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Recovery of gold from computer circuit board scraps: the study of the effect of different reductants

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Abstract

Computer circuit boards (CCBs) are valuable because of their precious metal contents. In this regard, the recovery of gold from CCBs has attracted great interest. In this work, we report the recovery of gold from CCBs with different reductants. The CCBs were first crushed mechanically to obtain particles with sizes less than 0.1 mm. The powders were then leached with nitric acid to remove undesired metals. The remaining was then treated with aqua regia to dissolve gold ion. The dissolved gold was then precipitated from the leachate with hydrazine, ferrous sulfate or oxalic acid and the effect of these reductants on the recovery of gold was studied. We were able to recover more than 99% of gold from CCBs with purity of about 99.5%.

Keywords: Computer circuit boards (CCBs) , precious metals, leaching, gold.

1. Introduction

Computer circuit boards (CCBs) are valuable waste materials because of their precious metal contents. From 20 to 50 million tons of waste electrical and electronic equipment (WEEE, e-waste) are generated each year, bringing significant risks to human health and the environment [1]. Besides, they contain several valuable metals which worth to be recovered. There have been several studies on the recycling of such materials by mechanical [2, 3], thermal [4] and chemical [5, 6] processes. According to Cui and Zhang [7] recycling of e-wastes can be broadly divided into three major steps: a) disassembly-mechanical pretreatment b) concentration and c) refining. Recently, Pilone and Kelsall [8] have reported multi-metal electro-deposition with a mathematical model. The metal content in an electronic scrap can be as high as 40% by weight [9, 10]**.** In general, an electronic scrap is composed of plastics (~30 %), refractory oxides (~30%), and metals (~40%). The metals are found in many electronic components such as edge connectors, integrated circuit, and transistors. Although the majority of the metals (about 39 % of the scrap weight) are base metals such as copper, iron, nickel, tin, lead, aluminum and zinc, major attention has been given to the recovery of the precious metals such as gold, silver and palladium [9, 10]. From these metals, gold recovery receives the most attention since a considerable quantity has been used in the electronics industry during the past three decades [11]. The development of low cost, and selective technologies for gold ions uptake from industrial effluents is extremely important from economical and environmental points of view, because the recovered ions can be converted into elemental gold [12]. In recent years, many papers have been published on gold adsorption using various biosorbents [13, 14]. Therefore, we decided to recover gold from CCBs, and optimize the recovery conditions. We were able to recover gold up 99% with purity of about 99.5%.

2. Experimental Methodology

2.1. Materials and Instruments

All of the chemicals were of the highest purity and were purchased from Merck. Jaw crushers (type BB1/A) and vibratory Disc Mill (Type RS 1,Retsch) used to crush the CCBs. Atomic Absorption spectroscopy studies were performed by an AVANTA PM. Instrument X-ray fluorescence studies were performed on an CXRF Philips Magix Pro. SEM EDAX (VEGA/TESCAN), XRD (SIEMENS: DiffraKtometer D 500) and ICP (ULTIMA 2C) were used for the analysis.

2.2. General Procedure For Gold Separation

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2.2.1. Crushing Procedure

The samples were mixed of TV board scraps, pc board scraps, mobile phone scraps, and printed circuit boards scraps. The physical forms of these precious metals may be plated gold or palladium on copper laminate and plated gold or silver on nickel or iron. The CCBs were first crushed with a jaw crusher to obtain particles with the diameter size of about 10-15 mm. These particles were then crushed with a vibratory disc mill for 3 min in 1400 rpm and the powdered materials were sized with a shaker. The results of the particle sizing after this step is shown in Table 1.The particles with the size of above 0.1 mm were re-crushed with the disc mill to obtain smaller size than 0.1 mm.

2.2.2. Leaching with nitric acid

Two 5g portions of the powders from the previous step were leached with nitric acid at 5 min intervals and at different temperatures to remove silver and other base metals. The remaining solid was filtered and kept for the next steps.

2.2.3. Leaching with aqua regia

The remaining solid from the previous step was leached again in aqua regia (30 mL of concentrated HCl and 3 mL of concentrated HNO_3) to dissolve gold. Leaching temperature and pulp density was optimized. The undesired solids were separated from the solution and the solution was diluted to 50 mL with double distilled water.

2.2.4. The removal of excess nitric acid

Two procedures could be employed to remove unreacted HNO_3. In one of the procedures H_2SO_4 and HCl is used while the other one employs $NaClO_4$ [15]. We used H_2SO_4 /HCl method. The solution from the previous step was heated with 7 mL of concentrated H_2SO_4 at 145 ˚C. This solution was also stirred at 50 rpm with a mechanical stirrer. Heating was conducted until about 5 mL of the starting solution remained. Then 3 mL of concentrated HCl was added. Brown bubbles of NO_2 were liberated. Heating was continued until 4 mL of the solution remained [15].

2.2.5. Precipitation of gold with different reductants

After the removal of excess nitric acid, the solution was diluted to 50 mL and then the solution was treated with one of the three reductants. The reductants in this study were oxalic acid, hydrazine or $FeSO_4$. In a typical experiment 20 mL of 2 percent (w/w) oxalic acid was added and the mixture was heated and stirred at 60 ˚C and 50 rpm for 17 hours. The precipitated gold was filtered and used for further analysis.

3. Results and discussion

3.1. Preparation and extraction of undesired materials

CCBs were first crushed mechanically with a jaw crusher. In order to obtain smaller sizes than 0.1 mm the particles after jaw crushing were re-crushed with a vibratory disc mill. The particles from these steps were analyzed with SEM EDAX, XRF and XRD to obtain the metal contents of the CCBs. Figure 1 and 2 show the results of SEM and XRD analyses. Table 2 also shows the results of XRF studies. According to XRD samples are consisted of copper, tin, lead, lead oxide, tin oxide, quartz and amorphous phases. The steps of the process are indicated in Figure 3.

Table 1.The result of sizing of the sample

Type of harp	Percent Weight (%)
1.25 mm	2.92
1.00 mm	3.23
800 µm	6.57
630 µm	5.24
500 µm	3.52
315 µm	5.27
0.1 mm	36.01
Smaller than 0.1 mm	37.24

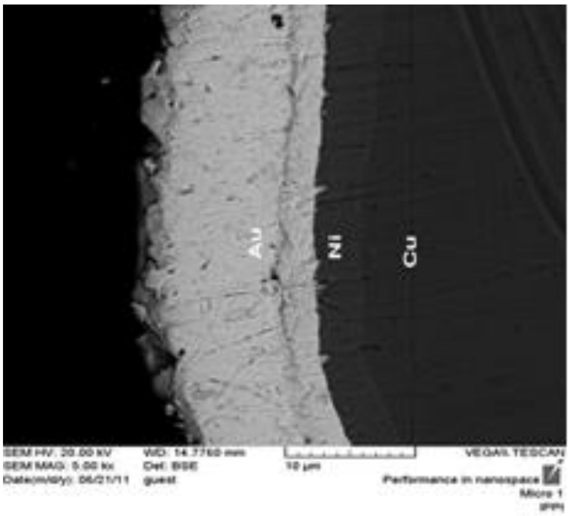

Figure 1. SEM EDAX micrograph of computer CPU with metal plating of: Au-Ni-Cu.

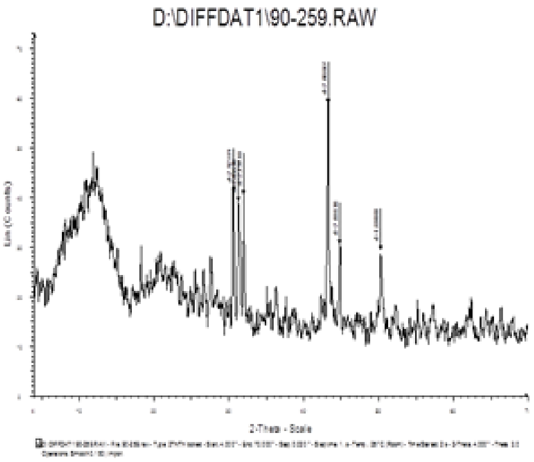

Figure 2. XRD of the sample.

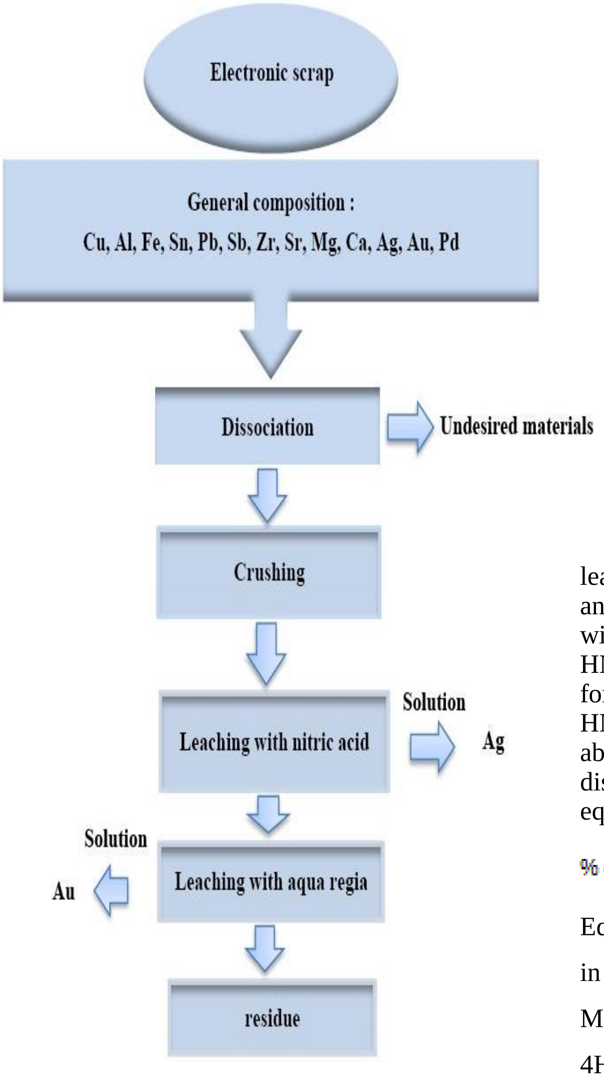

Figure 3. The flowchart of the extraction of gold from CCBs.

Table2. Analysis of the sample by XRF and ICP.

Component	%
SiO_2	43.16
Al_2O_3	3.58
Fe_2O_3	0.90
P_2O_5	0.14
SO_3	0.45
CaO	2.46
MgO	0.16
TiO_2	0.41
BaO	0.81
PbO	1.92
CuO	5.63
ZnO	0.47
NiO	0.48
Ag	0.17
Au	400 ppm
Pd	77 ppm
Br	2.44
I	0.74
Cl	<0.1
SnO_2	3.60
Sb_2O_3	0.77
SrO	<0.1
ZrO_2	<0.10

After these steps, the obtained particles were leached with HNO_3, HCl or H_2SO_4 to remove Ag, Cu, and base metals. Table 3 shows the results of leaching with these acids. As it could be seen from this table, HNO_3 was the most effective leacher and it was used for further experiments. The metal contents after HNO_3 leaching were evaluated by means of atomic absorption spectroscopy and ICP. The percent of dissolution was obtained [16] by the following equation:

$$\%\,dissolution = \frac{Dissolved\ amount\ in\ the\ solution\ (g)}{input\ amount\ (g)} \quad (1)$$

Equation (2) to (5) show the half-reactions occurred in the HNO_3 leaching process.

$$M \rightarrow M^{2+} + 2e^- \quad (2)$$

$$4H^+ + NO_3^- + 3e^- \rightarrow NO + 2H_2O \quad (3)$$

$$2H^+ + NO_3^- + e^- \rightarrow NO_2 + H_2O \quad (4)$$

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + 2H_2O + NO \quad (5)$$

3.2. Extraction of gold

3.2.1. Gold dissolution condition and determination of optimized conditions

33 mL of aqua regia (30 mL HCl and 3 mL HNO_3) was used to dissolve gold content of the precipitate after HNO_3 leaching step. Equations (6)-(8) show the half reactions [17].

$$2HNO_3+6HCl \rightarrow 2NO+4H_2O+3Cl_2 \quad (6)$$

$$2Au+9HCl+3HNO_3 \rightarrow 2AuCl_3+3NOCl+6H_2O \quad (7)$$

$$3HCl+HNO_3 \rightarrow Cl_2+NOCl+2H_2O \quad (8)$$

Note that nitrosyl chloride (NOCl) is formed by the reaction between hydrochloric and nitric acid, Eq. (8). The problems that hinder the leaching of scrap computer circuit boards using aqua regia are quite minor, provided that the precautionary measures are undertaken. First, the purity of the precipitated gold is decreased by the presence of silver chloride in the residue, but a chemical wash with nitric acid before aqua regia leaching minimizes silver contamination in the gold precipitate. Second, metastannic acid hinders the dissolution of gold. This acid is produced by the dissolution of the tin from solder. Production of metastannic acid is also limited by an initial leach with nitric acid. Despite these potential problems, aqua regia leaching was selected for the recovery of gold from computer chips because of its flexibility, ease and low capital requirements. Different parameters such as temperature and pulp density were optimized. Figure 4 shows the results for the optimization of pulp density. As it could be seen, pulp density of 1/3 g mL^{-1} was chosen as the optimized parameter. Figure 5 shows theresults for the optimization of reaction temperature and from this Figure, 70 ˚C was chosen as the optimized condition.

Table 3. Results of leaching of the sample with different acids.

Element		HNO_3		HCl		H_2SO_4	
	Amount (g) in 10g of sample	Dissolved amount (g)	% of dissolution	Dissolved amount (g)	% of dissolution	Dissolved amount (g)	% of dissolution
Pd	77×10^{-5}	73×10^{-5}	94.8	-	-	31×10^{-5}	40.3
Cu	0.450	0.400	88.9	-	-	0.351	78.0
Ag	0.170	0.160	94.1	-	-	0.088	51.8
Sn	2.840	2.540	89.4	1.99	70.1	1.680	59.2
Pb	0.178	0.107	60.1	-	-	0.086	48.3
Fe	0.060	0.046	73.0	0.047	74.6	0.049	77.8

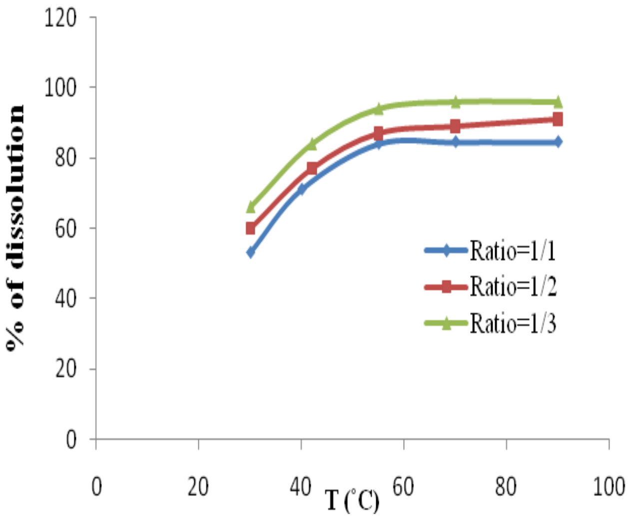

Figure **4.** Dissolution of CCBs in Aqua regia according to temperature. Ratios of 1/1, 1/2, and 1/3 note that CCBs of 10 g reacted with aqua regia of 10, 20, and 30 mL.

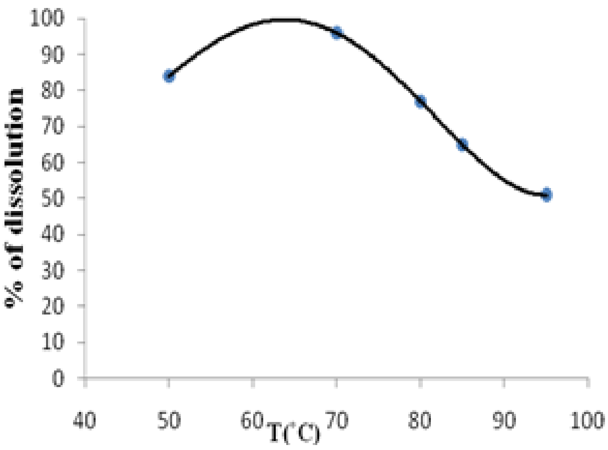

Figure 5**.** Dissolution of CCBs in Aqua regia according to temperature.

3.2.2. Gold precipitation

There are several reductants which are able to reduce gold ion to metallic gold. There are three important factors which help choose the suitable reductant: 1) purity of the precipitated gold 2) gold reduction rate and 3) physical form of the precipitated gold. In this research we used oxalic acid, hydrazine and $FeSO_4$ for the reduction of gold ion. In this research, we compared three reductants regarding different parameters such as temperature, reaction time, and percent of extraction and purity of gold. Tables 4, 5 and 6 show the results of comparisons.

Table 4. Precipitation of gold with $FeSO_4$ in different temperatures.

Reductant	Reaction temperature (ºC)	Stirring rate (rpm)	Reduction time	% Extraction
$FeSO_4$	50	50	20 min	99.90
$FeSO_4$	60	50	18 min	99.92
$FeSO_4$	70	50	17 min	99.92

Table 5. Precipitation of gold with N_2H_4 in different temperatures.

Reductant	Reaction temperature (ºC)	Stirring rate (rpm)	Reduction time	% Extraction
N_2H_4	50	50	7 min	98.31
N_2H_4	60	50	5.5 min	98.90
N_2H_4	70	50	5 min	99.90

Table 6. Precipitation of gold with $H_2C_2O_4$ in different temperatures

Reductant	Reaction temperature (ºC)	Stirring rate (rpm)	Reduction time	% Extraction
$H_2C_2O_4$	50	50	23 h	95.70
$H_2C_2O_4$	60	50	17 h	97
$H_2C_2O_4$	70	50	16.5 h	97

As it can be seen, the increase of temperature reduced the reaction time. The results show, higher and lower extractions of gold related to $FeSO_4$ and $H_2C_2O_4$ with yield of 99.9 % and 97 % respectively. This is very important because of high value of gold from economical viewpoint. In different temperatures, purity of gold from oxalic acid was higher than $FeSO_4$ and N_2H_4. In This work, conditions and results were studied to get the lowest extraction cost. Table 7 shows the results for these reductants. As it could be seen from this table, oxalic acid gives higher purity and lower cost but it has the limitation of reaction time and starting material concentration. $FeSO_4$ and hydrazine are able to reduce gold ion to metallic gold in lower initial concentration of gold ion more rapidly. The reactions of precipitated gold are as follows:

$$M^{n+}+ne^{-}\rightarrow M \qquad (9)$$

$$AuCl_4^{-}+3Fe^{2+}\rightarrow Au+3Fe^{3+}+4Cl^{-} \qquad (10)$$

$$H_2NNH_2\rightarrow N_2+4H^{+}+4e^{-} \qquad (11)$$

$$2Au^{3+}+3C_2O_4^{2-}\rightarrow 2Au+6CO_2 \qquad (12)$$

We were able to recover gold from CCBs up to 99%. The purity of the recovered was about 99.5 percent.

Table 7. The results and conditions of the precipitation of gold with different reductants.

Initial Au concentration (ppm)	Reductants	Reaction temperature (ºC)	Reduction time	Au content of the solution before reduction (mg)	Au content of the solution after reduction (mg)	Extraction %	Form of the precipitated Au	Purity %	Price (1 lit or Kg) $
485	$FeSO_4$ (10 mL, 0.05 g L^{-1})	50	20 min	12.125	0.012	99.9	Brown flakes	98.9	17.03
485	N_2H_4 (5 mL, 35%)	70	5 min	12.125	0.011	99.9	Brown flakes	99.0	42.58
700	$H_2C_2O_4$ (20 mL, 2%)	60	17 h	35	1.05	97.0	Au sand	99.5	13.84

4. Conclusions

Gold was successfully recovered from CCBs with high purity and low reaction times. The results obtained from the study of leaching of precious metals, and recovery of gold from scrap computer circuit boards allow the following conclusions to be drawn out:

1. Crushing of the samples to obtain particles with sizes less than 0.1 mm.

2. HNO_3 was found to be effective for the removal of undesired metals.

3. Aqua regia (30:3 HCl: HNO3) was chosen to dissolve gold content of CCBs.

4. $FeSO_4$ reduces gold ion to metallic gold rapidly with high purity. But if higher purities were needed, oxalic acid could be chosen with the sacrifice of time.

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References

[1] S. Herat, International regulations and treaties on electronic waste (e-waste), International Journal of Environmental Engineering. **4** (2009) 335-351.

[2] S. Zhang, E. Forssberg, Mechanical separation-oriented characterization of electronic scrap, Resour. Conserv.Recycl. **21** (1997) 247-269.

[3] S. Zhang, E. Forssberg, B. Arvidson, W.Moss, Aluminum recovery from electronic scrap by high-force eddy-current separators, Resour. Conserv.Recycl. **23** (1998) 225-241.

[4] W.J. Hall, P.T. Williams, Separation and recovery of materials from scrap printed circuit boards, Resour. Conserv.Recycl. **51** (2007) 691-709.

[5] K. Gloe, P. Muhl, M. Knoth, Recovery of precious metals from electronic scraps, in particular from waste products of the thick-layer technique. Hydrometallurgy. **25** (1990) 99-110.

[6] T. Oishi, K. Koyama, H. Konishi, M. Tanaka, J.C. Le, Influence of ammonium salt on electrowinning of copper from ammoniacal alkaline solution. Elecctrochim. Acta. **53** (2006) 127-132.

[7] J. Cui, L. Zhang, Metallurgical recovery of metals from electronic waste: A review, Journal of Hazardous Materials. **158** (2008) 228-256.

[8] D. Pilone, G.H. Kelsall, Prediction and measurement of multi-metal electro-deposition rates and efficiencies in aqueous acidic chloride media. Electrochim. Acta. **51** (2006) 3802-3808.

[9] J.H. Setchfield, Electronic Scrap treatment at Engelhard, Pergamon Press, Toronto, Canada. (1987).

[10] K. Feldmann, H. Scheller, Printed Circuit Board-a Challenge for Automated Disassembly and for the Design of Recyclable Interconnect Devices, IEEE Conference Publication, UK. (1959) 186-190.

[11] S. Zhang, E. Forssberg, Mechanical recycling of electronic scrap-the current status and prospects, Waste Management & Research. **16** (1998) 119-128.

[12] S. Syed, Recovery of gold from secondary sources — A review, Hydrometallurgy. **30** (2012) 115-116.

[13] M.A.Z. Abidin, A.A. Jalil, Recovery of gold (III) from an aqueous solution onto a durio zibethinus husk,Biochemical Engineering Journal. **54** (2011) 124-131.

[14] M. Gurung, B. Babu Adhikari, Recovery of Au (III) by using low cost adsorbent prepared from persimmon tannin extract, Chemical Engineering Journal, **174** (2011) 556-563.

[15] C.M. Hoke, Refining Precious Metals Wastes, New Jersey. (1940).

[16] Y.J. Park, D.J. Fray, Recovery of high purity precious metals from printed circuit boards. J. Hazard.Mater. **164** (2009) 1152-1158.

[17] C.A. Jacobson, Encyclopedia of chemical Reactions, Reinhold Publishing Co, New York. (1959).