Leaching of Gold from the Waste Mobile Phone Printed Circuit Boards (PCBs) with Ammonium Thiosulphate

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Abstract  The rapid growth in the use of electronic equipments, combined with early obsolescence has contributed enormously to the generation of large quantity of electronic (e) waste. One such e-waste, the mobile phone printed circuit boards (PCBs) contain various precious metals which can be extracted by different hydrometallurgical routes. The present work deals with the recovery of gold using ammonium thiosulfate as a leaching agent from waste mobile PCBs containing 0.021% Au, 0.1% Ag, 56.68% Cu, 1.61% Al, 1.42% Sn, 0.24% Fe, 0.22% Zn, 0.01% Pd etc.. The cutting granules of 0.5 -3.0 mm PCBs were used for leaching in a 500 mL glass beaker in open atmosphere. The effect of various parameters viz. ammonium thiosulfate concentration, copper sulfate concentration, pH and pulp density was studied. A leaching of 56.7% gold was obtained under the optimum condition of 0.1M ammonium thiosulfate, 40 mM copper sulfate, pH: 10-10.5, pulp density: 10 g/L at room temperature and stirring speed of 250 rpm in 8h duration. The maximum leaching of gold in the pH range 10-10.5 may be attributed to the higher stability of the ammonium thiosulfate. The decomposition of ammonium thiosulfate in the different pH ranges was chemically analysed by iodometric method. The ammonium thiosulfate contents in the leach liquors were in agreement with the quantity of gold leached in the respective pH ranges. In this process the copper sulfate worked as a catalyst. The experiment conducted with complete PCBs scrap exhibited a maximum leaching of 78.8% gold at the above optimised condition.

Keywords  Waste Mobile Phone, Printed Circuit Boards (PCBs), Ammonium Thiosulfate Leaching, Gold Leaching

1. Introduction

In recent years there has been tremendous growth in the use of many information and communication technology products, such as mobile phones, computers, television sets etc. The rapid advent of changing technology makes early obsolescence of these electronic equipments. This has contributed enormously to the large quantity of the electronic waste (e-waste) generated around the world. The United Nations estimates that collectively world is generating some 20-50 million tons of e-waste every year¹. The latest report by UN² predicts that by 2020, e-waste from old computers will jump 5 times in India compared to 2007. It also estimates that by the same year e-waste discharge from mobile phones in India will be 18 times higher than 2007. There are also growing concern about the e-waste generated in developed countries due to the lack of infrastructure for environmentally sound management of e-waste. The e-waste from such equipments contain many toxic elements such as lead, mercury, cadmium, nickel, chromium etc which has an adverse impact on our environment. Moreover, the e-waste also contains many valuable metals such as gold, silver, platinum, palladium etc. Therefore recycling and metal recovery from e-waste is required to protect the environment vis-à-vis resource conservation. Treatment of e-waste has been done mainly by the pyrometallurgical processes but due to emission of noxious gases and low recovery of metals, researchers are looking towards the hydrometallurgical processes because this route is easily controlled and better predictable.

Conventional recovery of gold was done by the cyanidation, a 100 years old leaching process for the recovery of the gold and other precious metals from the complex ores³. But due to toxicity of the cyanide, its use in this process has been prohibited in many countries. Thiourea is a non-cyanide lixiviant for gold leaching which efficiently recovers gold⁴ but this is not an economical route for the gold leaching due to its high consumption and cost. Thiosulfate leaching to recover gold from ores is known for several decades but extensive researches have been started only for the past two decades⁵. The process of recovering gold from mobile phone PCBs is an innovative approach to obtain the precious metals.
Literature reveals that only limited studies have been carried out to recover the metals from waste mobile phone PCBs. Ammonium thiosulfate \((\text{(NH}_4\text{)}_2\text{S}_2\text{O}_3)\) is a leachant which is non-toxic as well as economical. It works to stabilize gold as anionic complex which is mainly accountable for the gold recovery. Thiosulfate leaching has many advantages over the cyanidation process including higher leaching rates and less interference from foreign ions.

2. Theoretical Consideration

Thiosulfate when combines with the gold, a complex formation occurs i.e. aurothiosulfate \(\text{[Au(S}_2\text{O}_3)_2\text{]}^3^-\) which is accountable for the gold recovery as shown in equation (1). Copper sulfate was used as catalyst and oxidizing agent in the solution which forms a stable cupric tetra amine complex (eqn. 2) when reacts with ammonia\(^5,6\), which stabilizes the aurothiosulfate complex.

\[
4\text{Au} + 8\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Au(S}_2\text{O}_3)_2^{3-} + 4\text{OH}^- \quad (1)
\]

\[
\text{Au} + 5\text{S}_2\text{O}_3^{2-} + \text{Cu(NH}_3)_4^{2+} \rightarrow \text{Au(S}_2\text{O}_3)_2^{3-} + 4\text{NH}_3 + \text{Cu(S}_2\text{O}_3)_3^{5-} \quad (2)
\]

The cupric tetra-amine complex ions get regenerated by reaction between dissolved oxygen and \(\text{Cu(S}_2\text{O}_3)_3^{5-}\) as per reaction (3)

\[
\text{Cu(S}_2\text{O}_3)_3^{5-} + 4\text{NH}_3 + \frac{1}{2}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{Cu(NH}_3)_4^{2+} + 3\text{S}_2\text{O}_3^{2-} + \text{OH}^- \quad (3)
\]

3. Experimental

3.1. Raw Materials

| Elements | Weight (w/w %) | Elements | Weight (w/w %) |
|----------|---------------|----------|---------------|
| Cu       | 56.68         | Ag       | 0.1           |
| Ca       | 1.61          | Au       | 0.021         |
| Al       | 1.42          | Pd       | 0.01          |
| Sn       | 1.40          | Mn       | 0.005         |
| Fe       | 0.24          | Resin material | 38.29 |
| Zn       | 0.22          |          |               |

4. Results and Discussion

To make the recovery of gold viable from the mobile PCBs by ammonium thiosulfate, it is required to optimise the leaching conditions. Various leaching parameters such as effect of concentrations of ammonium thiosulfate and copper sulphate, effect of pH and pulp density were studied and the results are presented below.

4.1. Effect of Copper Sulfate

As stated in Section 2, the presence of copper (II) ions promotes the dissolution of gold in the thiosulfate solution. Copper sulfate variation was carried out in the range of 0-48 mM at the conditions i.e. ammonium thiosulfate: 0.1 M, pH: 10-10.5, pulp density: 60 g/L, temp: 25°C, stirring speed: 250 rpm in 8 h time duration as shown in Fig. 3. It was observed from the figure that the presence of copper ions in the solution enhances the dissolution of gold with the formation of the copper (II)-amine complexes. While there was negligible gold recovery in the absence of copper sulfate, it has been found to increase up to 30% with the addition of 48 mM copper sulfate. This can be attributed to the catalysing effect...
of copper sulfate present in the solution which enhances the dissolution of gold in thiosulfate system. Similar results have also been reported by some researchers.7-9

Figure 3. Effect of copper sulfate concentration on leaching of gold with time. [Ammonium thiosulfate : 0.1M, pH: 10-10.5, pulp density: 60g/L, temp.: 25℃, stirring speed: 250 rpm]

4.2. Effect of Ammonium Thiosulfate

The variation in the ammonium thiosulfate concentration was made over a range of 0.05-0.25M. The results are shown in the Fig 4. It is evident from the figure that maximum gold leached was 30.0% at the experimental conditions i.e. copper sulfate: 40mM, pH: 10-10.5, pulp density: 60g/L, stirring speed: 250rpm, temperature: 25℃ in 8h time duration. It is observed that the gold recovery increases up to 0.1M thiosulfate thereafter on further increase in thiosulfate concentration there is a decrease in the leaching of gold. This indicates that the higher thiosulfate concentration promotes the formation of unfavourable products such as trithionate, tetrathionate and polythionates.10 Thus by maintaining a proper concentration of thiosulfate-ammonia in the system, maximum gold can be leached from the mobile PCBs in the presence of copper which acts as a catalytic agent in the solution.5

Copper was also analysed from different ammonium thiosulfate leach liquors. It was found during the experiment that higher thiosulfate concentration was accountable for more weight dissolution of PCBs mainly due to copper dissolution (Table 2). At 0.1M ammonium thiosulfate concentration maximum total weight dissolution was 2.70g out of which the copper dissolution was 2.205 g which is a higher amount. At 0.05 M and 0.25 M thiosulfate, the copper dissolution was 0.103 g and 1.311 g, respectively which also supports the maximum leaching of gold at 0.1M thiosulfate.

Table 2. Copper dissolution (at various thiosulfate concentrations)

| Ammonium thiosulfate conc. | Copper dissolution(g) |
|-----------------------------|------------------------|
| 0.05M                       | 0.103                  |
| 0.10M                       | 2.205                  |
| 0.25M                       | 1.311                  |

4.3. Effect of pH Variation

pH of the solution was varied in the range of 8-11. The results for leaching of gold are shown in the Fig. 5. With increase in pH from 8.0 the gold percentage also increases but after pH 10.5 it shows decreasing trend. This shows that gold extraction occurs at very specific pH range i.e. 10-10.5.11 The maximum gold was found to be 30.0% at 0.1M thiosulfate, 40mM copper sulfate, 60g/L pulp density, 25℃ temperature in 8 h time duration. This can be explained with the fact that increasing the pH significantly increases the stability of Cu(NH3)42+ and Cu(S2O3)35- ions resulting in increase in dissolution of gold in ammonium thiosulfate. However, at higher pH values, there is a decrease in the stability of CuO and Cu2O leading to removal of copper from the leach solution. This decreases the availability of copper responsible of dissolution of gold. Moreover, the precipitation of copper oxides on gold surface may also hinder its dissolution.

After each experiment carried out for the pH variation, the leach liquor obtained was chemically analysed for the ammonium thiosulfate concentration by the iodometric titration method. In the iodometric analysis, a solution containing one gram of potassium iodide, 10 mL HCl (44g/L), 25 mL potassium iodate (3 g/L) was prepared and titrated with the thiosulphate leach liquor. Starch was used as indicator. The results shown in the Table 3 indicate that with increase in pH from 8.0 – 8.5 to 10.0 – 10.5, thiosulfate concentration also increases. This can be attributed to the maximum stability of thiosulfate in the pH range 10.0-10.5 (0.094 M). Further, at still higher pH of 10.5 – 11.0, the thiosulfate concentration in the leach liquor was found to decrease (0.086 M).

Table 3. Iodometric analysis of leach liquor at different pH ranges

| pH range   | Thiosulfate conc. in leach liquor (M) |
|------------|---------------------------------------|
| 8.0 – 8.5  | 0.034                                 |
| 9.0 – 9.5  | 0.042                                 |
| 10.0 – 10.5| 0.094                                 |
| 10.5 – 11.0| 0.086                                 |
4.4. Effect of Pulp Density

The variation in the pulp density was done in the range of 10g/L – 60g/L as shown in Fig. 6. It was observed from these experiments that the lower pulp density enhances the recovery of gold in the solution while at higher pulp density recovery percentage decreases. The maximum leaching was 56.7% gold at leaching conditions i.e. copper sulfate: 40mM, ammonium thiosulfate: 0.1M, pH: 10-10.5, temperature: 25°C, stirring speed: 250 rpm in time 8 h at a pulp density of 10 g/L. The lower pulp density has been found to be beneficial on the recovery of gold due to availability of larger quantity of the reagent per unit weight of PCBs granules than that of higher pulp density12 leaching.

4.5. Effect of Sample Variation

Complete PCB leaching (whole unit) of the mobile phone was also done to observe its effect on the leaching of gold. Results are compared with the shredded PCBs granules as shown in Fig. 7. About 78.8% of gold was leached with a complete PCB while in case of shredded sample it was 30.35% with the same pulp density (40 g/L) and other leaching variables. If the dissolution of copper is compared, it is observed as 1.53 g/L and 11.8 g/L, respectively for complete PCB sample and its granules. The high dissolution of copper is mainly due to large surface area involved for the leaching of granules than that of complete unit itself. However, the large dissolution of copper results in higher losses of thiosulfate ions by its conversion to tetrathionate and other polythionates. Such ions are not helpful in the in the extraction of gold and thus there is decrease in the recovery in gold from shredded PCBs granules.

5. Conclusions

Ammonium thiosulfate leaching of gold from waste mobile phones is an approach which has been tried to save the environment from the hazardous behaviour of the PCB metals as well as to recover the precious values of the PCB. On the basis of present study following conclusions can be drawn-

- The thiosulfate leaching of gold from waste PCBs exhibits that gold could be leached with good recovery under specific conditions. Recovery of gold was found to be highly dependent on the concentration of copper sulfate, ammonium thiosulfate, pH and pulp density.
- In the case of PCB granules, 56.7% gold could be leached under the optimised conditions viz., ammonium thiosulfate: 0.1M, copper sulfate: 40mM, pulp density: 10g/L, pH: 10-10.5, stirring speed: 250 rpm at room temperature in 8h time duration.
- In case of complete PCB unit the maximum gold leaching was 78.8% at thiosulfate: 0.1M, copper sulfate: 40mM, pH: 10-10.5, stirring speed: 250 rpm at room temperature in 8h time duration.

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REFERENCES

[1] S. Schwazer, A. De Bongo G. Giuliani, S. Kluser, P. Peduzzi, January, 2005, A National Policy: Managing Waste to 2020 – Submission, 1800 E-waste, Available:

[2] M. Schlnep, C. Hagelueken, R. Kuehrc, F. Magalinic, C. Maurer, C. Meskers, E. Mueller, F. Wang, Recycling from e-waste to resources, Report prepared by: Swiss Federal Laboratories for Materials Testing & research, Umicore Precious Metals and United Nation, Printed by: Oktoberdruck AG, Berlin, Germany, July 2009, p.49.

[3] S. Orgul, U. Atalay, 2002 Reaction chemistry of gold leaching in thiourea solution for a Turkish gold ore. Hydrometallurgy, 67, 71-77.

[4] D. Zipperian, S. Raghavan, J. P. Wilson, 1988, Gold and silver extraction by ammoniacal thiosulfate leaching from a Rhyolite ore, Hydrometallurgy, 19, 361–375.

[5] C. Abbruzzese, P. Fomari, R. Massidda, F. Veglio, S. Ubaldini, 1995, Thiosulfate leaching for gold Hydrometallurgy, 39, 265–276.

[6] M. G. Aylmore, D. M. Muir, 2001, Thiosulfate leaching of gold- a review, Miner. Eng. 14, 135–174.

[7] J. Ficeriova, P. Balaz, E. Boldizarova, S. Jelen, 2002. Thiosulfate leaching of gold from a mechanically activated CuPbZn concentrate, Hydrometallurgy, 67, 37-43.

[8] P. L. Breuer, M. I. Jeffrey, 2000, Thiosulfate leaching kinetics of gold in the presence of copper and ammonia, Miner. Eng., 13, 1071–1081.

[9] D. Feng, J.S.J. Van Deventer, 2006, Ammoniacal thiosulfate leaching of gold in the presence of pyrite, Hydrometallurgy, 82, 126-132.

[10] V. H. Ha, J. C. Lee, J. Jeong, H. T. Hai, M. K. Jha, Thiosulfate leaching of gold from waste mobile phones, Journal of Hazardous Material, 178, 1115 – 119.

[11] John O. Marsden, C. Iain House, 2006, Chemistry of Gold Extraction, Society of Mining, Metallurgy and Exploration, Inc. Colorado, USA12)

[12] P. Navarro, C. Vargas, A. Villarroel, F. J. Alguacil, 2002. On the use of ammoniacal/ammonium thiosulfate for gold extraction from a concentrate, Hydrometallurgy, 65, 37-42. http://www.grid.unep.ch/product/publication/download/ewaste.en(pdf.)