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Selective recovery and separation of copper and iron from fine materials of electronic waste processing

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ABSTRACT

As electronic waste (e-waste) is increasing, its by-products such as flue dust and wastewater, which are generated during its treatment process, are also increasing. In this study, the fine material generated in the processing of e-waste by both mechanical and thermal methods was investigated for the effective recovery and separation of valuable metals, including Cu and Fe, using both physical and chemical methods. The Fe in this sample was present mostly as magnetite, as determined by XRD, and was removed by magnetic separation. Three different acid solutions (HNO_3, HCl, and H_2SO_4) were used for selective Cu recovery. All experiments were conducted with varying length of time (1–10 h) and temperature ranges (20–60 °C). The kinetics of Cu dissolution in HNO_3 was studied, based on the shrinking core model, and the activation energy was about 5.0 kcal/mol. The dissolution of Cu in HNO_3 was faster than that of other metals such as Fe and Al. In the case of H_2SO_4, dissolution of Cu was not observed, while Fe was completely dissolved after about 4 h at 60 °C. Based on the results of various leaching and the kinetic study, a two-step process was performed for selective metal recovery. H_2SO_4 was used to dissolve Fe as the first leaching process and HNO_3 was used for Cu dissolution as the second leaching process. Through this two-step process, Fe and Cu leaching efficiencies were obtained at approximately 90% and 98%, respectively.

1. Introduction

As technology advances in both the electrical and electronics industries, a large amount of electronic waste (e-waste) is generated (Robinson, 2009; Widmer et al., 2005). E-waste contains components that are harmful to humans and affects environmental pollution (Kiddee et al., 2013). Therefore, some countries have established policies and legislation specific to e-waste (Nnoroma and Osibanjo, 2008). There are many options for the treatment of e-waste, including reuse, remanufacturing, recycling, incineration, and landfilling. Among them, recycling is most important in terms of environmental protection and valuable metal recovery-as long as it is both technically and economically viable.

Recently, some researchers have reported on recycling studies for e-waste based on hydrometallurgy (Le et al., 2011; Tuncuk et al., 2012; Xiao et al., 2013; Birloaga et al., 2014; Jadhav and Hocheng, 2015; Kumari et al., 2016). Compared to pyrometallurgical processes, hydrometallurgical processes have relatively low capital costs, minimal atmospheric pollution problems, and high selectivity in metal recoveries (Tuncuk et al., 2012; Jadhav and Hocheng, 2015). They seem to be suitable for small-scale applications and are generally energetically favorable (Gupta and Mukherjee, 1990; Tuncuk et al., 2012). Hydrometallurgy can be separated into three general processes for metal recovery; precipitation, solvent extraction (SX) and ion exchange (IX), all of which follow leaching by acid or caustic solutions (Cui and Zhang, 2008).

E-waste is generated from various types of electronic equipment, and the elements and compositions of e-waste depend on the materials that make up the electronic equipment. E-waste can contain up to 61% metals and 21% plastics (Widmer et al., 2005). In particular, Fe and Cu are the most common materials found in electrical and electronic equipment and account for the largest portion of the total metal weight of e-waste (Widmer et al., 2005; Cui and Zhang, 2008). Therefore, the effective separation of Cu and Fe is important in terms of e-waste management and recovery. In addition, the separation and recovery process used for Fe can be applied to other precious metal recovery processes.

Fine materials (< 600 μm particle size), such as flue dust, are generated in the processing of e-waste by mechanical and thermal methods. According to Balde et al. (2015) the total e-waste generated worldwide was estimated at approximately 41.8 million tonnes in 2014 and is expected to grow to 49.8 million tonnes in 2018. Therefore, flue dust,

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Table 1
Composition analysis of the samples with magnetic separation.

Sample (< 600 μm)	Mass (Wt. %)	Assay (wt.%)						Distribution (%) – (calculated)					
		Cu	Zn	Fe	Mn	Al	Ca	Cu	Zn	Fe	Mn	Al	Ca
Feed material	100	6.2	0.9	27.1	0.7	3.6	1.7	101.8	99.4	98.6	98.6	98.3	97.1
Non-mag fraction	41	14.1	0.6	6.3	0.1	5.9	2.3	93.2	27.3	9.5	5.9	67.2	55.5
Mag fraction	59	0.9	1.1	40.9	1.1	1.9	1.2	8.6	72.1	89.0	92.7	31.1	41.6

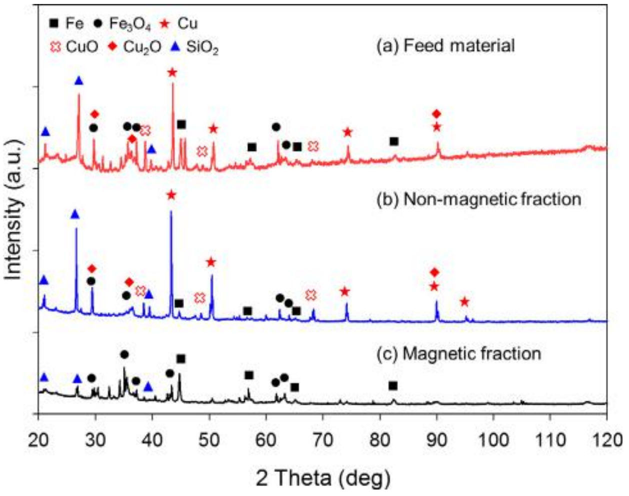

Fig. 1. XRD patterns of samples after magnetic separation.

which is the by-product of the e-waste treatment process, will also be increasing. Some researchers have investigated the recovery of valuable metals from Cu smelter slag by a leaching process (Banza et al., 2002; Vítková et al., 2011). Yang et al. (2010) reported the selective extraction of base metals, such as Co, Zn, and Cu from Cu smelter slag at atmospheric pressure. However, the recovery and separation valuable metals such as Cu, Fe, Al, Au and Ag from fine materials (including flue dust) in the processing of e-waste have not been well studied. Therefore, more research on their recovery process is necessary.

In this study, the selective recovery and separation of Cu and Fe from fine materials of e-waste were examined. Magnetic separation was used as a physical method to remove ferrous materials. Cu was selectively recovered by using a leaching method as a chemical process. An acid leaching process was carried out with a variation of time and temperature in HNO_3, HCl, and H_2SO_4 solutions. The Cu dissolution kinetics was measured, based on the shrinking core model, to obtain the activation energy. For the selective recovery of Fe and Cu, H_2SO_4 was used to dissolve Fe as the first leaching process and HNO_3 was used for Cu dissolution as the second leaching process.

2. Experimental

An e-waste recycling company provided the fine materials for this work. In order to optimize the effective recovery process, size separation (RX-29, W.S. Tyler) was performed as a pre-treatment process and the max. size of the sieve was 600 μm. Next, magnetic separation was carried out to remove ferrous materials. The LB-1 magnetic barrier separator (S.G. Frantz Co.) was used, which consists of an electromagnet with two long pole pieces. An additional piece of low-field control (LFC-3) equipment was used for the separation of ferromagnetic materials from other magnetic and non-magnetic materials. The forward slope of the chute regulates the travel speed of the sample stream as a vertical slope under which the sample moves. The side slope of the chute is the horizontal slope in the left and right directions, and sample moves into magnetic and non-magnetic fractions under the influence of gravity, depending on the side slope. The LFC-3 can generate and control low magnetic fields at currents from 0 to 100 mA. The forward slope (20°) and the side slope (15°) of equipment were fixed and the applied current was 25 mA. In addition, the crystalline phase of the flue dust before and after magnetic separation was confirmed by XRD (Empyrean, PANalytical) equipped with a Cr tube. HighScorePlus (PANalytical) was used as analysis software of the XRD patterns.

Samples were fused with a lithium borate mixture (40 wt% lithium tetraborate, 60 wt% lithium metaborate) at 1100 °C for 1 h. After the borate fusion process, the melt was dissolved in HNO_3 for ICP-OES (Optima 8000, Perkin Elmer) analysis. This fusion process has several advantages, in that minerals are readily dissolved, no pressure vessel is needed, and a clear aqueous solution is obtained for a variety of analytical procedures (Verbeek et al., 1982).

Three acidic solutions, HNO_3 (68–70%, GR ACS), H_2SO_4 (95–98%, J. T. Baker) and HCl (36.5–38.0%, GR ACS) were used as leaching reagents. During leaching, solids/liquid content was fixed at 20 g/L and the bath temperature was changed from 20 to 60 °C. A magnetic stir bar was also used to mix the solution during leaching, and the stirring speed was fixed at 200 rpm. In the case of a two-stage process, the solid/liquid ratio was increased to 100g/L to verify the effect of selective leaching. After leaching, the solid residue was separated from the leachate by vacuum filtration, and the leachate was analyzed by the ICP-OES process.

3. Results and discussion

3.1. Magnetic separation of the as-received sample

Table 1 shows the result of ICP-OES analysis of the sample with magnetic separation. The major elements of the feed material were Cu and Fe, and the compositions were about 6 wt% and 27 wt%, respectively. As shown in Fig. 1, the Fe in the feed material was confirmed to be magnetite (Fe_3O_4) in a metallic Fe phase. Fe_3O_4 is ferromagnetic and can be magnetized to become a permanent magnet (Wasilewski and Kletetschka, 1999). Therefore, it is easily separated by magnetic separation. In the non-magnetic fraction, the composition of Cu increased from 6.2 to 14.1 wt%, while the composition of Fe decreased from 27.1 to 6.3 wt%. However, approximately 6 wt% Fe still remained in the non-magnetic fraction after the magnetic separation. This finding is probably because some Fe particles and non-magnetic particles have aggregated and transferred to non-magnetic fractions. Therefore, the leaching process as a chemical method was used to selectively recover Cu and Fe in the non-magnetic fraction.

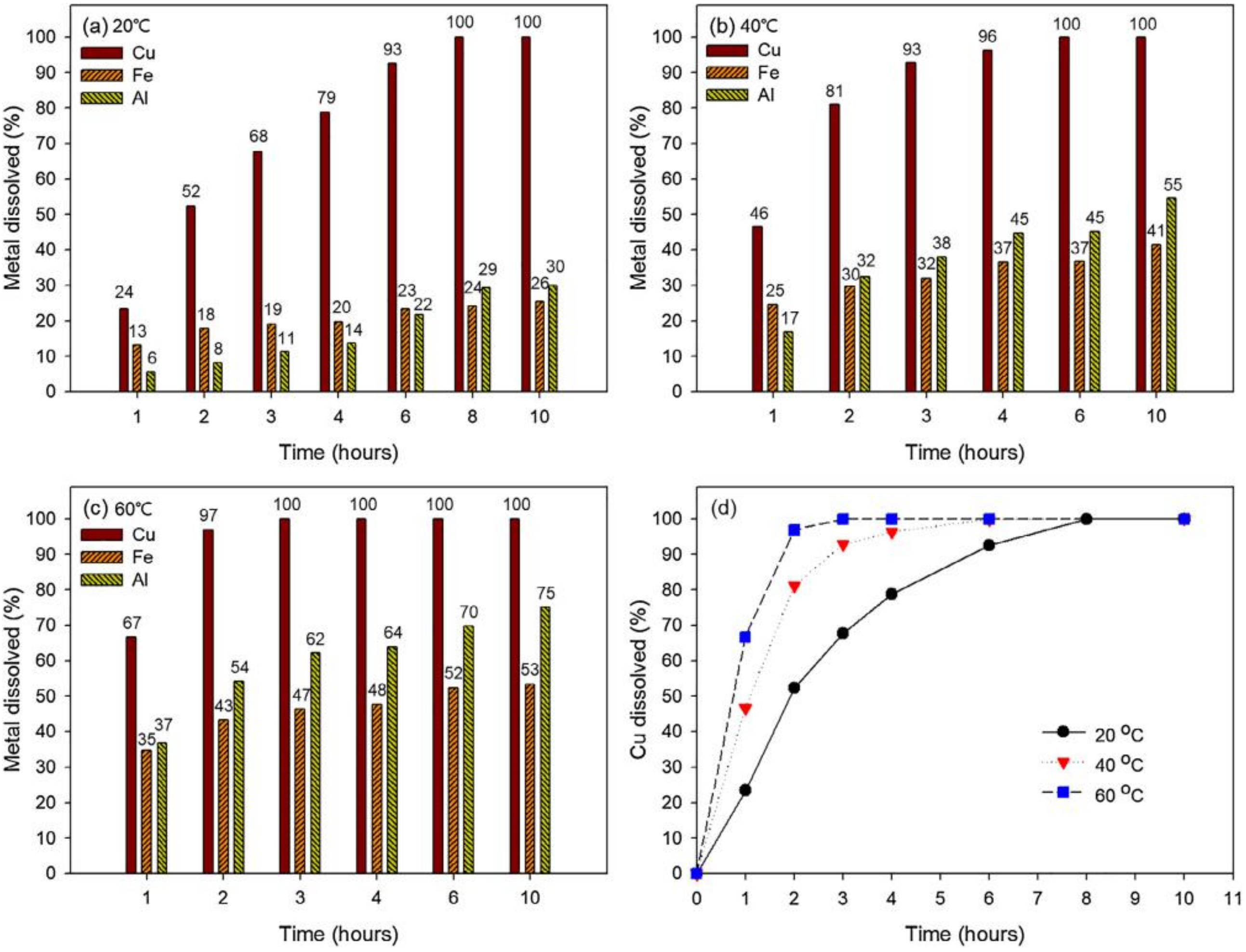

Fig. 2. Effect of temperature and time on e-waste leaching in a 1 M HNO_3 solution: (a) 20 °C, (b) 40 °C, (c) 60 °C, and (d) full Cu dissolution.

3.2. Effect of various acids leaching solutions

Fig. 2 shows the effect of temperature and time on HNO_3 leaching. As shown in Fig. 2(a)–(c), the dissolution of Cu in HNO_3 was faster than other metals. The Cu was completely dissolved over time at all temperatures. Fe was dissolved up to a maximum of 75% and Al was dissolved up to a maximum of 53% at 60 °C, respectively. The dissolution of Cu with time and temperature is shown in Fig. 2(d). The dissolved amount of Cu increased gradually with increasing time at 20 °C, and it was completely dissolved after 8 h. The dissolution rate of Cu became even faster at 40 and 60 °C, and it was completely dissolved after about 3 h at 60 °C.

HCl was chosen as the second reagent for leaching. The results are shown in Fig. 3 as a bar chart of metal dissolution over time. As shown in Fig. 3(a)–(c), the dissolution of Fe and Al in HCl was faster than Cu. In particular, Fe was completely dissolved at all temperatures and Al was dissolved at about 75% at 60 °C. Note that Fig. 3(a) shows that the rate of dissolution of Cu gradually increases after four hours, after the Fe dissolution was complete. The dissolution of Cu in HCl with time and temperature is shown in Fig. 3(d). The Cu dissolution gradually increased with both time and temperature. In the HCl solution, the dissolution of Fe and Al was higher than that of HNO_3, and the dissolution of Cu increased after the Fe was completely dissolved.

Fig. 4 shows the effect of temperature and time on 1 M H_2SO_4 leaching. In the case of H_2SO_4, the dissolution of Cu was hardly obtained, unlike HNO_3 and HCl. As shown in Fig. 4(a), the dissolution of Cu gradually decreased over time. In addition, the dissolution of Cu decreased with increasing temperature. At low concentrations of H_2SO_4, this effect can lead to the precipitation of hydrous ferric oxides that can adversely affect Cu extraction (Gupta and Mukherjee, 1990). Therefore, the dissolution of Cu can be suppressed. Thermodynamic equilibrium calculations of Cu and Fe were carried out in a temperature range of 20–60 °C using HSC Chemistry 5.1 software (Roine, 2002). Table 2 shows the results of the thermodynamic equilibrium reactions in H_2SO_4. As Table 2 indicates, the equilibrium reactions were spontaneous in the H_2SO_4 solution, except for the reaction of metallic Cu. In particular, the Gibbs free energy of metallic Fe had the most stable energy, at −78.989 kJ/mol. On the other hand, the value for metallic Cu was 36.727 kJ/mol, and therefore, it did not dissolve.

Some researchers have used various additives, such as dichromate ($K_2Cr_2O_7$) and hydrogen peroxide (H_2O_2) to improve the dissolution of Cu in H_2SO_4 solution (Altundogan et al., 2004; Deveci et al., 2010). However, the conversely inhibiting effects of Cu can enable the separation of Cu and other metals. The dissolution of Fe with time and temperature is shown in Fig. 4(d). The dissolution value increased gradually with increasing time at 20 °C. The dissolution rate of Fe was faster at 60 °C, and Fe was completely dissolved after about 4 h.

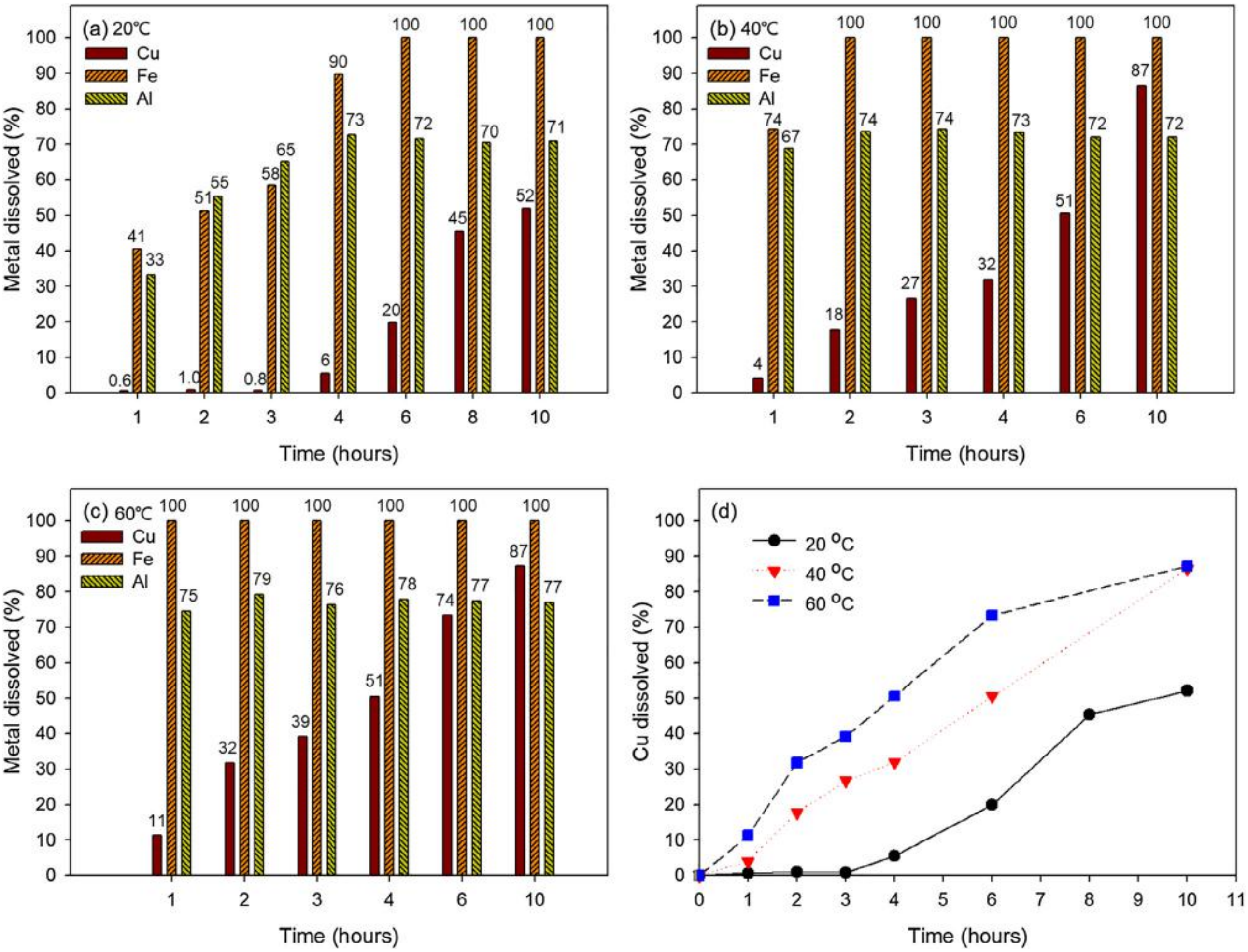

Fig. 3. Effect of temperature and time on e-waste leaching in a 1 M HCl solution: (a) 20 °C, (b) 40 °C, (c) 60 °C, and (d) Cu dissolution.

3.3. *Kinetic study of Cu leaching in HNO_3 solutions*

A kinetic study of Cu leaching on HNO_3 solutions was conducted with a shrinking core model (Habbache et al., 2009; Jung and Mishra, 2016). In HCl and H_2SO_4, kinetic studies were not conducted, because Cu was not completely dissolved. For the Cu-leaching kinetics, three different reaction equations of the shrinking core model were used, and can be expressed by the following equations:

$$1-3(1-x)^{\frac{2}{3}}+2(1-x)=kt \text{ (for pore diffusion control)} \quad (1)$$

$$1-(1-x)^{\frac{1}{3}}=kt \text{ (for chemical reaction control)} \quad (2)$$

$$x=kt \text{ (for fluid film diffusio ncontrol)} \quad (3)$$

where x is the fractional conversion of Cu, t is reaction time, and k is the rate constant. The rate of the process is controlled by the slowest of these sequential steps. For the exact shrinking core model applications, the regression lines of the three different equations were compared and, as a result, the R^2 value of the chemical control reaction was closest to 1. In the shrinking core model in which the rate limiting step is the chemical control reaction, Eq. (2) was applied, and linear fits were obtained, as shown in Fig. 5(a). From the slopes of the linear line, a rate constant (k) was obtained. An activation energy (E_a) can be obtained from an Arrhenius equation with temperature and k, and may be expressed by the following equations (Laidler, 1984):

$$k=A\ exp(-E_a/RT) \quad (4)$$

where k is the rate constant, A is the frequency factor, E_a is the activation energy, R is the universal gas constant, and T is the reaction temperature. The Arrhenius plot is shown in Fig. 5(d), and the calculated activation energy from the slope ($-E_a/RT$) was about 5.0 kcal/mol. This value corresponds to the activation energies of the diffusion control and/or mixed control of diffusion processes and chemical processes. Diffusion control processes generally have low activation energy values, and their value is typically smaller than 5 kcal/mol. Chemical reactions normally have activation energy values between 10 and 25 kcal/mol (Haung and Twidwell, 1980).

3.4. *Selective metal recovery by a two-stage process*

Based on the results of leaching in various acids and the kinetic study, a continuous two-stage process was performed for selective metal recovery. To verify the effect of selective leaching, the solid/liquid ratio was increased to 100 g/L and the temperature and time were fixed at

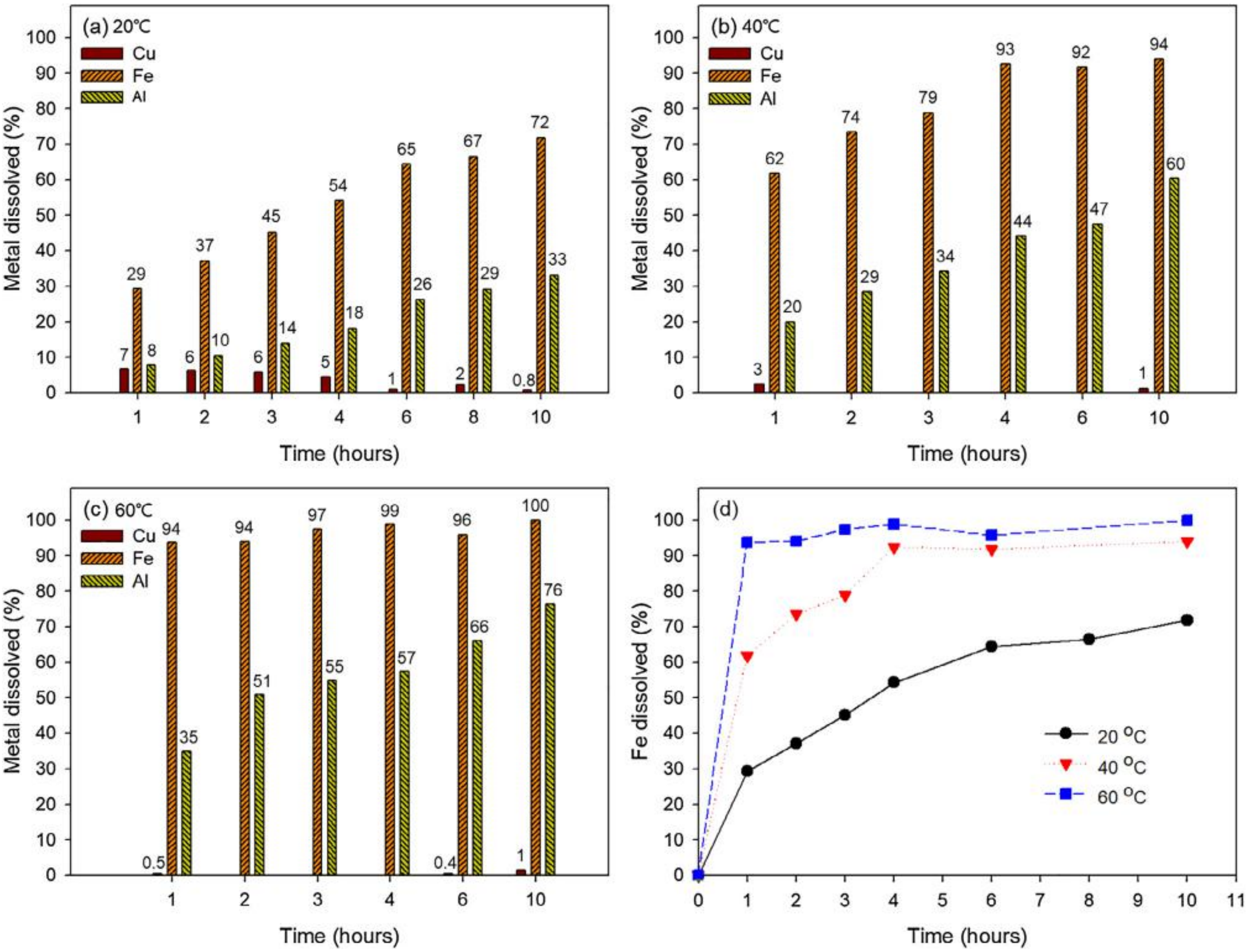

Fig. 4. Effects of temperature and time on e-waste leaching in a 1 M H_2SO_4 solution: (a) 20 °C, (b) 40 °C, (c) 60 °C, and (d) Cu dissolution.

Table 2
Gibbs free energy of the reaction calculated with temperature (kJ/mol).

Reaction equation	Temperature, °C		
	20	40	60
$Cu + 2H_2SO_4 (aq) \rightarrow CuSO_4 (aq) + 2H_2O (l) + SO_2 (g)$	36.727	31.848	26.283
$CuO + H_2SO_4 (aq) \rightarrow CuSO_4 (aq) + H_2O (l)$	−44.014	−42.636	−41.536
$Cu_2O + H_2SO_4 (aq) \rightarrow Cu + CuSO_4 (aq) + H_2O (l)$	−24.330	−22.621	−21.195
$Fe + H_2SO_4 (aq) \rightarrow FeSO_4 (aq) + H_2 (g)$	−78.989	−78.364	−78.364
$Fe_3O_4 + 4H_2SO_4 (aq) \rightarrow Fe_2(SO_4)_3 (aq) + FeSO_4 (aq) + 4H_2O (l)$	−24.756	−12.324	−1.023

60 °C for 4 h. In the leaching experiment in H_2SO_4 (Fig. 4), the Cu was not dissolved, while Fe and Al were dissolved along with other metals. Therefore, H_2SO_4 was used as the first-stage process for selective metal recovery. As shown in Fig. 6(a), 90% of Fe and 47% of Al were dissolved, and the Cu was almost insoluble. Compared with the results of Fig. 4(c), the dissolution efficiency of Fe decreased from 100% to 90%. It is probably due to the increased solid/liquid ratio (20–100 g/L). Some researchers also reported the decrease in the leaching efficiency with increasing solid/liquid ratio (Le et al., 2011; Jung and Mishra, 2016). The second-stage process with HNO_3 is shown in Fig. 6(b). The purpose of the second-stage process is to obtain the high dissolution efficiency of Cu. In the single stage of Cu, 100% leaching efficiency was obtained in HNO_3 at 60 °C for 3 h (Fig. 2(c)). However, in the second stage, the leaching time was increased to 4 h in consideration of the increased solid/liquid ratio. As a result, the selective Cu dissolution was obtained at 98% in the final leaching solution. Based on Fig. 2(c), after 4 h the dissolution of Fe and Al were 48% and 64%. On the On the other hand, the second-stage experiment showed the dissolution of Fe and Al as 5% and 23%, respectively. The reason for the decrease of Fe and Al dissolution is due to the compositional change of feed sample. Approximately 90% of Fe and 47% of Al were removed after the first-stage process. As a result, the leaching efficiency changed after the final experiment due to the change of composition and the solid/liquid ratio of the residue. The recovery efficiency of these selective metals depends on the composition and concentration of the sample. Therefore, further research is needed to improve the leaching efficiency and to increase their purity.

Based on the above investigations, a process for selective metal recovery can be proposed. Fig. 7 shows a schematic design of the

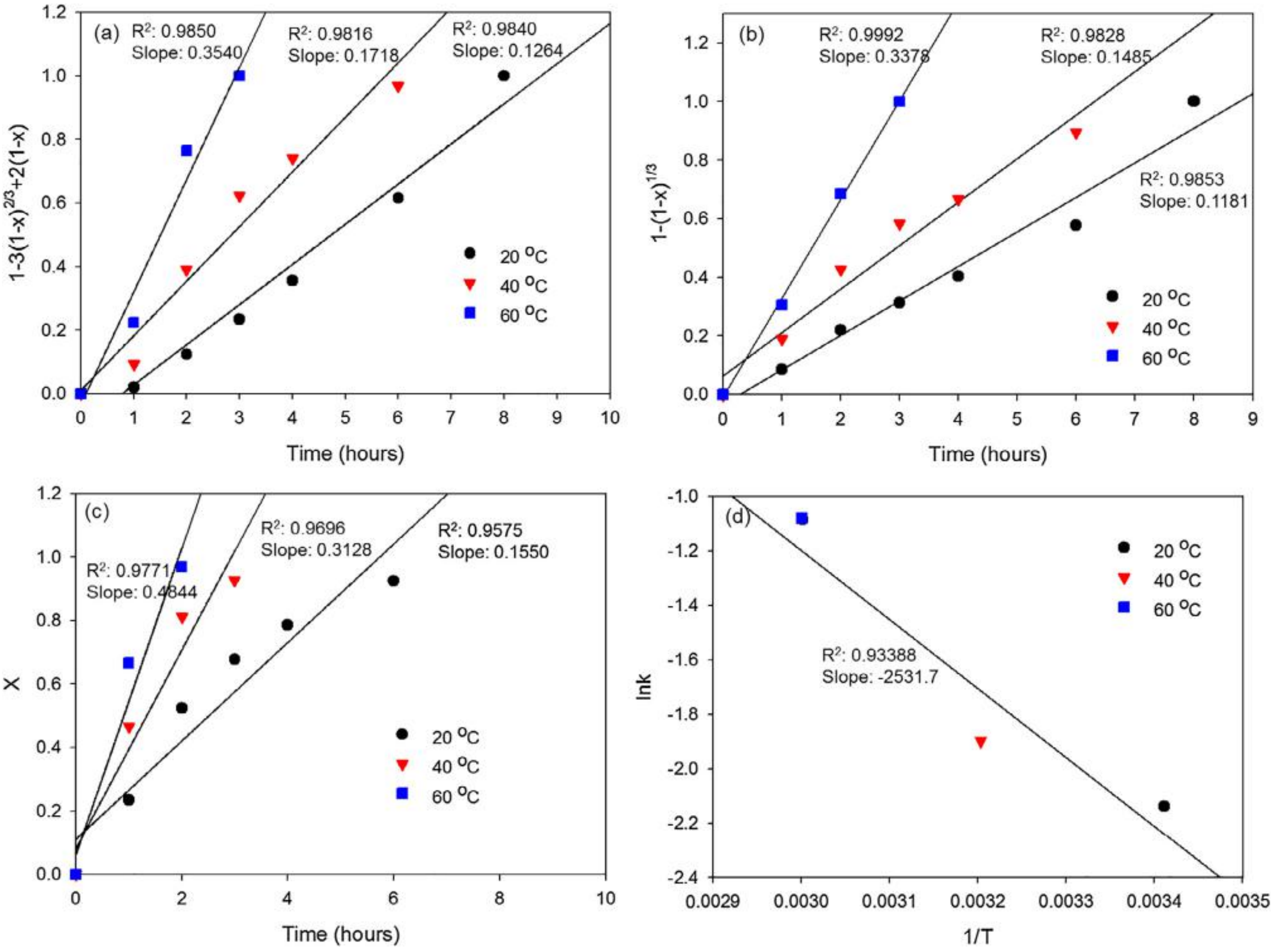

Fig. 5. Application of the shrinking model and Arrhenius plot with HNO_3: (a) pore diffusion control plot, (b) chemical reaction control plot, (c) fluid film diffusion control plot, (d) Arrhenius plot, based on chemical reaction control.

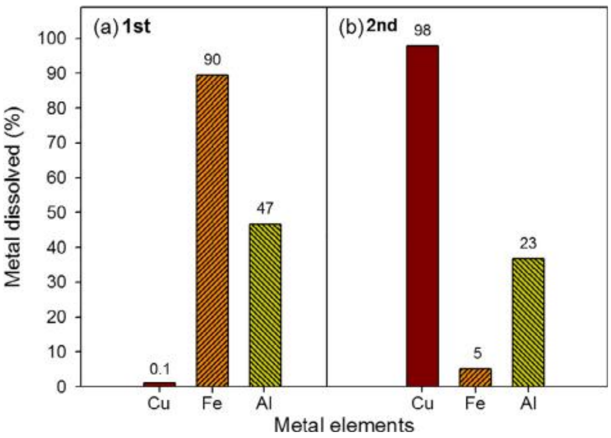

Fig. 6. Efficiency of metal leaching by two-stage process: (a) first stage 1 M H_2SO_4; (b) second stage 1 M HNO_3.

process. From each leachate, Fe and Cu metals can be obtained by electrolysis or precipitation, and then the remaining solutions can be returned to leaching steps.

4. Conclusion

In this study, fine materials, including flue dust from e-waste processing, were investigated for recovery and separation of valuable metals, and the optimum conditions for Fe and Cu selective leaching were determined. In a single process, Cu showed the highest dissolution efficiency compared to Fe and Al in HNO_3. On the other hand, Fe had the highest dissolution efficiency and Cu was almost insoluble in H_2SO_4. Through this results, H_2SO_4 was used to dissolve Fe as the first leaching process and HNO_3 was used for Cu dissolution as the second leaching process. As a result, Fe and Cu leaching efficiencies were obtained at approximately 90% and 98% by the two-stage leaching

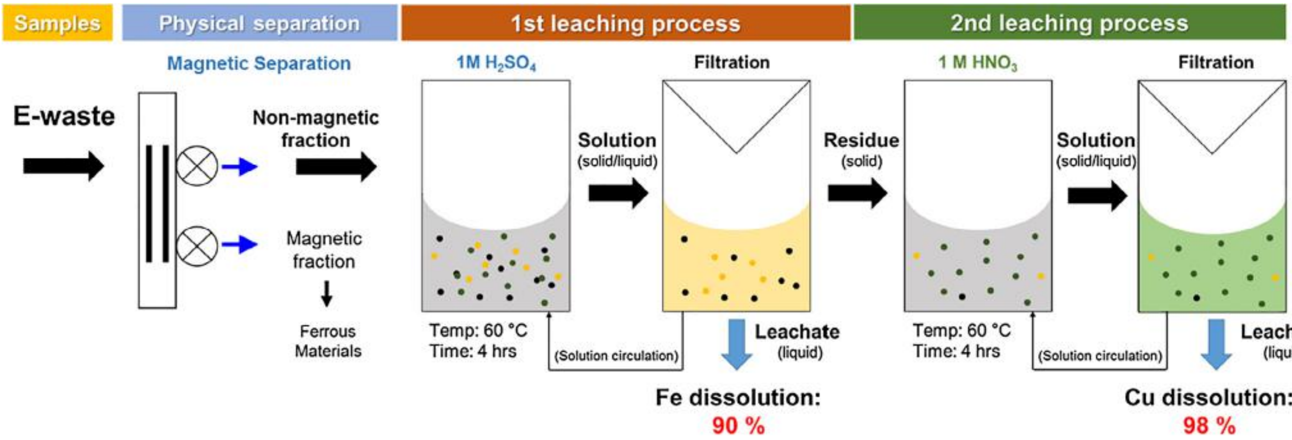

Fig. 7. A process flowsheet proposed for selective metal recovery from e-waste.

process, respectively. Although the dissolution efficiency of Fe and Cu depends on the concentration and composition of the feed material, the multistage leaching process using this acid solution could be applicable to other recovery studies.

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