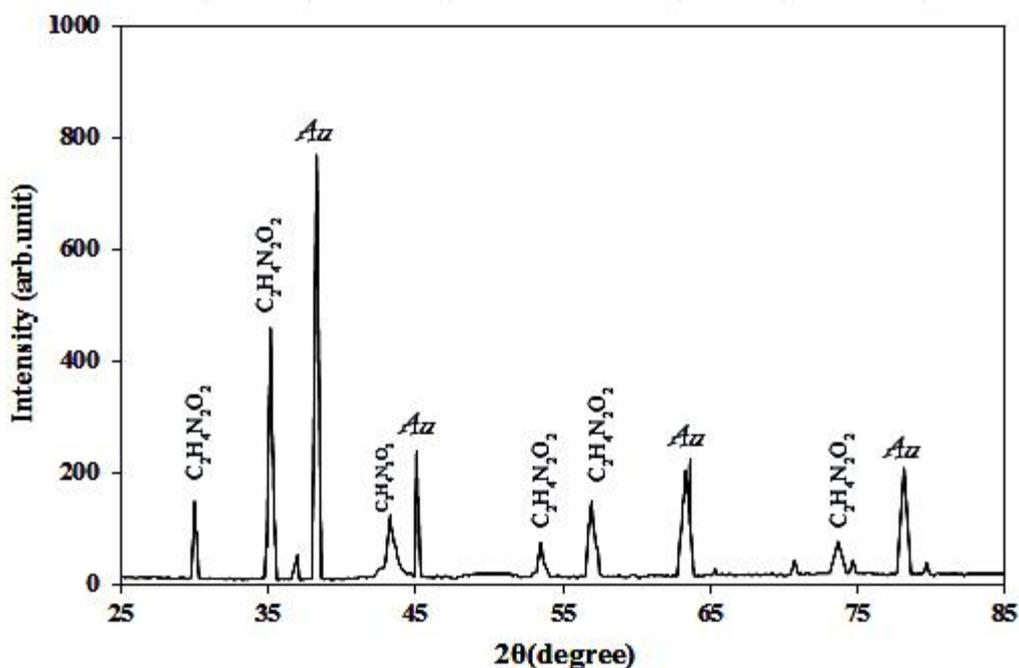
Figure 7. XRD results for the precipitates.

4-Conclusions

The thiourea-to-hydrogen peroxide concentration ratio is the most important factor affecting the reaction chemistry of gold at the pH range of 1-1.5.

The best conditions for gold dissolution were obtained to be 1.25 to 1.5 for the pH range,

TU/H$_2$O$_2$=2, and solution volume being equal to 30 ml (pulp density= 1/6 g/ml, 24h for leaching time and 400rpm for agitation rate). The least thiourea consumption was obtained in this solution volume.

Adding ammonia to the gold–thiourea solution increased the solution pH to over 8, and the existing gold in the solution precipitated completely in the metallic form; this is a very simple method for gold recovery from its solution.

Gold recovery from copper anode slime was successfully conducted and with a proper efficiency. This new technology is viable for obtaining high purity gold from anode slime and other sources.

Although the consumption levels of thiourea are higher than cyanide, thiourea seems to be more promising in terms of compatibility with small amounts of dissolved metal ions, and thus suitable for pure gold recovery.

References

[1] L. Pan, F. Wang, X. Bao, "Solvent Extraction of Gold(I) from Alkaline Cyanide Solution with Furfuryl Thioalcohol", Sep. Purif. Technol., Vol. 48, 2013, pp. 2007.

[2] S. Xiaowei, C.Y. Guan, K.N. Han, "Electrochemical behavior of the dissolution of gold-silver alloys in cyanide solutions", J. metall mater trans B, Vol. 27, 1996, pp. 355.

[3] R.Y. Wan, J.D. Miller, "Solvation extraction and electro-deposition of gold from cyanide solutions", J. Metals, Vol. 38, 1986, pp. 35.

[4] M.B. Mooiman, J.D. Miller, "The chemistry of gold solvent extraction from alkaline cyanide solution by solvating extractants", J. Hydrometallurgy, Vol. 27, 1991, pp. 29–46.

[5] Y.F. Shen, W.Y. Xue, "Recovery palladium, gold and platinum from hydrochloric acid solution using 2-hydroxy-4-sec-octanoyl diphenyl-ketoxime", Sep. Purif. Technol., Vol. 56, 2007, pp. 278.

[6] A.M. Donia, A.A. Atia, K.Z. Elwakeel, "Recovery of gold(III) and silver(I) on a chemically modified chitosan with magnetic properties", J. Hydrometallurgy, Vol. 87, 2007, pp. 197.

[7] S. Park, J.C. Lee, B.S. Kim, "Collection of high purity gold from wastewater using ZnO nanopowders synthesized by solution combustion method", J. Mater. Sci., Vol. 40, 2005, pp. 5327.

[8] S. Syed, "Recovery of gold from secondary sources—A review", J. Hydrometallurgy., Vol. 116, 2012, pp. 30–51.

[9] P. A. Farinha, M.J. Correia, J.R. Carvalho, "Leaching of gold from a Portuguese concentrate with thiourea", J. Miner. Eng., Vol. 5, 1992, pp. 953.

[10] Ö. Yavuz, R. Ziyadanoğullari, "Recovery of Gold and Silver from Copper Anode Slime", Sep. Purif. Technol., Vol. 35(1), 2000, pp. 133.

[11] X. Yang, M.S. Moats, J.D. Miller, X. Wang, X. Shi, H. Xu, "Thiourea–thiocyanate leaching system for gold", J. Hydrometallurgy., Vol. 106, 2011, pp. 58.

[12] Z. Wang, Y. Li, C. Ye, "The effect of tri-sodium citrate on the cementation of gold from ferric/thiourea solutions", J. Hydrometallurgy, Vol. 110, 2011, pp. 128.

[13] V. Gaspa, A.S. Mejerovich, M.A. Meretukov, J. Schmiedl, "Practical application of potential-pH diagrams for Au-CS (NH2) 2-H20 and Ag-CS (NH2) 2-H20 systems for leaching gold and silver with acidic thiourea solution", J. Hydrometallurgy, Vol. 34, 1994, pp. 369.

[14] H. Gavin, A.J. Monhemius, "Alternatives to cyanide in the gold mining industry: what prospects for the future?", J. Clean PROD., Vol. 14, 2006, pp. 1158.

[15] A. Aydin, E. Kaki, A. A. Aydin, "gold leaching by use of an n, n-disubstituted thiourea", Sep. Purif. Technol., Vol. 36(14), 2001, pp. 3239.

[16] Z. Wang, D. Chen, L. Chen, "The analysis of gold leaching systems based on thermodynamics", Nonferrous Met. (Extractive Metallurgy), Vol. 3, 2006, pp. 36.

[17] S. Orgul, ö. Atalay, "Reaction chemistry of gold leaching in thiourea solution for a Turkish gold ore", J. Hydrometallurgy., Vol. 67, 2002, pp. 71.

[18] T.S. Urbanski, P. Fornari, C. Abbruzzese, "Gold electro-winning from aqueous – alcoholic thiourea solution", J. Hydrometallurgy, Vol. 55, 2000, pp. 137.

[19] J. Li, J. D. Miller, "Reaction kinetics of gold dissolution in acid thiourea solution using ferric sulfate as oxidant", J. Hydrometallurgy, Vol. 89, 2007, pp. 279.

[20] R. Ranjbar, M. Naderi, H. Omidvar, Gh. Amoabediny, "Gold recovery from copper anode slime by means of magnetite nanoparticles (MNPs)", J. Hydrometallurgy, Vol. 143, 2014, pp. 54.

[21] H. Wang, C. Sun, S. Li, P. Fu, Y. Song, L. Li, W. Xie, "Study on gold concentrate leaching by iodine-iodide", Int. J. Miner. Metall. Mater., Vol. 20, 2013, pp. 323.

[22] Y. Li, J. Liu, W. Guan, "Cyanidation of gold clay ore containing arsenic and manganese", Int. J. Miner. Metall. Mater., Vol. 17, 2010, pp. 132.

[23] C.M. Juarez, A.J.B. Dutra, "Gold electro-winning from thiourea solutions", J. Mineral Eng., Vol. 13(10), 2000, pp. 1083.

[24] J., Harvanova, M. Stofkova, M. Stofko, "influence of agitation and temperature upon extraction of gold to thiourea solution", J. Acta metallurgica slovaca, Vol. 4, 1997, pp. 260.