J. of Korean Inst. of Resources Recycling
Vol. 17, No. 3, 2008, 48-55
≫ 硏究論文 ≪

핸드폰 基板으로부터 구리와 은의 窒酸 浸出 硏究†

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Leaching of copper and silver from ground mobile phone printed circuit boards using nitric acid†

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요 약

핸드폰 기판 내 구리와 은의 침출거동에 미치는 질산농도, 반응온도, 교반속도, 광액농도의 영향을 조사하기 위하여 질산을 이용한 핸드폰 기판침출실험을 수행하였다. 질산농도와 반응온도의 증가에 따라 침출율은 빠르게 증가하였다. 최적 침출 조건인 80°C, 2 mol/L HNO_3, 120 g/L의 조건에서 구리와 은의 침출율은 반응시간 20분 동안 98~99%에 달하였다. 수축핵 모델(Shrinking core model)에 기초하여 각 침출실험결과를 분석하고 속도상수를 결정하였다. 활성화에너지는 2 mol/L 질산용액을 이용하여 온도범위 35~80°C에서 분석한 결과, 구리와 은에 대하여 각각 45.5 kJ/mol과 60.5 kJ/mol을 나타내었다.

주요어 : 핸드폰, 인쇄기판, 은, 구리, 재활용, 질산

Abstract

Leaching of copper and silver from mobile phone PCBs (printed circuit boards) with nitric acid was performed to investigate the effects of nitric acid concentrations, leaching temperatures, agitation speeds, and pulp densities on the leaching behaviors of Cu and Ag. The leaching rate considerably increased with increasing acid concentration and temperature. The leaching ratios of Cu and Ag were found to be 96.4% and 96.5%, respectively, under the optimum condition; at 80°C with 2 mol/L HNO_3 and 120 g/L in pulp density within 30 minutes. The kinetic parameters were determined based on the shrinking core model with reaction control corresponding to small particles. The activation energies for the leaching of copper and silver were found to be 45.5 kJ/mol and 60.5 kJ/mol at 35-80°C with 2 mol/L HNO_3, respectively.

Key words : mobile phone, printed circuit boards, silver, copper, recycling, nitric acid

1. Introduction

Electronic waste (e-waste) is the fastest growing waste stream in the industrialized life[1]. Thus, the management of electronic waste is becoming the seriously environmental problem over the world, mainly due to the hazardous materials contained in the electronic waste. Therefore, great attention has been paid to the recycling of e-waste rather than to simply disposing of it in land-fill sites. The recycling of printed circuit boards (PCBs) inside e-waste is important since they contain valuable metals such as copper and precious metals.

Many researchers have investigated the recycling of PCBs to recover valuable metals. Hall *et al.* conducted the separation and recovery of valuable material from scrap PCBs by pyrolysis[2]. Sheng *et al.* used aqua regia

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Table 1. Weight and value distribution of metals in several electronic equipments[9].

Weight-%	Fe	Al	Cu	Plastics	Ag [ppm]	Au [ppm]	Pd [ppm]
TV-board	28%	10%	10%	28%	280	20	10
PC-board	7%	5%	20%	23%	1000	250	110
Mobile phone	5%	1%	13%	56%	1380	350	210
Value-share	**Fe**	**Al**	**Cu**	**Sum PM**	**Ag**	**Au**	**Pd**
TV-board	4%	11%	42%	43%	8%	27%	8%
PC-board	0%	1%	14%	85%	5%	65%	15%
Mobile phone	0%	0%	7%	93%	5%	67%	21%

to recover gold from computer PCBs[3]. Veit *et al.* utilized magnetic and electrostatic separation for recycling of PCBs[4]. Oishi *et al.* recovered copper from PCBs using ammoniacal sulfate or chloride solution[5]. Eswaraiah *et al.* classified metals and plastic from PCBs using an air classifier[6]. Kim *et al.* investigated the leaching of copper from waste PCBs using electro-generated chlorine in hydrochloric acid[7]. Lee *et al.* have proposed strategic processes for recycling of waste PCBs which classified the recycling technologies into two methods: (1) pyrometallurgical process typically practiced at copper smelters and (2) combined process of mechanical pretreatment and hydrometallurgical processes[8]. Lee *et al.* also reported that, because the pyrometallurgical approach has notable disadvantages such as air pollution and loss of noble metals, mechanical pretreatment in combination with hydrometallurgical process has been developed as environmentally friendly technology[8].

Although many researches have been conducted for the recycling of PCBs inside waste electrical and electronic equipments (WEEE), there have been a few researches focusing on recycling of mobile phone PCBs. The recycling of mobile phone PCBs is very attractive since their high contents of precious metals such as gold, silver and palladium as can be seen in Table 1[9]. In the previous work, the liberation of the mobile phone PCBs was studied for subsequent hydrometallurgical process to recover precious metals. The separation of base metals such as copper and noble metals such as gold, silver, and palladium was achieved decreasing loss of precious metals[10].

In order to recover the precious metals efficiently, 2-step leaching was suggested using nitric acid for the dissolution of Cu and Ag and aqua regia for that of Au and Pd. In the present study, the effects of HNO_3 concentration, leaching temperature, agitation speed and pulp density on leaching behaviors of Cu and Ag were investigated.

Table 2. Chemical composition of leaching sample used in study.

Metal	Au	Ag	Pd	Cu	Fe	Ni	Zn	Pb
Wt.%	0.20	0.75	0.05	14.1	1.08	1.62	0.49	2.94

2. Experimental

2.1. Materials

Mobile phone PCBs were shredded into approximately 5 mm fragments by scutter shredder and ground finely by mixer-mill (MM 301, Retsch) for 4 minutes. Then PCB powder was screened with 150 μm (100 mesh) Tyler sieve using vibratory sieve shaker (J-VSS, Jisico) for 2 hours at a speed of 130 vibrations per second. The undersize fraction containing precious metals with chemical composition shown in Table 2 was used as the sample for this study.

2.2. Procedures

All leaching experiments were performed with a 500 ml four-necked thermostatic Pyrex reactor. The center hole of the reactor was fitted with a stirrer, and two side holes were done with a temperature controller and reflux condenser, respectively. Fig. 1 shows the schematic diagram of leaching apparatus used in this study. Firstly 300 ml nitric acid solution was added into the reactor, and then heated to the desired temperature

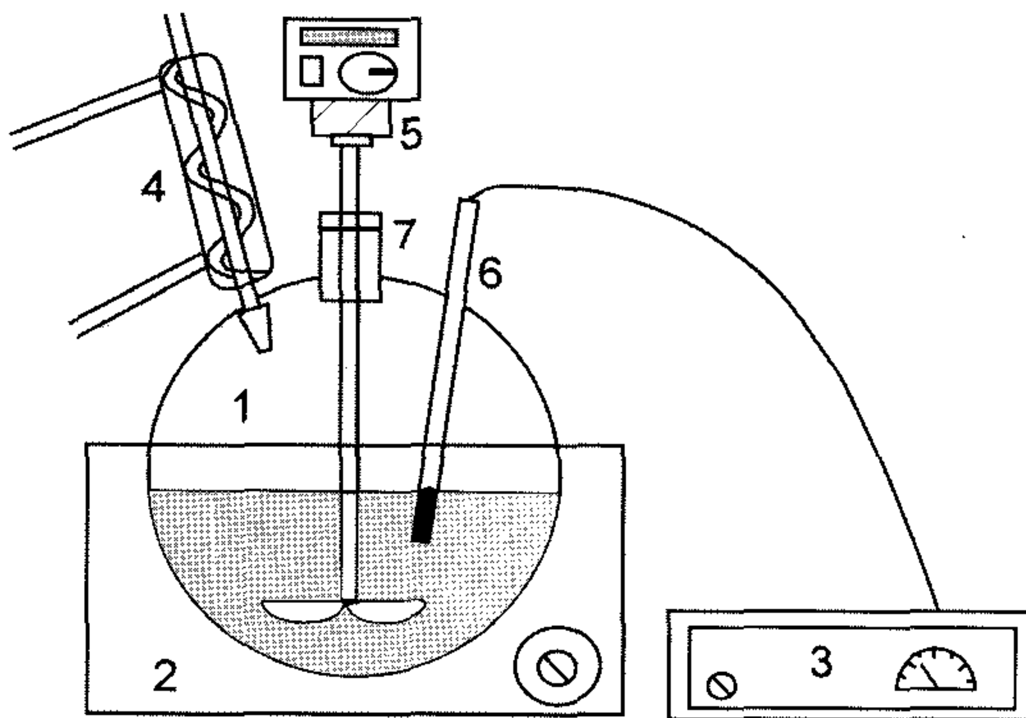


Fig. 1. Schematic diagram of the leaching apparatus. 1. Reactor, 2. Heating mantle, 3. Temperature controller, 4. Reflux condenser, 5. Stirrer, 6. Thermometer, 7. Mercury seal.

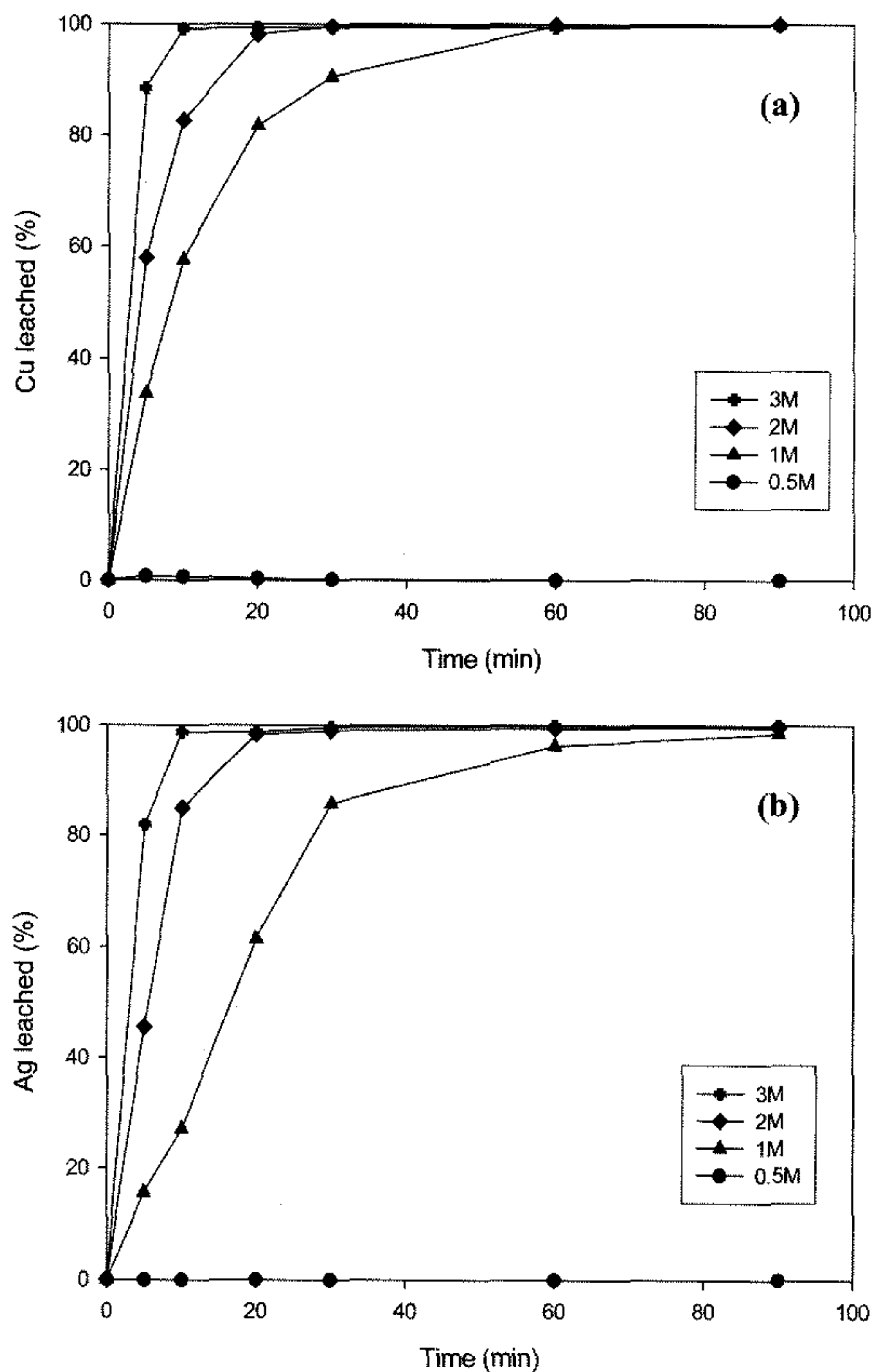


Fig. 2. Effect of HNO_3 concentration on the leaching process. (a) Copper leaching; (b) Silver leaching (temperature: 80°C, agitation speed: 400 rpm, pulp density: 10 g/L).

with a heating mantle. Finally, the ground PCBs were introduced into the reactor. The solution was stirred during all leaching tests.

During the test, 2 ml of solution leached was sampled periodically at a desired time by a syringe. The samples were filtered with membrane filter (0.45 μm) and diluted with 5% HNO_3 solution. The concentrations of Cu and Ag were analyzed by using an atomic absorption spectrometer (AAnalyst 400, PerkinElmer) and inductively coupled plasma spectrometer (ICP-AES, JY-38 plus, Jobin-Yvon).

3. Results and discussion

3.1. Effect of acid concentration

In order to investigate the effect of acid concentration on the leaching, the ground PCBs were leached under the following condition; 80°C in temperature, 400 rpm in agitation speed, 10 g/L in pulp density, and 0.5 mol/L~3.0 mol/L in nitric acid concentration. The leaching behaviors of Cu and Ag with time are shown in Fig. 2. Both Cu and Ag were not leached when HNO_3 concentration was 0.5 mol/L. The leaching rate of Cu and Ag increased rapidly with increasing acid concentration to more than 1 mol/L HNO_3. The leaching rate of Cu and Ag reached to 98% at 2 mol/L HNO_3 within 20 minutes, so that 2 mol/L HNO_3 was selected as the suitable concentration for the leaching process.

3.2. Effect of temperature

The effect of temperature on the leaching of Ag and Cu was examined in the leaching tests conducted at 400 rpm in agitation speed and 35°C~80°C in temperature with 10 g/L in pulp density and 2 mol/L HNO_3. The effect of temperature is shown in Fig. 3. At 35°C, the dissolution of Cu and Ag was quite slow and the leaching rates reached to only 74% with Cu and 43% with Ag, respectively. However, the leaching rates of Cu and Ag increased rapidly at more than 50°C with increasing temperature. Almost 99% of Cu and Ag was leached at 80°C within 30 minutes, while it took around one hour to leach the same amount at 70°C. In this study, 80°C was selected for leaching of Cu and Ag from the moblie phone PCBs.

3.3. Effect of agitation speed

The leaching tests were conducted at 80°C in temperature and 50 rpm~300 rpm in agitation speed

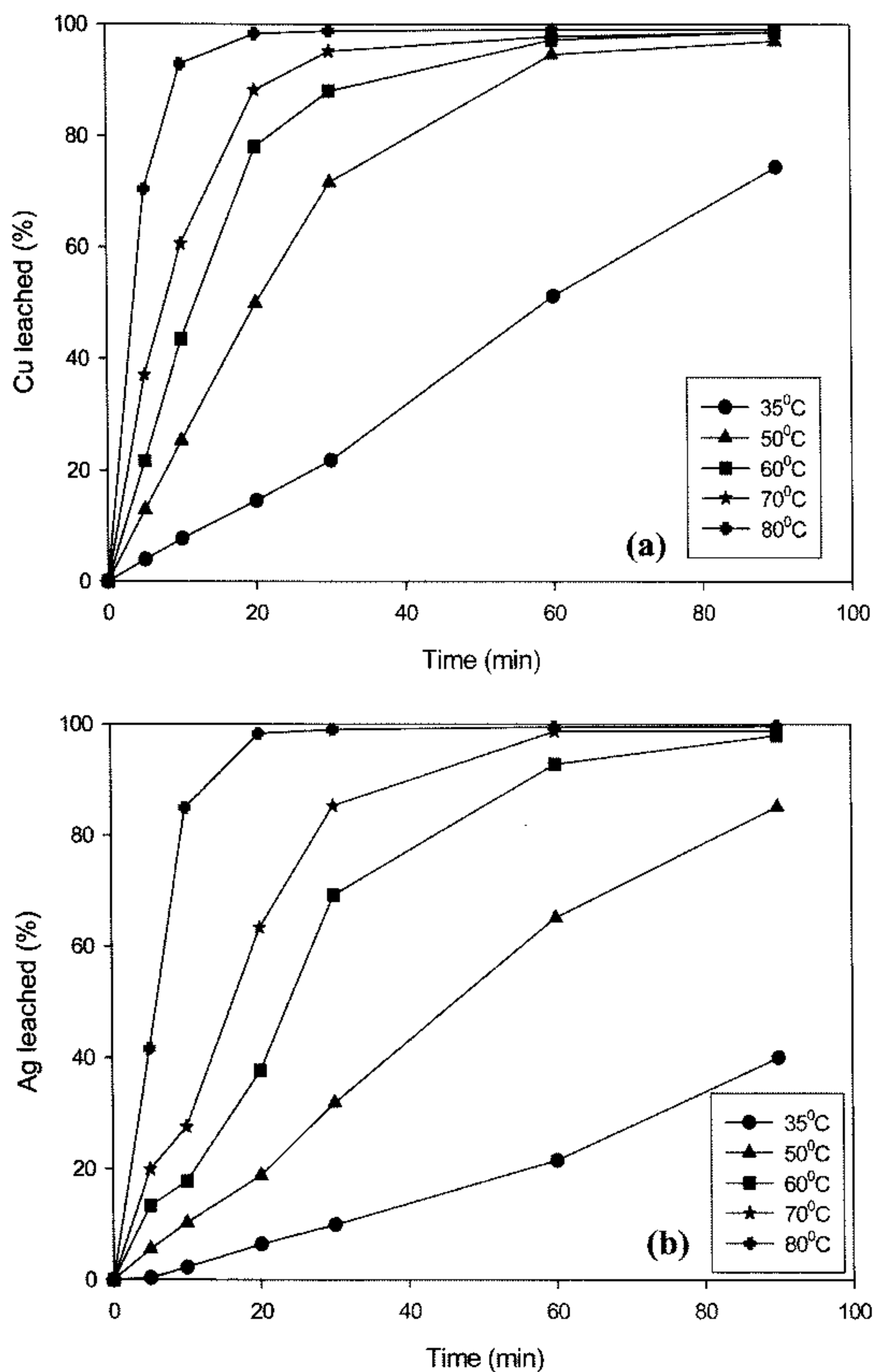


Fig. 3. Effect of temperature on the leaching process. (a) Copper leaching; (b) Silver leaching (acid concentration: 2 mol/L, agitation speed: 400 rpm, pulp density: 10 g/L).

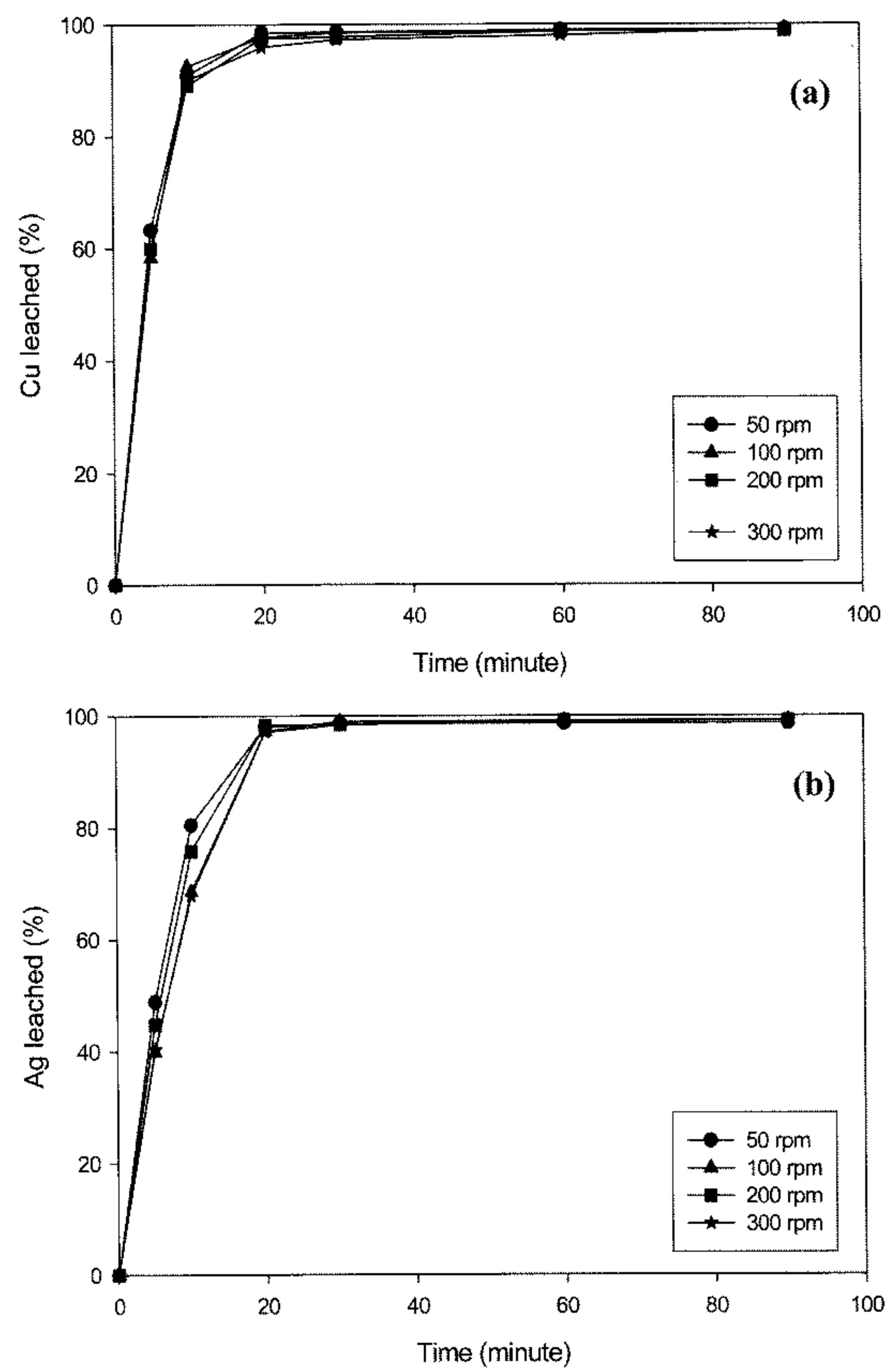


Fig. 4. Effect of agitation degree on the leaching process. (a) Copper leaching; (b) Silver leaching (temperature: 80°C, HNO_3 concentration: 2 mol/L, pulp density: 10 g/L).

with 10 g/L in pulp density and 2 mol/L HNO_3. Fig. 4 shows the effect of agitation speed on the leaching process of Cu and Ag. The leaching rate and total dissolution of Cu and Ag almost didn't change with various agitation speeds. This result would suggest that the effect of agitation speed on the leaching process would be negligible under the experimental conditions in this study. These results indicate that the rate controlling step in the leaching process is the dissolution reaction, rather than the diffusion of reagent and leached solution through the pores of material being leached.

3.4. Effect of pulp density

The leaching test was conducted at 80°C and 300 rpm in agitation speed with 2 mol/L HNO_3, and the pulp density was varied from 30 to 170 g/L. The effect of pulp density on leaching of Cu and Ag is presented in Fig. 5. The increase in pulp density had a negative effect on the total dissolution. This effect was relatively smaller in the leaching of copper than in that of Ag. At 90 and 120 g/L pulp density, 96~98% of copper and silver was dissolved within 30 minutes while only 95% of copper and 91% of silver were dissolved in the case of 170 g/L. From these data, the pulp density of 120 g/L was found to be suitable for the leaching process. Normally, the increase of solid has a detrimental effect on total dissolution as well as on the leaching rate. But in this test, the increase of pulp density did not lower the leaching rate because of the heat produced by the exothermic dissolution reaction, which quickly raised the temperature over 100°C within the first 10 minutes leading to the increase of leaching rate.

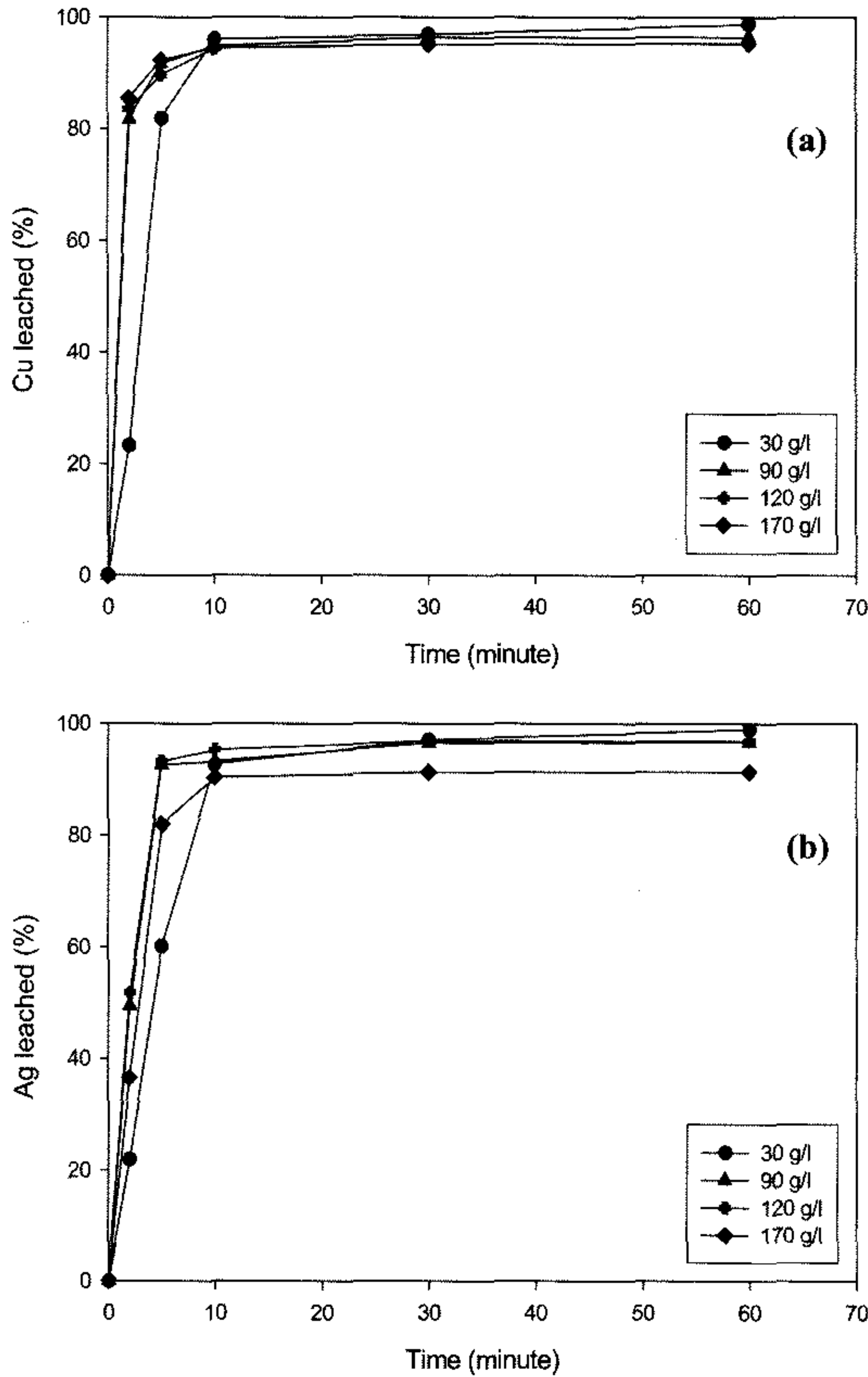


Fig. 5. Effect of pulp density on the leaching process. (a) Copper leaching; (b) Silver leaching (temperature: 80°C, HNO_3 concentration: 2 mol/L, agitation speed: 300 rpm).

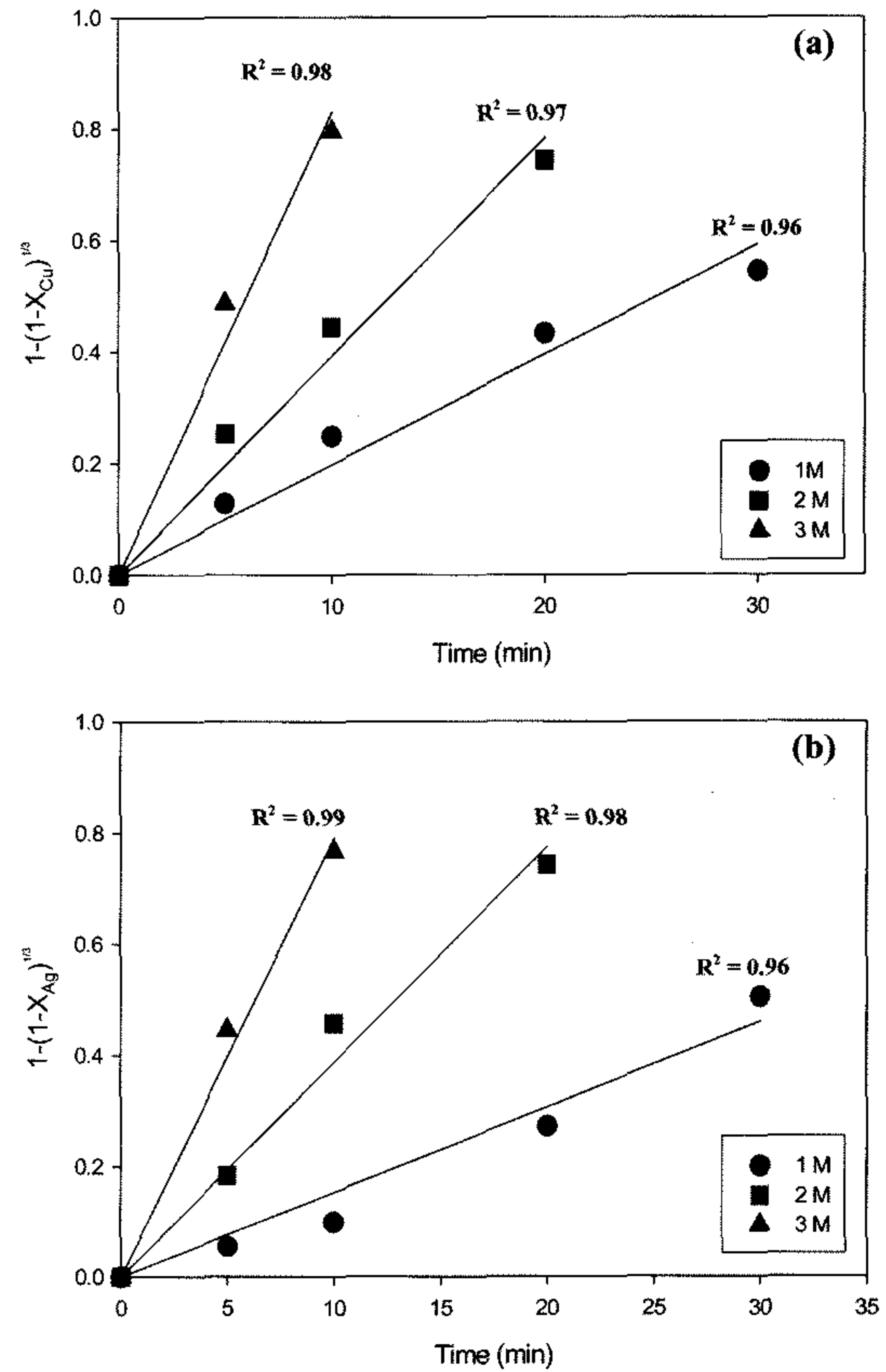
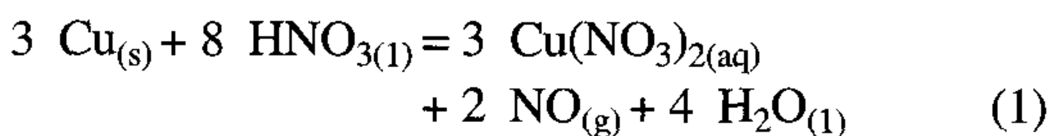


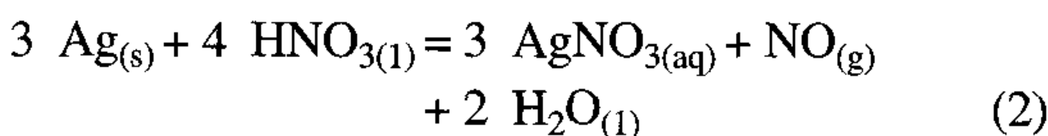
Fig. 6. Plot of results in Fig. 2 according to Eq. (3). (a) Copper leaching; (b) Silver leaching.

3.5. Reaction kinetics

Copper and silver are known to react slowly with diluted nitric acid, generating NO gas; and very vigorously with concentrated (70%) nitric acid, producing NO_2 gas[11]. As a result, the most probable reaction stoichiometry for nitric acid leaching of copper and silver in the reaction conditions of this study is given by Eqs. (1) and (2)



$$3\ Cu_{(s)} + 8\ HNO_{3(l)} = 3\ Cu(NO_3)_{2(aq)} + 2\ NO_{(g)} + 4\ H_2O_{(l)} \quad (1)$$



$$3\ Ag_{(s)} + 4\ HNO_{3(l)} = 3\ AgNO_{3(aq)} + NO_{(g)} + 2\ H_2O_{(l)} \quad (2)$$

The appreciable effect of temperature on the copper and silver dissolution suggests that this process is surface reaction controlled[12]. The experimental data were analyzed by using the relationships between time and conversion for the shrinking core model[13] as the following equation.

$$1-(1-X)^{1/3} = k_{app}t \quad (3)$$

where t is the leaching time (min), X is the fraction reacted, and k_{app} is the apparent reaction rate constant (min^{-1}) which is given by

$$k_{app} = bkf([HNO_3]) = bk[HNO_3]^n\ (min^{-1}) \quad (4)$$

where b is stoichiometry factor for the reactions ($b = 3/8$ for copper dissolution; $b = 3/4$ for silver dissolution), k is the intrinsic rate constant ($min^{-1}.mol^{-1}$), f represents the HNO_3 concentration dependence of the rate, and n is the reaction order for HNO_3 concentration.

The reacted fractions (X) were calculated with the data in Fig. 2 and 3. The variation of $1-(1-X)^{1/3}$ with time is shown in Figs. 6 and 7, respectively. As can be

seen in Figs. 6 and 7, correlation coefficients (R^2) show 0.96 to 0.99, and this indicates that the model fits the data well.

The apparent reaction rates (k_{app}) were obtained from data in Fig. 6. Fig. 8 shows the k_{app} versus HNO_3 concentration where correlation coefficents were 0.95 and 0.97 for the leaching of copper and silver, respectively. The straight lines obtained indicate that the leaching of copper and silver is first order with respect to HNO_3 concentrations considered in this study. Thus, Eq. (4) can be rewritten as

$$k_{app,Cu} = (3/8)k[HNO_3] \ (min^{-1}) \quad (5)$$

$$k_{app,Ag} = (3/4)k[HNO_3] \ (min^{-1}) \quad (6)$$

where $k_{app,i}$ represents the apparent reaction rate constant of species i.

From the slope of the curves in Fig. 7, the kinetic constants k for the various temperatures can be determined, which were used to draw the Arrhenius plots as shown in Fig. 9. The calculated activation energies were 45.5 kJ/mol for Cu and 60.5 kJ/mol for Ag, respectively. These results show a typical value for a process controlled chemical reaction[12]. The line through data can be expressed by the following equation:

$$k_{Cu} = 21.3 \times 10^4 \exp[-5467.6/T] \ (min^{-1} \cdot mol^{-1}) \quad (7)$$

$$k_{Ag} = 29.5 \times 10^6 \exp[-7283.5/T] \ (min^{-1} \cdot mol^{-1}) \quad (8)$$

where k_i represents the intrinsic rate constant of species i. Using Eqs. (3), (5), (6), (7) and (8), the leaching rate is represented by the following equation:

$$1-(1-X)^{1/3} = k_{app}t \quad (9)$$

with $k_{app,\,Cu} = 7.99 \times 10^4 \exp[-5467.6/T]$ (min^{-1}) and $k_{app,\,Ag} = 22.12 \times 10^6 \exp[-7283.5/T]$ (min^{-1}).

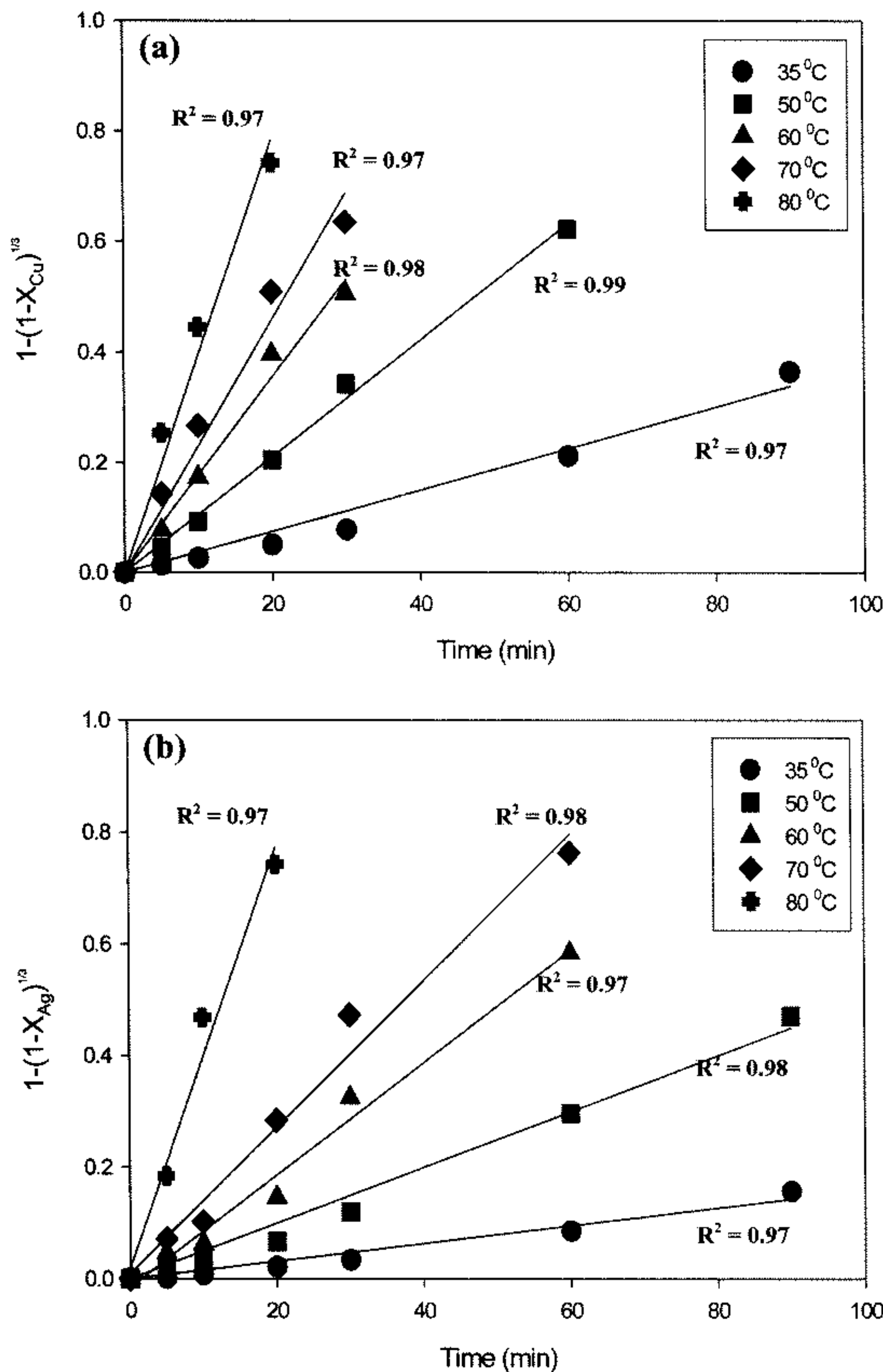


Fig. 7. Plot of results in Fig. 3 according to Eq. (3). (a) Copper leaching; (b) Silver leaching.

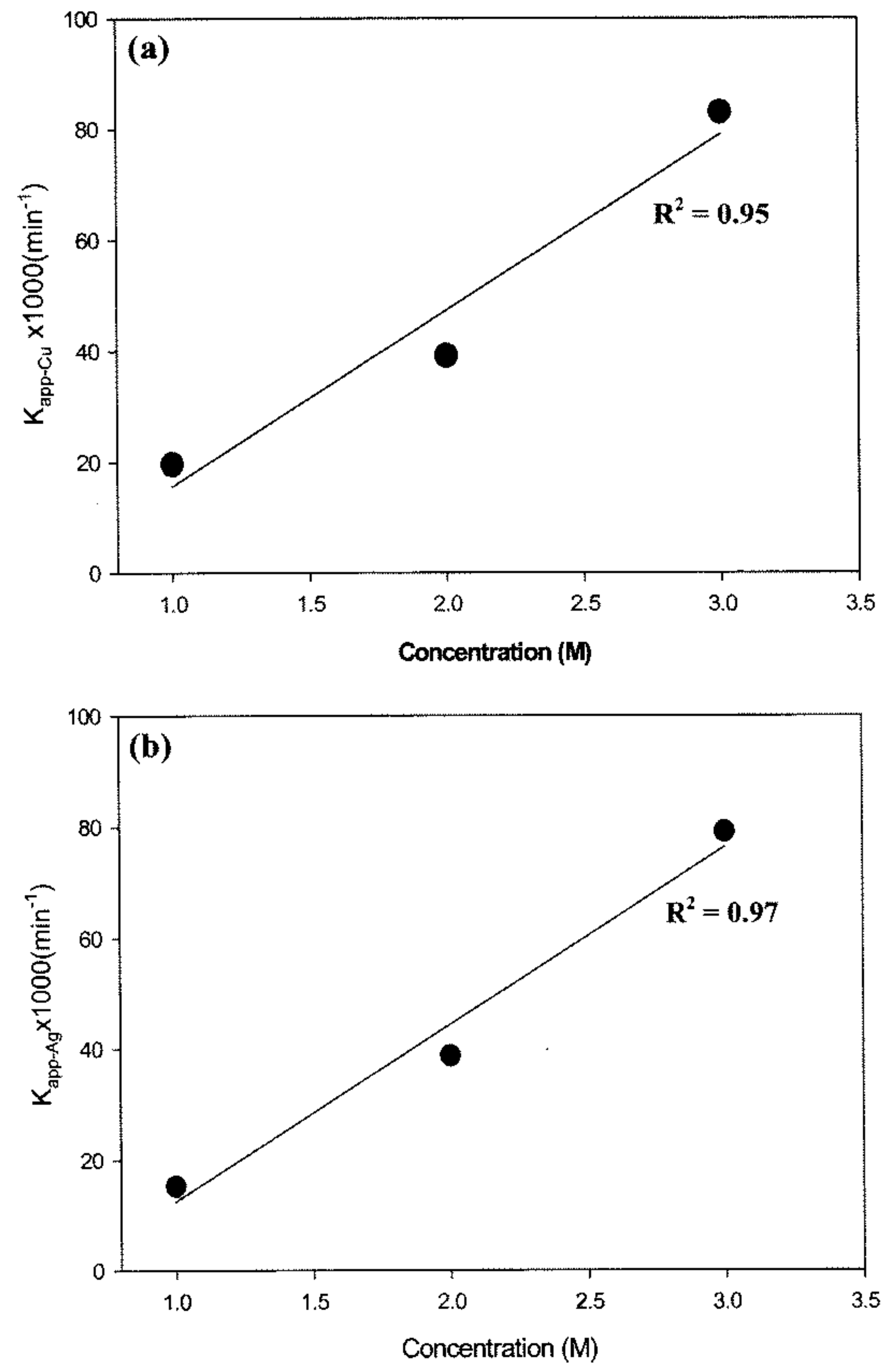


Fig. 8. Dependence of k_{app} on the HNO3 concentration from the results shown in Fig. 6. (a) Copper leaching; (b) Silver leaching.

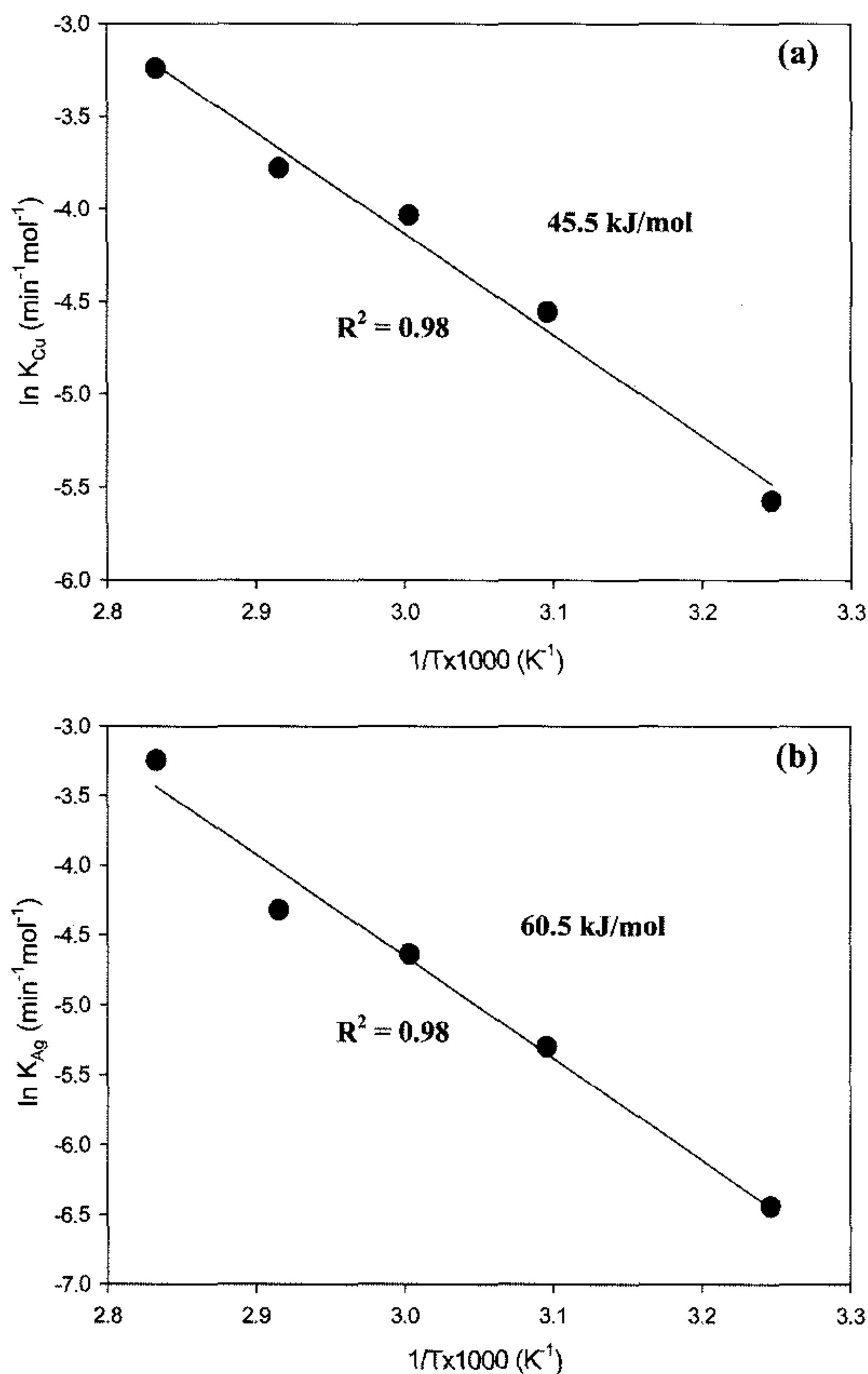


Fig. 9. Arrhenius plot for the dissolution of Cu and Ag. (a) Cu dissolution, (b) Ag dissolution.

4. Conclusions

From the experimental data on the leaching of copper and silver in nitric acid the following conclusions can be obtained.

The leaching rate of copper and silver with nitric acid was significantly affected by acid concentration and temperature. The increase of pulp density decreased the total dissolution of metals. Leaching rate was found to be independent of agitation speed in the experimental ranges. The optimum condition for leaching of Cu and Ag was found at 80°C with 2 mol/L HNO_3, and 120 g/L in pulp density for 30 minutes, under which the leaching rates could be reached to 96.5% for Ag and 96.4% for Cu.

The reaction kinetics was analyzed by using shrinking core model: $1-(1-X)^{1/3} = k_{app}t$. The calculated activation energy for the dissolution of Cu and Ag were 45.5 kJ/mol and 60.5 kJ/mol, respectively, which are typical value for a process controlled by chemical reaction. The rate of Cu and Ag dissolution was found to be of first order with respect to HNO_3 concentration. The rate of the leaching reaction of Cu and Ag could be represented by the following equation:

$$1-(1-X)^{1/3} = k_{app}t$$

with $k_{app,\,Cu} = 7.99 \times 10^4 \exp[-5467.6/T]$ (min^{-1}) and $k_{app,\,Ag} = 22.12 \times 10^6 \exp[-7283.5/T]$ (min^{-1}).

Acknowledgements

This paper is based on work supported by Resources Recycling R&D Center (KOREA) under the project entitled "Development of total recycling technology for WEEE".

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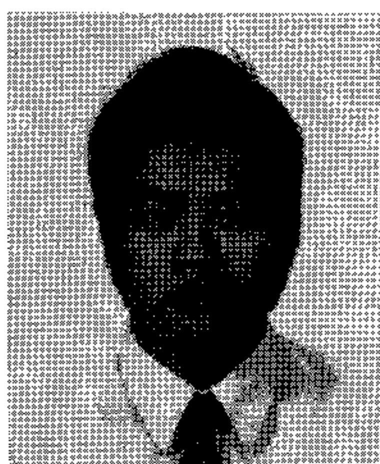

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