KINETIC STUDY OF SILVER LEACHING FROM SEMICONDUCTOR WASTE

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ABSTRACT
Semiconductor waste can cause serious problem in term of storage and pollution since it contains high concentration of heavy metals. However, this waste is also one of the potential silver recovery source. During the last decade, recovery has become more favorable in waste treatment. Kinetic study has been performed during leaching process. This study involves non-catalytic reaction of particles with surrounding fluid and shrinking core model approach has been used to describe the actual kinetics of the process. Some parameters were investigated, such as types of leaching agent, HCl and NaCl concentration, liquid to solid ratio and stirring speed as well. Several mathematical models have been selected to represent the actual kinetics. The experimental data was obtained at 200 liquid to solid ratio and 200 rpm of stirring speed using mix solution of 0.5 M HCl – 3.0 M NaCl as leaching medium. From the experiment it was shown that the shrinking core model was able to describe the silver leaching behavior and indicated that the outward diffusion of silver chloro complex is the rate-controlling step.

Keywords : silver, semiconductor waste, leaching

1. INTRODUCTION

Silver is one of the most useful precious metals, due to its excellent physicochemical properties. Semiconductor waste is one of the potential silver recovery sources. Silver is normally used to plate the semiconductor components in order to improve the electrical contact of the component. The semiconductor waste consists of several components, which the major elements existed are copper (Cu), calcium (Ca), ferrum (Fe), silver (Ag) and stanum (St). This waste causes a serious environmental problem due to the high heavy metal content.

Several silver recovery technologies have been reported. Flotation technique is able to recover silver from wet extraction of zinc at yield more than 89.5% [1]. However, this technique consume high volume of feed material in order to be used economically. Pyrometallurgical process for precious metal recovery has been used commercially, but a large capital is required for the processing equipment. Low metal content and liquid form of feed material are also limiting for wider application of this technique. Biological process to recover silver using microorganisms exhibits low selectivity and operative only at low silver concentration. Another technology, solid liquid extraction technique well known as leaching, is widely used in hydrometallurgy field for silver recovery. Some advantages has been shown such as easily and economically performed operation, high selectivity and purity of silver recovered.

2. KINETIC MODELS OF LEACHING PROCESS

Leaching process involves dissolving the required metal from a solid substance into a solution, using appropriate solvent. Kinetic modeling of leaching is very important in order to get better understanding on the mechanism involved; therefore this study is intended to investigate the kinetic of leaching process. The kinetics of silver leaching is affected by several parameters, which include leaching agent types, HCl and NaCl concentrations, and liquid to solid ratio. The shrinking unreacted-core model selected to represent the leaching process, thus can be classified further into chemical reaction and diffusion through liquid films control model

To study the kinetic of leaching process, five models have been selected from the literature [2,3,4]. These models describe the leaching rate controlled by chemical reaction and diffusion as shown in Table 1.

Table 1. Matematical models to represent the leaching process

	Model	Matematical Model	
Chemical reaction control	1	$1-(1-\alpha)^{1/3}=\left(\frac{V_m C k_o k'}{r_o}\right)t$	$\alpha=1-\left[1-\left(\frac{V_m C k_o k' t}{r_o}\right)\right]^3$
	2	$1-(1-\alpha)^{1/3}=\left(\frac{k_s C}{b\rho_B r_o}\right)t$	$\alpha=1-\left[1-\left(\frac{k_s C t}{b\rho_B r_o}\right)\right]^3$
Diffusion through liquid film control	3	$1-(1-\alpha)^{1/3}=\left(\frac{C V_m D}{\delta b r_o}\right)t$	$\alpha=1-\left[1-\left(\frac{C V_m D t}{\delta b r_o}\right)\right]^3$
	4	$1-(1-\alpha)^{2/3}=\left(\frac{2CD}{b\rho_B r_o^2}\right)t$	$\alpha=1-\left[1-\left(\frac{2CDt}{b\rho_B r_o^2}\right)\right]^{3/2}$
	5	$\ln(1-\alpha)=-\left(\frac{KA}{V}\right)t$	$\alpha=1-\exp\left[-\left(\frac{KAt}{V}\right)\right]$

3. MATERIAL AND METHOD

3.1. Materials

The investigation were performed with solid semiconductor waste after being preheated at 105°C to remove the water content. Table 2 shows the composition of the waste, analyzed using EDAX.

Table 2. Major elemental composition of semiconductor waste sample determined by EDAX

Element	% (w/w)
Cu	34.96
Sn	17.83
Ag	7.55
Fe	5.15
Ca	3.44

3.2. Methods

The dry sample was added into 500 ml beaker at specified L/S ratio containing 300 ml of leaching agent. The mixture was then stirred by magnetic stirring at selected stirring speed. During the stirring, 5 ml of leaching solution was withdrawn by pipettes at selected time intervals. The sampels was then separated by centrifugation at 4500 rpm for 15 minutes. The collected supernatants were then used for metal determination by using Atomic Absorption Spectrophotometer model Philips PU9200X.

4. RESULTS AND DISCUSSION

4.1. The effect off leaching agent types and concentration.

As reported by Dutrizac [5] and Kolodziej [6] in their studies, silver can be practically extracted from solid especially in the form of AgCl and Ag. The chloride medium produces more stable soluble silver than in any other medium such as sulphate. In Table 3, it is shown that HCl has the highest capability to leach silver from semiconductor waste.

Table 3. Effect of leaching agent types on silver leachability in semiconductor waste

Leaching agent types	Leached silver	
	ppm	%
4 M HCl	197	52.19
4 M HNO_3 + 4 M HCl	167	44.24
4 M HNO_3	132	34.97
4 M H_2SO_4	116	30.73

The extent of silver leaching is mainly due to the presence of Cl^- ion. Higher free chloride ion available can increase the solubility of AgCl and Ag by forming silver chloro complexes according to the following reactions :

$$Ag^+ + Cl^- \Leftrightarrow AgCl$$

$$AgCl + Cl^- \Leftrightarrow AgCl_2^-$$

$$AgCl_2^- + Cl^- \Leftrightarrow AgCl_3^{-2}$$

$$AgCl_3^- + Cl^- \Leftrightarrow AgCl_4^{-3}$$

According to Dinardo [7], the equilibrium constant of those reactions are very low. Therefore a concentrated chloride solution is required to achieve any significant silver solubility, of which the dominant form of silver chloro complexes is $AgCl_4^{-3}$. At higher Cl^- concentration, the equilibrium is forced to generate more soluble silver complexes following Le Chatelier principles.

The percentage of leached silver is still low, since the amount of free chloride ions available is limited. However, higher percentage of HCl is not preferable in industrial application due to serious corrosion problem might appear in piping. Therefore, another source of chloride, NaCl is chosen. A study of silver recovery from copper smelter flue dust [8] deduced that the minimum NaCl concentration required was 125 g/L in order to obtain a significant silver removal. The total free Cl^- ions contributed by combining HCl and NaCl is higher compared to HCl system, thus higher soluble silver chloro complexes as illustrated in Fig. 1.

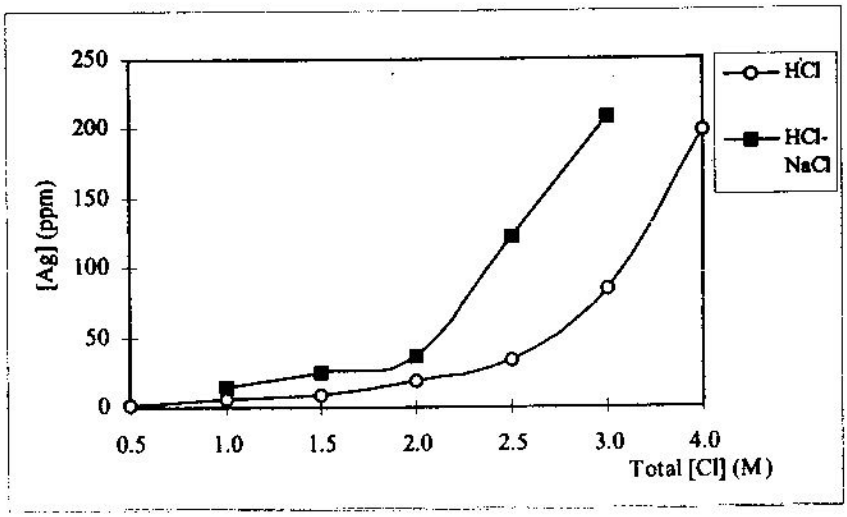

Fig. 1. Effect of total Cl^- concentration contributed by HCl and HCl-NaCl on silver leaching

This combined system will also provide a more selective process on silver as shown in Table 4.

Table 4. Comparison of silver leaching selectivity

Metal	4 M HCl	0.5 M HCl – 3 M NaCl
Ag	52.19	54.89
Cu	51.77	47.31
Fe	68.35	44.66
Sn	23.58	44.10
Ca	8.56	0.60

4.2. Effect of liquid to solid ratio (L/S).

The ratio of liquid to solid affects the degree of solution viscosity and the total surface area of the particle contact to the leaching agent [9]. A sufficient low viscosity is required for the leaching solution to circulate freely. Fig. 2 illustrates that at the constant concentration of Cl^-, the increase of silver content will reduce the rate of silver leaching due to insufficient available free Cl^- ions around solid particle.

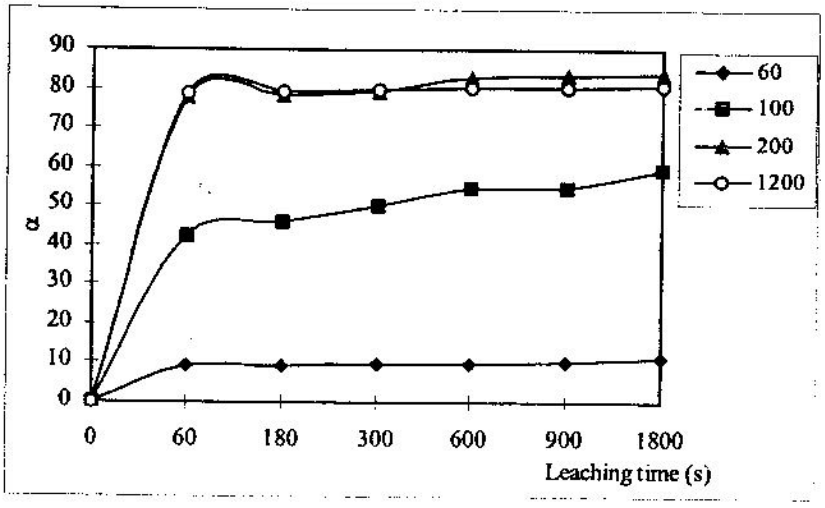

Fig. 2. Effect of L/S ratio on the extent of silver leaching.

4.3. Rate-controlling determination.

Each kinetic model is plotted as conversion against leaching time. Fig. 3. illustrates the behavior of model 1 to model 5 along with the silver leaching experiment data. It was found that the experimental data deviates greatly from model 1 and model 2, which represent chemical rate-controlled model. However, it is close to the diffusion rate-controlled model. Thus, the silver leaching kinetics under chloride medium suggested to be controlled by diffusion through liquid boundary layer rather than chemical reaction. In further evaluation, Model 5 is eliminated due to its high deviation from the experimental data.

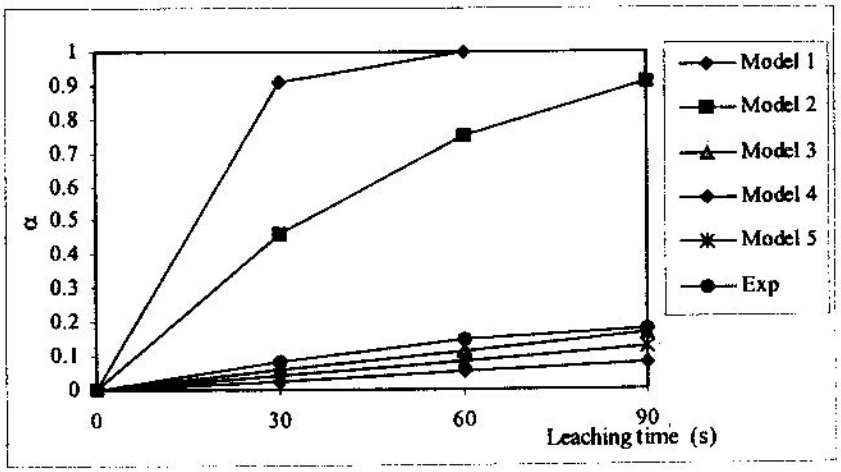

Fig. 3. A comparison of conversion at various leaching time for different models and experimental data.

4.4. Effect of stoichiometric factor.

The effect of stoichiometric factor of model 3 and model 4 during leaching process, is illustrated in Fig. 4 and 5. It is clearly indicates that model 4 is unacceptable to be the kinetic model for silver leaching process since the experimental data is only fitted between the low stoichiometric factor of 1 and 2. The correlation for model 3 is evaluated by assuming that the diffusion thickness is 1×10^{-4}m which approximate to the thickness of the unstirred condition [2]. For model 3, it was found that the silver leaching reaction is preferable with the formation of silver chloro complexes $AgCl_3^{-2}$ and $AgCl_4^{-3}$ which is in agreement with the results reported by Dinardo [7].

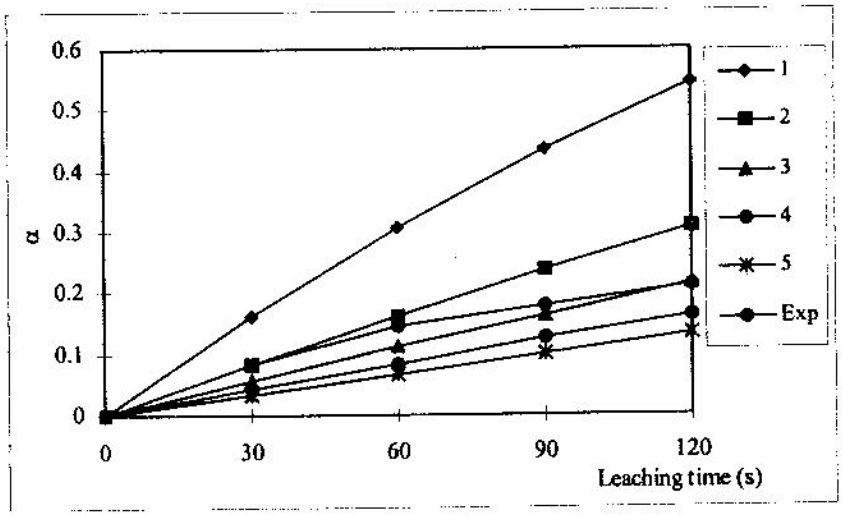

Fig. 4. Effect of stoichiometric factor on conversion at various leaching time for model 3.

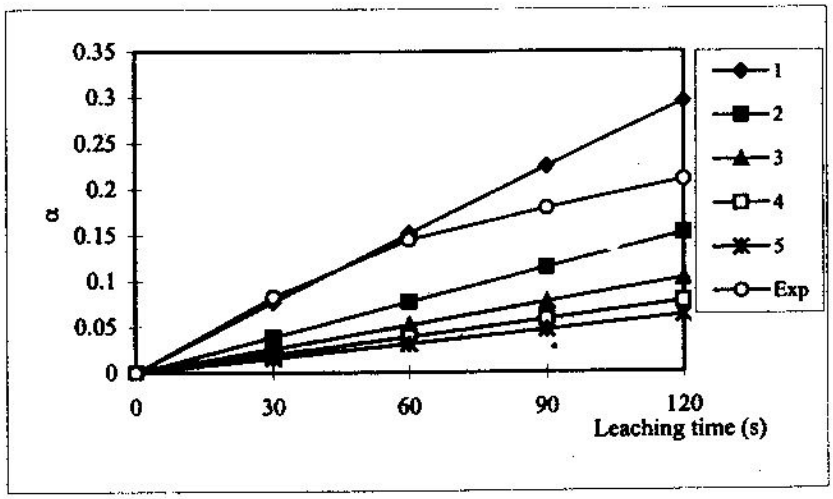

Fig. 5. Effect of stoichiometric factor on conversion at various leaching time for model 4.

4. CONCLUSION

Semiconductor waste is treated in a solution of 0.5M HCl – 3.0M NaCl with a liquid to solid ratio of 200. The low acid concentration is preferable in industrial application because it can reduce any risk of corrosion in piping system. While, the high concentration of chloride ion from NaCl is used to activate the progressive formation of soluble silver chloro complexes, $AgCl^{-(n-1)}$ from Ag and AgCl. In kinetic modeling, the shrinking core model was able to describe the silver leaching behavior and indicated that the outward diffusion of Ag(I) chloro complex through liquid boundary layer is the rate controlling step. In term of selectivity, 0.5M HCl – 3.0M NaCl of leaching system was able to perform better silver leaching than HCl alone at any leaching agent concentration.

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NOTATION

α	=	reacted fraction or conversion
V_m	=	molar volume of unreacted Ag + AgCl, m^3mol^{-1}
C	=	concentration of Cl^-, $molm^{-3}$
k_0	=	number of reactive sites per unit area, m^{-2}
k'	=	rate constant, m^3s^{-1}
r_0	=	initial radius of solid sphere, m
t	=	time, s
k_s	=	first order reaction rate constant, ms^{-1}
b	=	stoichiometric factor
ρ_B	=	molar density of Ag + AgCl in solid, $molm^{-3}$
D	=	diffusion coefficient, m^2s^{-1}
δ	=	diffusion boundary layer thickness, m
K	=	mass transfer coefficient (k_0k'), ms^{-1}
A	=	total surface area of particle, m^2

V = total volume of solution, m^3
k_i' = slope

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