INDONESIAN MINING JOURNAL Vol. 14, No. 3, October 2011 : 123 - 132

LEACHING THE LEAD FROM ANODE SLIME BY AMMONIUM ACETATE SOLUTION

ISYATUN RODLIYAH[1], NGURAH ARDHA[1], NURYADI SALEH[1] and M. ZAKI MUBAROK[2]
[1] R & D Centre for Mineral and Coal Technology
Jalan Jendral Sudirman 623 Bandung 40211
Ph. +6222-6030483, Fax. +6222-6003373
e-mail: isyatun@tekmira.esdm.go.id
[2] Metallurgical Engineering, Department of Mining and Petroleum Engineering, ITB
Jalan Ganesha 10 Bandung 40116

ABSTRACT

Selective leaching the lead from anode slime from PT. Smelting (PTS) was investigated. The presence of large amount of lead in electrometallurgical anode slime courses of extraction of precious metals (Au, Ag) and other valuable metals (Bi, Se, Te, Pt and Pd) from the slime is more difficult. A process for taking off lead content in anode slime was subjecting the latter to first and second-stage leaching in a medium of an ammonium acetate solution at temperature not exceeding 80°C. Whereby lead dissolution is maximized and other metals are minimized. The effects of various parameters such as solvent concentration, leaching time, temperature, and solid/liquid ratio on the percent extraction of lead were studied. The highest recovery of lead is attained 94.9% Pb at the leaching temperature of 70°C, solvent concentration of 8 M and percent solid 20% after 120 minutes of leaching time. The leaching kinetics of lead sulfate in an ammonium acetate solution followed the ash diffusion control model and this further confirms that the activation energy of leaching is found to be 4.8 kcal/mol, to show that rate reaction can increased by mixing.

Keywords: lead, anode slime, recovery, ammonium acetate

INTRODUCTION

Indonesia is known as the highest copper producer in Asia and the 3rd one in the world (7%) after Chili (36%) and United State (8%)[anonim,2006]. Most of copper concentrates in Indonesia is produced by PT. Freeport Indonesia and PT. Newmont Nusa Tenggara but only less than 30% of the concentrate is smelted and refined by PT. Smelting (PTS) in Gresik Indonesia. The smelter produces approximately 260,000 tons fine copper (Cu 99.99%) per annum and 1500 to 1800 tons by product (anode slime) per annum. However, the slime is processed in other countries. The valuable metals present in anode slime are Au, Ag, platinum group metals (PGMs), Pb, Cu, Se, Te, etc. Chemical composition of anode slime has been analyzed by the R & D Centre for Mineral and Coal Technology. It contains 52.58% Pb; 1.57% Au; 4.52% Ag; 8.83% Se; 4.1% Bi; 0.12% Te; 0.49% Cu; 0.17% Sn; and 1.74% As. Lead is a dominant one in the slimes as $PbSO_4$ [Azhari et al., 2010].

Previous study, reported by Hoh et al. (1982), states that the presence of large amount of lead in anode slime would lowering the recovery of precious metals and other valuable metals and increase the solvent consumed; more over silver recovery becomes more complicated. It is also interesting to study that anode slime containing lead would affect bismuth extraction, because bismuth solubility would decrease in the presence of lead sulfate.

Hydrometallurgy process of lead extraction has been studied using many acids such as chloride, nitrate, sulfate, and alkylamine followed by carbonation [Bratt, 1970; Striffler, 1980]. An alternative leaching system employs ammoniacal ammonium sulfate, which dissolves lead sulfate well and cheaper than the alkylamine solution [Habashi, 1997]. Earlier research of extraction lead has been done by Hartanto (2008) to study the possibility of extracting lead from Electrostatic Precipitator (S-EP) dust in PTS through leaching by sulfuric acid

Received : 08 July 2011, first revision : 15 August 2011, second revision : 10 October 2011, accepted : October 2011

followed by reduction of lead sulfate-rich residues using coke. The result reached was not satisfied, due to the lead content in the leach residue was attained about 32%. The low content of lead in the leach residues may be due to the high amount of elements in the dust such as Fe, As, Sb, Se, Ni, Zn. Furthermore, the study had been done by Zulkarnain (2009), to extract lead from (S-EP) dust of PTS through hydrometallurgy route by ammonium acetate solution (CH_3COONH_4) under atmospheric pressure. The results showed that 95% lead could be extracted from the two-stage leaching. Several researches investigated that anode slimes could be leached on solvent-based ammonium solution [Hoh et al., 1982].

This paper discusses of lead extraction from anode slimes using ammonium acetate solution through two-stage leaching. In this process, second-stage leaching had accomplished because at first-stage leaching after a certain time interval tends to form passive layer in solid surface and causes lead in slime difficult to dissolve. In this case it is necessary to add fresh ammonium acetate solution to break the layer. The dissolution reaction of lead can be expressed as follows:

$$PbSO_4 \text{ (solid)} + 2\ CH_3COONH_4 \text{ (liquid)} = Pb(CH_3COO)_2 \text{ (liquid)} + (NH_4)_2SO_4 \text{ (liquid)} \ldots\ldots (1)$$

METHODOLOGY

The anode slime sample was obtained from copper electrorefining process of PTS. At first, 800 g slime was dried at 120°C for 2 hours, then ground to -150 mesh using a laboratory-scale ballmill. The slime was the dissolved in ammonium acetate solution and filtered. The residue was leached by fresh ammonium acetate solution and filtered. Chemical analysis for both leach solutions and residues were employed using Atomic Absorption Spectrophotometer (AAS) to show the leachable lead. Flow diagram of lead extraction process is shown in Figure 1. Percent extraction (recovery) of lead is calculated as follow:

$$\%\text{ extraction of Pb} = \frac{\text{leached Pb content (g)}}{\text{Initial weight of Pb (g)}} \times 100\ \%$$

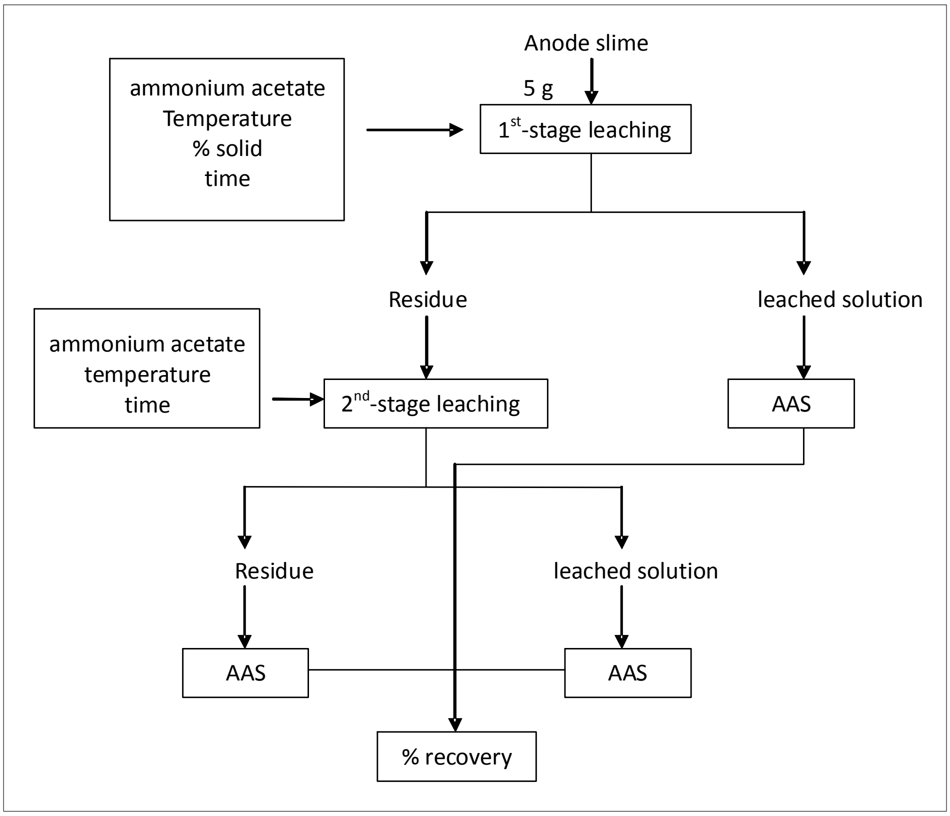

Figure 1. Flow diagram of lead extraction process

The first-stage leaching performs ammonium acetate concentrations of 2, 3, 5, 7, 8, and 10 M, leaching temperature 30, 40, 50, 70, and 80°C and solid to pulp ratio of 5, 10, 20, 25 and 30% by weight. The second-stage leaching retains ammonium acetate concentrations of 5, 7, and 8 M and leaching temperature of 50, 70, and 80°C. Physical parameter set in this research was stirring speed 100 rpm. The process variables studied in leaching of lead can be shown in Table 1.

Table 1. The process variables in lead leaching

First-stage lead leaching

Variables	Time (minute)	Conditions tested	Constant conditions		
[CH_3COONH_4]	15 30 45 60 90 120 150 180	2 M 3 M 5 M 7 M 8 M 10 M	temperature 40°C	%solid 20%	Stirring speed 100 rpm
temperature	15 30 45 60 90 120	30°C 50°C 70°C 80°C	Concentration CH_3COONH_4 8 M	%solid 20%	Stirring speed 100 rpm
% solid	120	5% 10% 25% 30%	consentration CH_3COONH_4 8 M	temperature 70°C	Stirring speed 100 rpm

Second-stage lead leaching

Variables	Conditions tested	Constant conditions			
[CH_3COONH_4]	5 M 7 M 8 M	temperature 40°C	Stirring speed 100 rpm	Leaching time 120 minutes	%solid 20%
temperature	50°C 70°C 80°C	CH_3COONH_4 8 M	Stirring speed 100 rpm	Leaching time 120 minutes	%solid 20%

An attempt was made to study the dissolution kinetics of Pb in the leaching of anode slime with ammonium acetate solution using the shrinking core model. This is the most widespread model describing fluid-solid reacton kinetics of dense particles. The standard equations for dense constant-size spherical particles of this model are :

$t \infty x$ (i) film diffusion control

$t \quad 1 - 3 (1 - x)^{2/3} + 2(1 - x)$. (i) ash diffusion control

$t \quad 1 - (1 - x)^{1/3}$. (i) chemical reaction control

x in the above equations is the fraction of metals extracted at time t.

Reaction can only take place if the value of activation energy of the reaction is accomplished. The value of activation energy is in accordance with the Arrhenius equation, namely:

$k_g = A_g \exp^{-Ea/RT}$ or $\ln k_g = \ln A_g - (Ea/RT)$, for film diffusion control

$D_{eff} = D_o \exp^{-Ea/RT}$ or $\ln D_{eff} = \ln D_o - (Ea/RT)$, for ash diffusion control

$K'' = A_s \exp^{-Ea/RT}$ or $\ln k'' = \ln A_s - (Ea/RT)$, for chemical reaction control

RESULTS AND DISCUSSION

A representative sample was analyzed for chemical composition using X-Ray Fluoroscence (XRF). It contained 52.58% Pb; 1.57% Au; 4.52% Ag; 8.83% Se; 4.1% Bi; 0.12% Te; 0.49% Cu; 0.17% Sn; and 1.74% As . Results of chemical analysis are shown in Table 2.

Table 2. Chemical composition of anode slimes from PT. Smelting (PTS)

No.	Element	grade (%)
1	Gold (Au)	1.57
2	Silver (Ag)	4.52
3	Selenium (Se)	8.83
4	Lead (Pb)	52.58
5	Copper (Cu)	0.49
6	Tellerium (Te)	0.12
7	Bismuth (Bi)	4.1
8	Arsen (As)	1.74
9	Tin (Sn)	0.17
10	Antimony (Sb)	0.12
11	Nickel (Ni)	0.02
12	Fe_2O_3	0.01
13	Al_2O_3	0.15
14	SiO_2	0.45
15	SO_3	14.43
16	Cl	1.42
Total		**94.78**

According to Habashi (1993), there are several factors that could affect leaching process. Those are concentration of solvent, temperature, leaching time, particle size, and percent solid. In this experiment, particle size was not tested because the sizes at the slime have dominant size of -150 mesh about 59%. Figure 2 showed that percent extraction of lead would decline after 120-minute leaching time. Therefore, the subsequent experiments of leaching time was set up firmly to 120 minutes.

Figure 2 reveals that lead sulfate dissolves in concentrated ammonium acetate solution. It was firmly characterized by percent lead extraction which increased rapidly from 20% lead extracted for concentration 7 M up to 37% for concentration 8 M. Reaction rate increases with concentration as described by the rate law and explained by collision theory [Levenspiel, 1999]. The reaction rate (r) of the lead extraction according to the reaction (1) and equation (1a):

$$PbSO_4 \text{ (solid)} + 2\ CH_3COONH_4 \text{ (liquid)} = Pb(CH_3COO)_2 \text{ (liquid)} + (NH_4)_2SO_4 \text{ (liquid)} \quad \text{.......................................(1)}$$

$$r = -\frac{d[PbSO_4]}{dt} = -(1/2)\frac{d[CH_3COONH_4]}{dt} = \frac{d[Pb(CH_3COO)_2]}{dt} = \frac{d\,[(NH_4)_2SO_4]}{dt} \quad (1a)$$

In the solid-liquid reaction that occur during leaching, 4 stages could control rate reaction if the liquid is stirred to eliminate concentration gradients in the bulk solution. Those are:

- diffusion of the lixiviant through the liquid phase boundary film to the surface of particle;
- diffusion of the reactants and the product within the solid;
- chemical reaction at the unreacted solid interface;
- diffusion of the reaction product through the liquid phase boundary film into the bulk solution.

It is also shows that the highest percent extraction of lead is obtained at concentration of ammonium acetate 8 M. When the concentration was increased up to 10 M, lead extracted tends to decrease significantly. In this condition, the solution has probably been saturated. As a result the solution is no longer dissolve lead sulfate. According to Hoh et al. (1982), lead sulfate can only be dissolved in rather concentrated ammonium acetate solution (±10 M). Zulkarnain (2009), used the optimum concentration of ammonium acetate 3 M. This was caused by Pb content in S-EP dust about 16%, whereas in the present experiment Pb content is about 52%.

After setting the optimum concentration of ammonium acetate to 8 M at the first-stage leaching, effect of temperature on lead percent extraction was then studied. Result is shown in Figure 3. The figure confirms that the lead percent extraction increases from 30% Pb at 50°C up to 42% Pb at 70°C. In this experiments, the highest percent

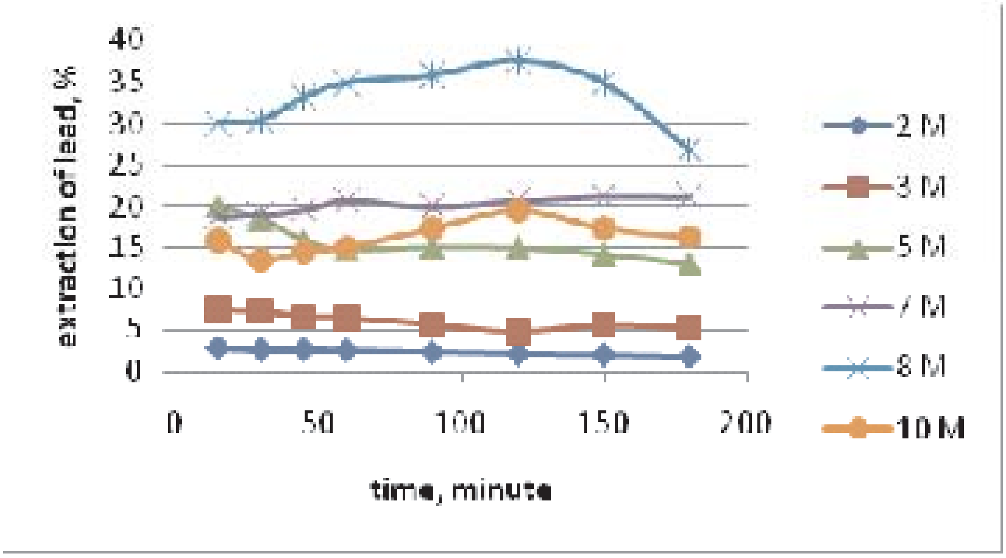

Figure 2. Effect of concentration of ammonium acetate on lead extraction in first-stage leaching

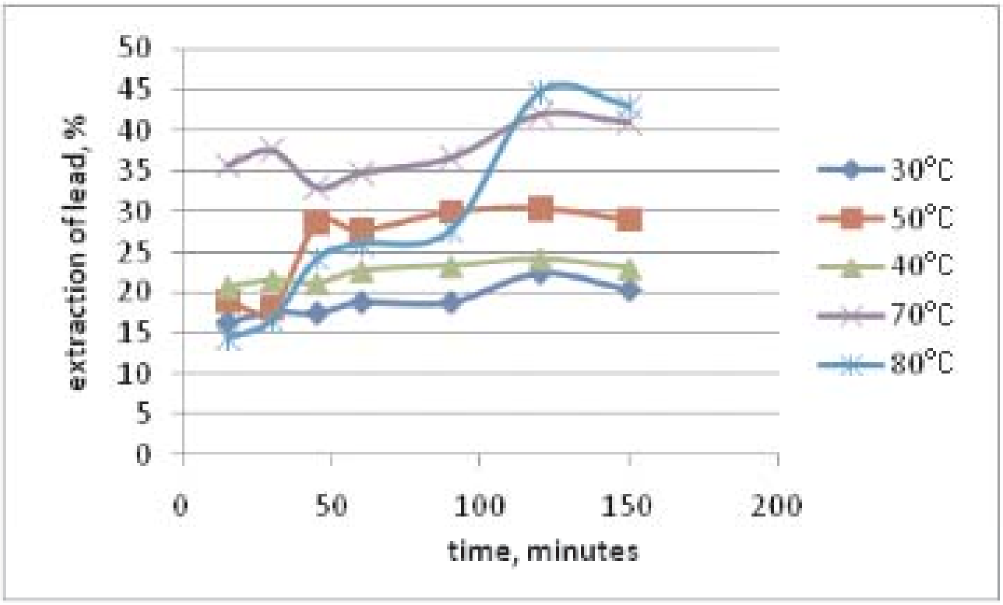

Figure 3. Effect of temperature on lead extraction in first-stage leaching

extraction is attained at 80°C namely 44%, however, due to the difference is in significant with percent extraction at 70°C (i.e, 42%), the next experiments is firmly set at 70°C.

Most solvent has limited solubility on a number of specific solvent and specific temperature [Habashi, 1997]. It can be seen from the experiments results that raising percent extraction at 80°C is in significant (only 2%).

After getting the optimum temperature (70°C) in first-stage leaching, next experiment was studying the effect of percent solid on lead percent extraction. The result is presented in the Figure 4. It can be seen that the highest percent extraction can be obtained if using lowest percent solid. However, decreasing percent solid also increasing solvent consumption. In this case, decreasing percent solid would increase concentration ratio of solvent on anode slime by dry weight. The lower percent solid then more increase the concentration but the higher the solvent concentration, the faster the reaction. Higher concentration increases the number of molecules will that in turn lies tightly. The molecules are then more easy to collide. It causes higher rate reaction and higher lead percent extraction as well. In the present experiment, measured percent solid is 20%, because it produces the high percent extraction of lead and it is not too solvent consuming.

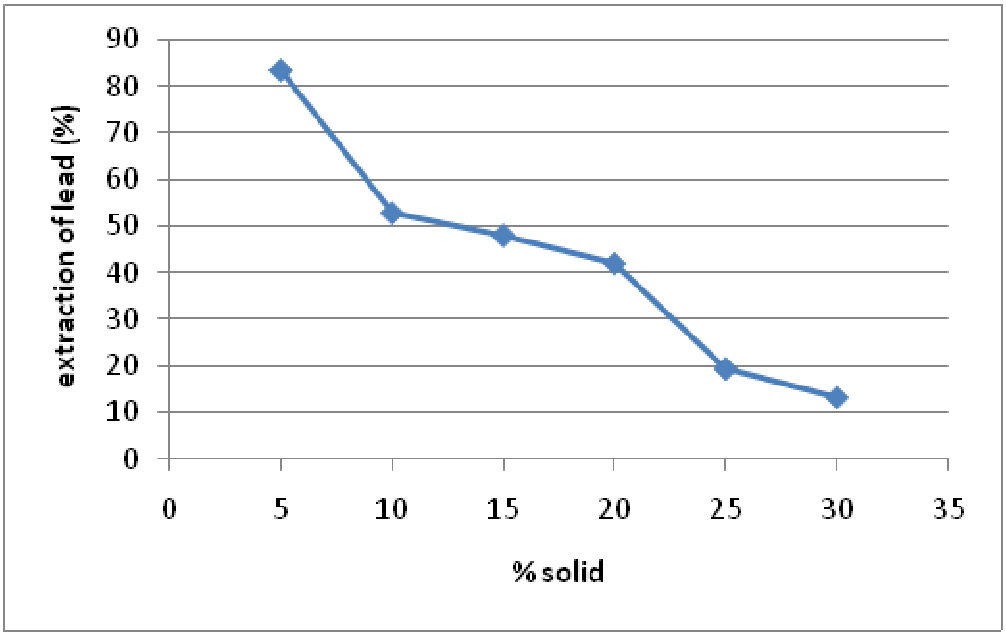

Figure 4. Effect of percent solid on lead extraction in first-stage leaching

The first-stage leaching of lead have been carried out especially for the parameters of solvent concentration, leaching temperature, and percent solid then obtained the highest percent extraction of lead 42%, which was reached for 8 M, at temperature 70°C, and percent solid 20%. Furthermore, the residue from the first-stage leaching will further be leached for the second-stage by studying the effects of such concentration of ammonium acetate and leaching temperature. The second-stage leaching experiment results can be seen in Figure 5.

It can be seen from Figure 5 that the highest lead percent extraction of 86% is reached at solvent concentration of 8 M. It reveals from both first-stage and second-stage leachings are that solvent concentration of 8 M is the optimum condition. After getting the optimum concentration, the next experiment was studying the effect of temperature on second-stage leaching. The results can be seen in Figure 6. The figure shows that the highest lead percent extraction was reached at 70°C. It is similar to that of first-stage leaching where the highest percent extraction was also reached at 70°C.

Lead obtained from leached solution can be recovered by crystallization. The crystallized lead acetate from solution is heated by distillation until the total volume is reduced to one-third of initial volume then cooled down. Meantime, lead acetate is crystallized out from its stock solution. After filtration and drying, lead acetate with the purity greater than 99.9% is obtained [Hoh et al., 1982]. The resultant clarified solution can be recycled to be re-used to the leaching step.

From the experimental results (Figure 3) in comparison with shrinking core model, the kinetics of Pb (Figure 7), it was found that the data could best fitted according to the ash diffusion control model, i.e., $1 – 3(1-x)^{2/3} + 2(1-x)$ “ t.

During the leaching process, insoluble gangue metals (Au, Ag, Se, Pt, Pd) was formed and this product layer might have contributed to ash diffusion reaction of Pb. It means that the lowest stage

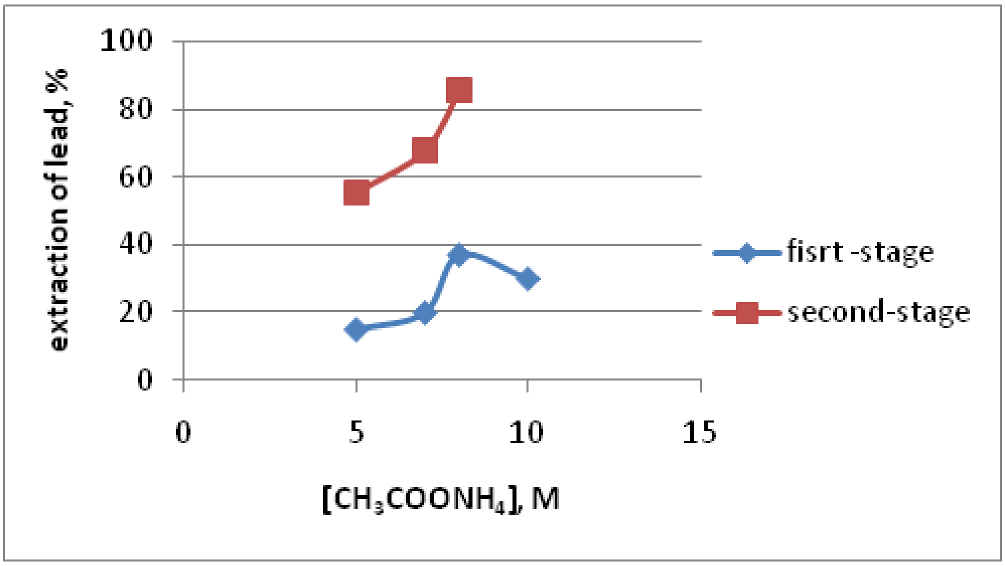

Figure 5. Effect of concentration of ammonium acetate on extraction of lead in first and second-stage leaching after 120-minute leaching

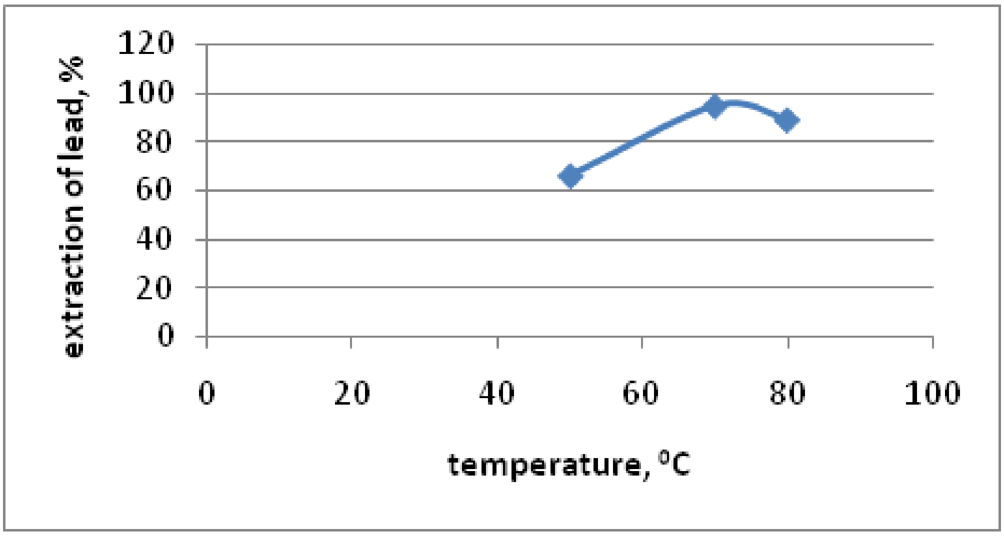

Figure 6. Effect of temperature on lead extraction in second-stage leaching after 120-minute leaching

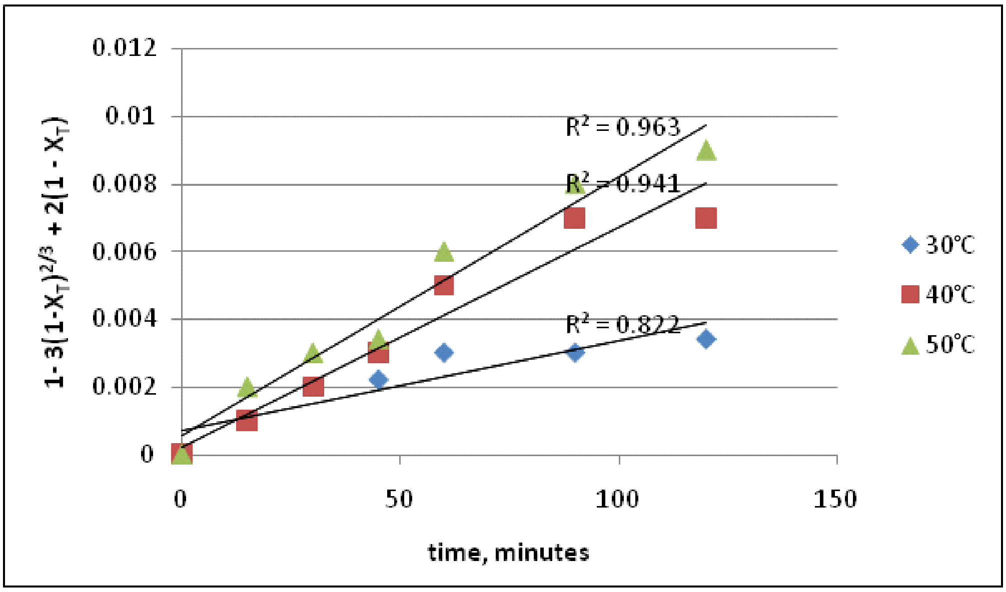

Figure 7. Leaching kinetics Pb with ammonium acetate solution

of leaching lead sulfate is ash diffusion stage. To raise rate reaction of lead leaching can be conducted by mixing process.

Calculation of activation energy for ash diffusion control model is as follows:

$$\ln D_{eff} = -\frac{Ea}{RT} + \ln D_o$$

Where

$$D_{eff} = \frac{m\rho_R R^2}{12\ C_{NH4-Ac}}$$

Where D_{eff} is the diffusion coefficient, ρ is the particle density, R is the radius particle, C is concentration of ammonium acetate and m is gradient from graphic of $1 - 3(1-x)^{2/3} + 2(1-x)$ on time at various temperatures. The values of ln D_{eff} were plotted against 1/T (Arrhenius plot) in Figure 8.

The activation energy of reaction was calculated. The results is about 4.8 kkal. The activation energy value of diffusion controlled process is generally <5kkal [Habashi, 1993]. Therefore, this further confirms that the leaching of Pb using ammonium acetate solution are followed by ash diffusion control reaction kinetics.

From the experiments of two-stages leaching of lead by ammonium acetate was reached lead recovery of 94.9%. Ammonium acetate is needed to leach of lead sulfate can be calculated is shown as Table 3.

Table 3. Total ammonium acetate is needed and lead acetate is produced per year

Wet anode slime	2000 tpa (ton per annum)
Dry anode slime	1800 tpa
Lead sulfate in anode slime (grade 52.58%)	954 tpa
Total Ammonium acetate (p.a)	241 tpa
Total Ammonium acetate (32% by weight)	753.125 tpa
Lead acetate (product)	951.6 tpa

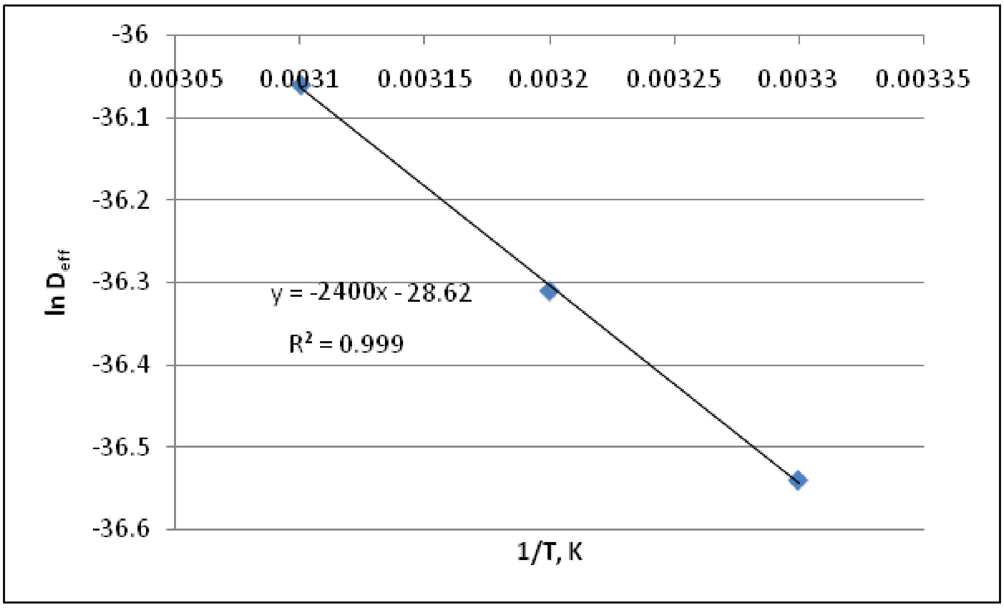

Figure 8. Leaching kinetics for Pb

CONCLUSIONS

It can be concluded that:

1. Lead sulfate may dissolve in ammonium acetate concentration at 5-8 M. Leaching in second-stage processes is necessary to produce higher lead extraction. Temperature, solvent concentration, percent solid and leaching time considerably affects percent extraction.
2. The optimum percent extraction which reached 94.9% is achieved in second-stage leaching for solvent concentration of 8 M, at temperature 70°C, percent solid 20% and after 120 minutes leaching time.
3. Reaction kinetic for Pb at 70°C follows the ash diffusion control model. This was further confirmed by the activation energy value of reaction about 4.8 kcal/mol.

REFERENCES

Anonim, 2006. Merukh Bangun Dua Smelter US$ 10 M. http://www.ima-api.com. Access in February 19th, 2011 at 14.00.

Azhari, Saleh, N., Pramusanto, and Dahlan, Y., 2010. Intern Report Ekstraksi logam berharga dari lumpur anoda (*anode slime*) produk samping pemurnian tembaga*. Laporan Teknik Penelitian Pengolahan Mineral*, Puslitbang Teknologi Mineral dan Batubara (Tekmira).

Bratt and Pickering. 1970. Production of lead via ammoniacal ammonium sulfate leaching. *Metallurgical Transaction,* Vol.1, pages 2141.

Habashi, F., 1997. *Handbook of Extractive Metallurgy Vol. II*. Gordon and Breach Science Pub. Inc, New York.

Habashi, F., 1993. *A Textbook of Hidrometallurgy*. Metallurgie Extractive Quebec, Enr., Kanada.

Handogo, B., and Situmorang, T. B., 2008. PT. Smelting, Production Performance and Plant Expansion Milestone*. Indonesian Process Metallurgy*. ITB, Bandung.

Hartanto, T. 2008. Studi pendahuluan recovery timbal dari debu S-ESP furnace PT. Smelting Gresik melalui proses pelindian dan reduksi residu pelindian dengan menggunakan kokas*. Tesis Teknik Metalurgi, Fakultas Teknik Pertambangan dan Perminyakan*. ITB, Bandung.

Hoh, Chuang, Lee, Ma, Tieh; Wang, Wei-ko, 1982. *Treatment of copper refinery anode slime*. United State Patent. 4352786.

Levenspiel, O. 1999. *Chemical Reaction Engineering. 3th edition.* John Wiley & Sons. New York.

Striffler; Windson; Kolakowski. 1980. *Production of lead monoxide from leas sulfate with acidic ammonium acetate*. United States Patent. 4,220,628.

Zulkarnain, A., 2009. Studi pendahuluan pelindian timbal dari debu ESP S-Furnace PT. Smelting Gresik dalam larutan amonium asetat*. Tesis Teknik Metalurgi, Fakultas Teknik Pertambangan dan Perminyakan*. ITB, Bandung.