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≫研究論文≪

Recovery of Gold from Electronic Scrap by Hydrometallurgical Processes

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ABSTRACT

A series of processes has been developed to recover the gold from electronic scrap containing about 200~600 ppm Au. First, mechanical beneficiation including shredding, crushing and screening was employed. Results showed that 99 percent of gold component leaves in the fraction of under 1 mm of crushed scrap and its concentration was enriched to about 800 ppm without incineration. The crushed scrap was leached in 50% aqua regia solution and gold was completely dissolved at 60°C within 2 hours Other valuable metals such as silver, copper, nickel and iron were also dissolved The resulting solution was boiled to remove nitrous compounds in the leachate. Finally, a newly designed electrolyzer was tested to recover the gold metal. More than 99% of gold and silver were recovered within an hour by electrowinning process.

1. Introduction

Electronic scrap has been increasingly generated due to a rapid growth of the electronics industries. The scrap includes the rejected products from IC (integrated circuits) manufacturing process and the computer industry as well as the disposal of obsolete PCB (printed circuit boards), connectors, cabling, metal cases, etc.[1] Among these, the amount of IC chip scrap in Korea reached about 1,500 ton/year in 1994 and has kept increasing.[2] Despite a variety of gold content from 200 to 600 g/ton depending on different forms and kinds of IC chip, this scrap becomes an important secondary resource for gold because the reclamation of metals is more easily achieved compared to other electronic scrap.

Therefore, the recycling of valuable metals from this scrap plays an important role considering that deposits of precious metals are becoming scarcer. In addition, the increase of the scrap causes a serious environmental problem and this scrap has to be recycled according to environment protection law.

Several processes have been employed for the recovery of gold from electronic scrap.[3-4] Although some drawbacks in causing other types of pollution and increased metal loss are involved, pyrometallurgical methods can treat all forms of scrap. Usually, collector metals such as copper or iron were smelted with or without flux and then the recovery of gold was accomplished from the slag or metal portion. On the other hand, only small scale plants for hydrometallurgical processes have been developed despite better environmental protection, easier separation and higher recovery rate. A variety of ways to recover valuable metals from leach liquor of the scrap have been developed such as precipitation with Na_2SO_3,[5] ion exchange method,[6] supported liquid membrane technique,[7] cementation,[8] solvent extraction,[9] and electrolysis.[10] Besides these, processes involving electrochemistry and biotechnology have been applied to enhance the gold recovery and purity from the scrap.

The aim of this study was to develop a process which included mechanical treatment, leaching and electrowinning. The complete recovery of gold component from the scrap is accomplished using a newly designed electrolyzer which enhances the mass transfer rate. Reaction chemistry during electrolysis can be expressed as follows,

cathode	$M^{n+}+n\ e^- = M$	(1)
anode	$n\ Cl^- = n/2\ Cl_2 + ne^-$	(2)

where M indicates the metals to be electrodeposited and n is the number of electrons involved in electrochemical reaction

2. Experimental

2.1. Sample preparation by physical separation

The metal composition of the scrap used in this ex-

Table 1. Chemical analysis of metals in IC scrap

Element	Cu	Ni	Fe	Sn	Pb	Al	Au	Ag
Content (wt%)	14.19	3.86	5.36	1.46	0.52	0.08	0.43	0.11

periment is shown in Table 1. Physical separation was performed to reduce bulk and to classify the material fractions. Cutter, hammer and ball mills were used for size reduction. After grinding, crushed scrap was classified by ASTM standard sieve and chemical composition as a function of particle size was determined to optimize each unit process. The chemical analysis was carried out by Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICPA).

Samples for subsequent experiments were prepared as follows: After size reduction down to about 1 mm, crushed scrap was separated by airflow classifier. The fraction under 1 mm in size was used for leaching and electrowinning experiments and that over 1 mm for the magnetic separation in which cross-belt magnetic separator was used.

2.2. Aqua regia leaching

Leaching tests were carried out in a 1000 ml three-neck flask which was kept in a constant temperature bath as shown in Fig. 1. Crushed scrap was charged into 50% aqua regia (3:1 mixture of concentrated HCl and HNO_3) and pulp density was adjusted to 20 g/l. The rotation speed and reaction temperature were kept constant during the reaction. In order to study the effect of temperature, temperatures were varied from 15 to 60°C. A 5 ml aliquot of sample solution was withdrawn at the regular time intervals for chemical analysis using an ICPA.

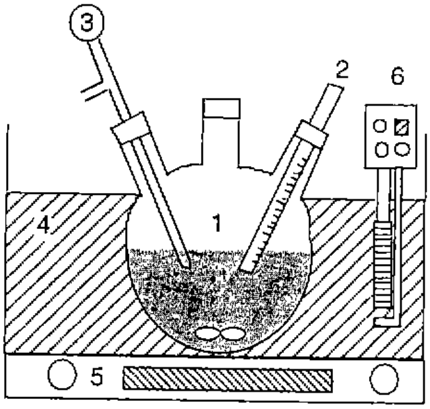

Fig. 1. Schematic diagram of leaching apparatus.

2.3. Electrowinning

Synthetic solution as well as leach liquor from the leaching of the scrap were tested to recover valuable metals from the solution. The synthetic solutions were prepared using analytical grade $HAuCl_4 \cdot 4H_2O$ mixed $CuSO_4$ to the desired concentration and pH was adjusted with hydrochloric acid The leach liquor from the leaching was heated up to 70°C for 2 hours to boil off NO_x prior to electrolysis.

Electrowinning was performed at room temperature with a newly designed electrolyzer using an insoluble anode which evolves chlorine gas. The leach liquor was cycled with a pump and the concentration of various metal ions was measured with an atomic absorption spectrophotometer (Perkin-Elmer 3100).

3. Results and Discussion

3.1. Mechanical separation

The optimization for the combination of unit operations, such as shredding, crushing and grinding has been made through experiments.

The cutting mill reduced the scrap to about 5~7 mm in size, hammer mill to less than 3 mm and ball mill to less than 1 mm. After grinding, the size distribution of crushed scrap was measured and the results are shown in Table 2. Despite size reduction, 24 5% of scrap still remains over 1 mm in size, because the ductile metallic portion is not easily crushed.

The metallic and gold content along with size distribution is given in Table 3. Most of the metallic part of scrap re-

Table 2. Particle size distribution of crushed IC scrap

Particle size (mm)	Distribution (wt%)
+3	7 50
3~1	17.0
1~0 6	24 0
0.6~0 5	12 9
0 5~0.3	14.1
0.3~0 25	4.00
0.25~0.21	3 50
− 0.21	17.0

Table 3. Distribution of metals in crushed IC scrap

Particle size (mm)	Distributions		Composition	
	Metals (wt %)	Au (wt%)	Metals (wt %)	Au (ppm)
+3	26.6	0.1	97.8	2.84
3~1	60.2	0.9	95.8	24.2
1~0.6	11.1	29.0	12.9	546
0.6~0.5	1.70	16.0	3.70	566
0.5~0.3	0.44	17.0	0.87	535
0.3~0.25	0.01	4.0	–	446
0.25~0.21	–	3.0	–	387
−0.21	–	30.0	–	756

ports to the fraction over 1 mm in size, however, the Au content is quite low. Most of gold (more than 99%) remains in the portion below 1 mm in size, especially more than 30% is found in the size fraction less than 0.21 mm. The Au content of this size fraction is 756 ppm, which is the highest of the size fraction. This is due to the fact that most of Au are present in the form of bonding wire or thin film which is easily separated during grinding.

The chemical composition of the metallic fraction is shown in Table 4. It mainly consists of Cu, Ni and Fe which are easily separated by applying the magnetic field. Based on the results, the optimized processes for mechanical pretreatment are shown in Fig. 2

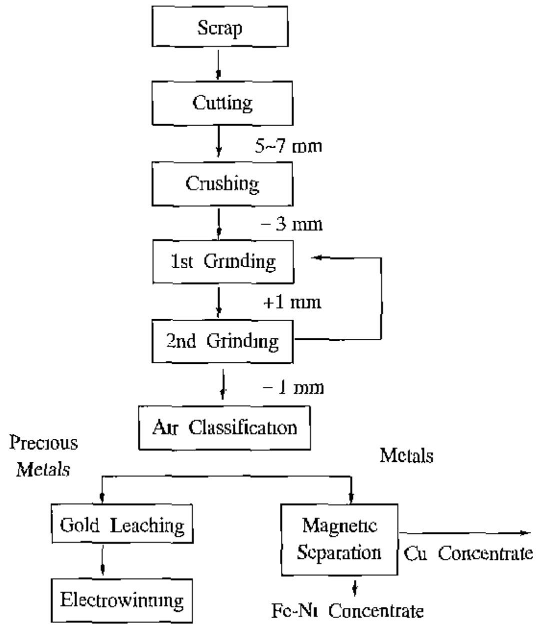

Fig. 2. Flowsheet for recovery of metals from IC scrap.

Table 5. Chemical composition of metals in crushed IC scrap below 1 mm in size

Element	Cu	Ni	Fe	Au	Ag
Content (wt%)	2.73	0.47	0.20	0.074	0.089

3.2. Leaching

For complete extraction of gold, aqua regia was used and leaching behavior was investigated with respect to temperature only The material used in this leaching tests was the crushed scrap under 1 mm in size obtained through mechanical treatment The chemical analysis is shown in Table 5

Fig. 3 shows that only 10~20% of metals were extracted at 15°C even after 2 hours reaction in 50% aqua regia leaching. When the temperature was increased to 40°C, all Cu and about 85% of other metals including Au and Ag were dissolved. Finally, most of metals except Ag were completely leached out at 60°C A lower extraction of silver in aqua regia leaching can be explained by the precipitation of silver chloride in strong chloride solution.

Because selectivity in the dissolution of metals was not considered in this test, subsequent leaching experiments were carried out at 60°C.

3.3. Electrowinning

Electrolysis was carried out with variations of the applied potential and flow rate. Fig 4 shows the effect of flow rate which was correlated in terms of linear velocity of solution at the applied potential of 3.5 V and pH of 2.0. The linear velocity was defined as the ratio of the flow rate to the cross sectional area of inlet in the electrolyzer. The elec-

Table 4. Chemical composition of metals in crushed IC scrap

Size \ Element (wt %)	Cu	Ni	Fe	Sn	Pb	Al	Au (ppm)	Ag
+3 mm	49.2	16.9	23.9	0.81	0.01	0.19	2.84	0.72
−3 mm	52.3	12.9	17.8	6.83	2.57	0.32	24.2	0.28

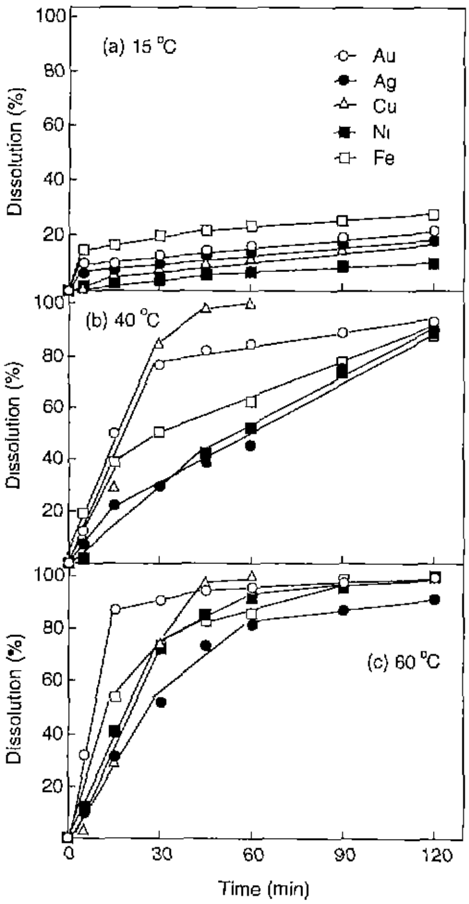

Fig. 3. Metals dissolution from the crushed IC scrap (20 g *solid*/l, 50% aqua regia).

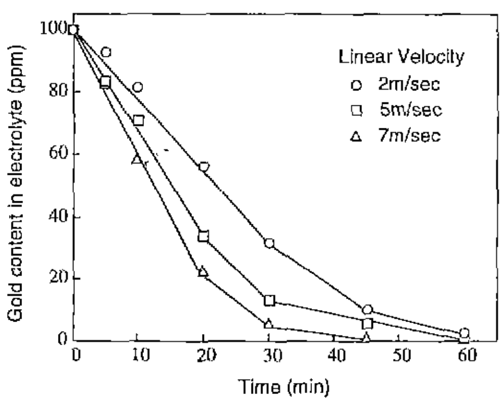

Fig. 4. Gold content with a variation of the flow rate (pH 2, 3.5 V, room temperature).

trolyzer was designed to provide a highly turbulent flow conditions to increase the mass transfer rate. The con-

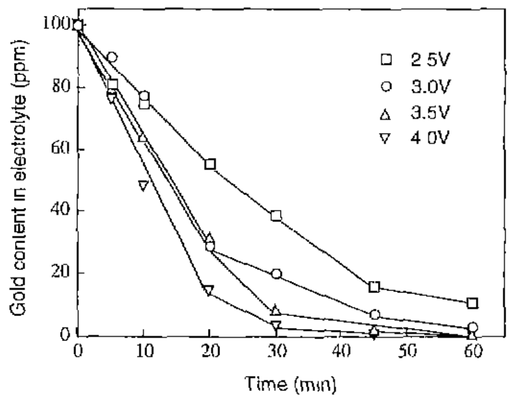

Fig. 5. Gold content with variation of the applied voltage (pH 2, 7 m/sec flow rate, room temperature).

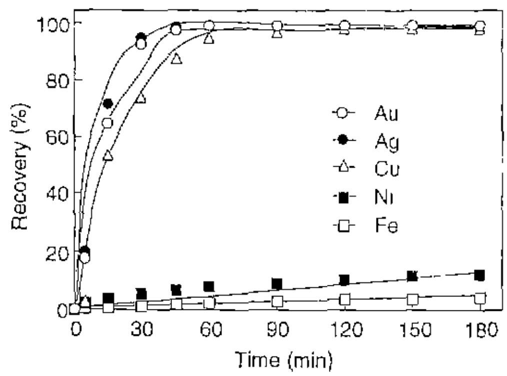

Fig. 6. Metals recovery from leach liquor of crushed IC scrap (pH 2, 7 m/sec flow rate, 3.5 V).

centration of Au and Cu drops almost exponentially and the recovery of these metals exceeds 99% within a hour.

The effect of applied potential on Au recovery is illustrated in Fig. 5, and the removal rate of metals from synthetic solution increased with the applied potential. As shown in this figure, the rate of electrodeposition of metals at 4.0 V is a little higher than that of 3.5 V. As a result, the optimum applied potential would be 3.5 V with considering the energy consumption.

The leach liquor from the leaching of electronic scrap was tested with an electrolyzer and the results are presented in Fig. 6. The initial concentrations of various metals were: Au 738 ppm, Ag 887 ppm, Cu 27.25 g/l, Ni 1.995 g/l and Fe 4.72 g/l, respectively. Ninety nine percent of the precious metals were recovered within a hour. During this same period, 97% of Cu and less than 10% of Ni and Fe were recovered. Although the selectivity for precious metals over the base metals is not good enough, it might be possible to separate the precious metals from the base metals using a staged operation with different applied voltage in each electrolyzer.

4. Conclusions

The series of processes has been developed to recover the gold from electronic scrap containing initially about 200~600 ppm Au. The following conclusions were made,

1. By the combination of unit processes such as shredding, crushing and grinding, most metallic part of IC-based scrap was classified into over 1 mm in size. And more than 99% of Au remained in the portion of below 1 mm
2. Cu, Ni and Fe were easily separated by magnetic separation for the fraction of crushed scrap over 1 mm in size.
3. The crushed scrap under 1 mm in size was leached in 50% aqua regia solution and Au was completely dissolved at 60°C within 2 hours Other valuable metals such as Ag, Cu, Ni and Fe were also dissolved.
4. The Au metal was recovered by a newly designed electrolyzer which provides a highly turbulent flow condition. The optimum applied potential and flow rate are 3.5 V and 7 m/sec considering the energy consumption and recovery rate.
5. More than 99% of Au and Ag were recovered from the leach liquor of crushed scrap within an hour through the electrolyzer.

References

1 G. Edson "Recovery of Precious Metals from Electronic Scrap," Recovery and Refining of Precious Metals (Skytop, PA, 1980), Paper 10.
2. J.C. Lee, *et al.* · "Separation of Metals from Integrated Circuit Chip Scrap by Mechanical Beneficiation", J. of Korean Inst. of Resources Recycling, 3(1). 38-43 (1994).
3 E.Y L. Sum · "The Recovery of Metals from Electronic Scrap", JOM, 43(4), 53-61 (1991).
4. J.E. Hoffmann "Recovering Precious Metals from Electronic Scrap", JOM, 44(7), 43-48 (1992).
5. J. Zakrewski, *et al.* : Pol. PL 146.269 (C1.C23F1/16) (1989).
6. A Celi Ger. Offen. DE 3,732,177 (C1 C22B7/00) (1989)
7. CEE-R & D : Commision of the European Communities (Contract # RNF-012-I(S), Recycling of Non-ferrous Metals Contact Group Meeting, Brussels, Jan. 30-31, (1985).
8 J. Loebel and L Meisnner : Ger(east). DD. 253,048 (C1. C23F1/16) (1988).
9. E. Jackson Hydrometallurgical Extraction and Reclamation (Ellis Horwood. 1986), 204-208.
10. H E. Hilhard, *et al.* · U.S. Bureau of Mines RI 8940, (1985).