International Journal of Technology (2017) 1: 19-26
ISSN 2086-9614

A MODIFIED SHRINKING CORE MODEL FOR LEACHING OF ALUMINUM FROM SLUDGE SOLID WASTE OF DRINKING WATER TREATMENT

Agus Mirwan[1], Susianto[1], Ali Altway[1], Renanto Handogo[1*]

[1]*Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia*

(Received: February 2016 / Revised: October 2016 / Accepted: January 2017)

ABSTRACT

The kinetics of aluminum leaching from sludge solid waste (SSW) using hydrochloric acid at different leaching temperatures (30–90°C) was studied. A mathematical model was developed based on a shrinking core model by assuming first-order kinetics mechanisms for leaching and an equilibrium linear at the solid-liquid interface. The proposed model is suited to fit experimental data with three fitting parameters and to simulate the leaching of aluminum from SSW, which was validated with the mass transfer coefficient (k_c, cm/s), diffusion coefficient (D_e, cm^2/s), and reaction rate constants (k, cm/s). The evaluated k_c, D_e, and k are expected to follow an increasing trend with increasing temperature. The correlation coefficient ≥ 0.9795, the root mean square error ≤ 0.399, the mean relative deviation modulus $\leq 6.415\%$, and the value of activation energy is 13.27 $kJmol^{-1}$. The proposed model could describe the kinetics of aluminum leaching from the SSW DWT in accordance with test parameters and relevant statistical criteria. Valuable information on the results of this work can be given for the purposes of the simulation, optimization, scaling-up, and design of the leaching process.

Keywords: Aluminum; Leaching; Recovery; Shrinking core model; Sludge solid waste

1. INTRODUCTION

Sludge solid waste of drinking water treatment (SSW DWT) is the waste by-product of the drinking water treatment processes produced daily and largely produced during clarification (e.g., coagulation-flocculation and solid-liquid separation with sedimentation process) while removing colloidal impurities from raw water (Nair & Ahammed, 2015; Zhou et al., 2015). It is a fundamental process that uses a large amount of general aluminum salt coagulants, such as commercial aluminum sulfate and polyaluminum chloride (Nair & Ahammed, 2015). A large amount of the coagulant used in DWT is proportional to the amount produced in SSW. Regarding the global production of SSW, approximately 10,000 tons are produced per day, of which European countries, such as Ireland, Germany, the Netherlands, the United Kingdom (UK), and Portugal, take up 10.38%, the United States 72.6%, and China and Taiwan 0.003% (Babatunde & Zhao, 2007). In Indonesia, especially Banjarmasin, South Kalimantan, more than 6.91×10^6 tons (70 wt.%) of SSW is produced every year. At present, the majority of SSW is still disposed in landfills, in sanitary sewers, and by land applications, such as land treatment facility and waste pile, assuming that the SSW is not poisonous (Babatunde & Zhao, 2007). Given the high demand for a high quantity of and high-quality drinking water, coupled with the increasing generation of SSW and environmental restrictions on their disposal up until recently,

---

*Corresponding author's email: renanto@chem-eng.its.ac.id, Tel. +6231-5946240, Fax. +6231-5999282

Permalink/DOI: https://doi.org/10.14716/ijtech.v8i1.3233

various studies have been done in search of options for reusing coagulants (Zhou et al., 2015). The reduction and re-use of SSW have been considered and have provided varying achievement levels.

The main constituents of SSW-DWT are SiO_2 and Al_2O_3; however, during the addition of aluminum salt in the water treatment process, aluminum hydroxide [$Al(OH_3)$] precipitates have formed (Cheng et al., 2012; Nair & Ahammed, 2015). Aluminum extraction from SSW is performed mainly by hydrometallurgical methods, in which SSW is first leached by a hydrochloric acid solvent. During the leaching process, soluble aluminum hydroxides can form and stay in the solution. In the separation process, precipitates of aluminum hydroxides are transferred to the leaching filter cake.

Based on differential mass-balance, mass-transfer, and equilibrium relationships, a mathematical model has been proposed. The shrinking core (SC) model describes how irreversible desorption is followed by the diffusion process through pores inside a porous solid (Goto et al., 1996), which reacts with a solvent to leave a reacted layer around the unreacted core. This model assumes that a solute is extracted around a shrinking core. The SC model has been widely used in hydrometallurgy for the leaching process to obtain metal or any other material that is valuable (Safari et al., 2009; Baba & Adekola, 2012; Cheng et al., 2012). It has been successfully applied to the leaching of zinc from a zinc ore containing silica (Safari et al., 2009), to the study of the dissolution kinetics of a Nigerian galena ore (Baba & Adekola, 2012), and to the study of aluminum leaching from sludge (Cheng et al., 2012). Some studies have described that the leaching process is dominated by three of the rate-controlling step mechanisms, i.e., diffusion through a liquid film surrounding a particle, diffusion through a product layer, and a surface chemical reaction at the unreacted core (Levenspiel, 1998; Baba & Adekola, 2012; Cheng et al., 2012). Most of them concentrate on the determination of rate-controlling steps using three reaction mechanisms with the entire leaching process time for removing and recovering metals from different materials. In the development of the leaching process, the leaching kinetics of aluminum from SSW is necessary for process optimization and reactor design. Despite many studies' using different methods for removing and recovering metals from sludge, however, an appropriate model for aluminum leaching kinetics is not available.

The objective of this study was to determine the influence of different temperatures from 30 to 90°C on the aluminum leaching rate from SSW. We also aimed to develop a mathematical model based on the SC model used in supercritical fluid extraction and based on the enforceability of the proposed model for aluminum leaching kinetics with temperature dependence, where the mass transfer coefficient, reaction rate constant, and diffusion coefficients were used as fitting parameters.

2. EXPERIMENTAL METHOD

2.1. Material

SSW was collected from the sludge ponds of DWT Banjarmasin, Indonesia; washed and dried under direct sunlight for 24 hours; and then oven-dried at 105°C for 3 hours. It was milled in a grinder and then sieved to select particles that were 0.074–0.044 mm in width, with a particle size of 0.0585 mm, before the leaching process was carried out.

2.2. Leaching Procedure

About 5 g (measured exactly) of grinded and classified SSW was extracted with 250 ml of 4 M hydrochloric acid (HCl) (prepared from Sigma-Aldrich with a purity of ≥ 32%) in an Iwaki Pyrex boiling flask. The flask had one neck for a thermometer and for the inlet or withdrawal of samples at regular time intervals (3–60 minutes). The reaction mixture was stirred at 300 r.min−1 using a magnetic stirrer and was heated (Dragon Lab, MS-H-Pro, People's Republic of China) indirectly through a water bath at different temperatures (30, 50, 70, and 90ºC). At selected time intervals (5, 10, 20, 30, 40, 50, and 60 minutes), all samples were collected using a syringe and filtered for analysis to determine the aluminum content in the solution using an inductively coupled plasma cluster optical emission spectrometer (ICP-OES) (9060-D Teledyne Leeman Labs. the USA). Each analysis was repeated three times and deputized with average values.

The total amount of aluminum can be leached out in the acid condition and calculated based on standard methods (Cheng et al., 2012). SSW was added in nitric acid with a ratio of 1:1 and filtered. The filtrate was analyzed using ICP-OES to determine the amount of soluble aluminum. The result indicated that approximately 61.8 mg of aluminum ions can leach from 1 g of WTS, and the aluminum leaching recovery (x) can be stated as $x = (X/X_0) \times 100$, where X_0 denotes the total aluminum obtained through the acid leaching process, and X is the amount of aluminum obtained at different conditions (mg/g).

2.3. Model Development

According to Cheng et al. (2012), a lower pH between 1 and 3 in aluminum dissolution can be obtained with a higher aluminum recovery ratio of approximately 70–90%. Furthermore, at normal temperatures, Al_2O_3 cannot react with acid so that the solid-phase amorphous aluminum hydroxide contained in sludge can be leached out by the acidification process. Chemical reactions that occur in SSW and hydrochloric acid are stated as follows:

$$Al(OH)_3\ (s) + 3HCl\ (aq) \rightarrow AlCl_3\ (aq) + 3H_2O \qquad (1)$$

Aluminum ions were formed by appending acid ions to dissolve aluminum hydroxide from SSW. By a dispersion mechanism, aluminum ions can be dissolved and leached out from SSW (Cheng et al., 2012). The hydrochloric acid ions were first diffused through the film surrounding the SSW particles to the surface of the solid. The acid ions continued to penetrate and to diffuse through the blanket of a product layer to the surface of the unreacted core and reacted with the aluminum precipitates. Ultimately, the aluminum ions were diffused out of the SSW particles to the surrounding fluid. The common SC model in the leaching process is illustrated in Figure 1.

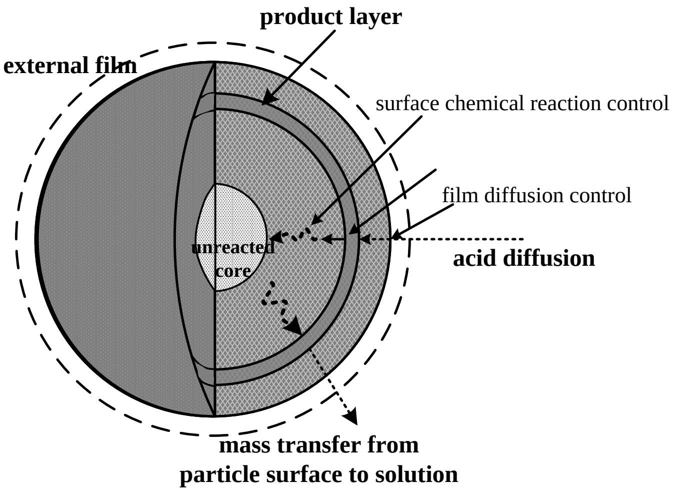

Figure 1 Schematic drawing of the SC model

2.4. Mathematical Modeling of Leaching Kinetics

SC model assumptions are as follows: SSW has spherical particles; the particles are completely mixed so that their spherical shape can be maintained; the temperature is fixed during the leaching process; other substances in the SSW do not have a significant effect on the kinetics (Safari et al., 2009).

The total mass balance equation for leaching is as follows:

$$\frac{dC_{AL}}{dt}=\frac{k_c}{R}\frac{(1-\varepsilon_L)}{\varepsilon_L}(C_{A(R)}-C_{AL}) \tag{2}$$

Variations in time from the solid phase (aluminum concentration in a particle of SSW) are related to the mass transfer rate of solute as follows:

$$\frac{d\overline{q}}{dt}=\frac{4\pi R^2 k_c \rho_s}{b\times solids\ mass}(C_{A(R)}-C_{AL}) \tag{3}$$

The diffusion in the outer particle is given by

$$-\frac{d}{dr}\left(-D_e 4\pi r^2 \frac{dC_{A(R)}}{dr}\right)=0 \tag{4}$$

The average value of the solute concentration as follows

$$\frac{\overline{q}}{q_0}=\left(\frac{r_c}{R}\right)^3 \tag{5}$$

Boundary conditions and initial conditions are given as follows:

$$r=r_c \rightarrow D_e\frac{dC_{A(R)}}{dr}=kC_{A(R)} \tag{6}$$

$$-D_e\frac{dC_{A(R)}}{dr}=k_c(C_{A(R)}-C_{AL}) \tag{7}$$

$$r_c=R \text{ and } \overline{q}=q_0 \text{ at } t=0 \tag{8}$$

The model parameters, k_c, k, and D_e, can be obtained from fitting the experimental data to Equations 6 to 8. Through the integration of Equation 4, the following is obtained:

$$C_{A(R)}=-\frac{k_1}{r}+k_2 \tag{9}$$

By the substitution of Equation 6 to Equation 9, the following is obtained:

$$k_1=\frac{kk_2r_c^2}{(D_e+kr_c)} \tag{10}$$

The mass of solute of the aluminum leaching recovery is calculated by combining Equations 7, 9, and 10. Furthermore, solving Equation 9 to find k_1 and k_2 would result in obtaining $C_{A(R)}$. Before that, Equation 11 is substituted into Equation 10.

$$k_2 = \frac{k_c C_{AL}(D_e + kr_c)R^2}{D_e(kr_c^2 + R^2 k_c) + k_c k(r_c R^2 - r_c^2 R)} \tag{11}$$

$$C_{A(R)} = -\frac{kk_c C_{AL} R^2 r_c^2}{D_e(kr_c^2 + R^2 k_c) + k_c k(r_c R^2 - r_c^2 R)r} + \frac{k_c C_{AL}(D_e + kr_c)R^2}{D_e(kr_c^2 + R^2 k_c) + k_c k(r_c R^2 - r_c^2 R)} \tag{12}$$

2.4.1. Statistical analysis

According to Bucić-Kojić et al. (2013), the proposed model parameters determined by three statistical criteria, namely c_{coef}, *RMSE*, and *E*, were calculated by the following:

$$c_{coef} = \sqrt{1 - \frac{\sum_{i=1}^{N}\left(C_{pred,i} - C_{\exp,i}\right)^2}{\sum_{i=1}^{N}\left(C_{\exp,i} - C_{\exp,\mathrm{sr}}\right)^2}} \tag{13}$$

$$RMSE = \sqrt{\frac{1}{N}\cdot\sum_{i=1}^{N}\left(C_{pred,i} - C_{\exp,i}\right)^2} \tag{14}$$

$$E = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{C_{\exp,i} - C_{pred,i}}{C_{\exp,i}}\right| \tag{15}$$

The suitability of the data and models was good when $RMSE \rightarrow 0$, $c_{coef} \rightarrow 1$, and $E < 10\%$ (Bucić-Kojić et al., 2013).

3. RESULTS AND DISCUSSION

The model parameters were adjusted to the aluminum content in untreated leaching (q_0 = 61.8 mg of aluminum ions for all investigated temperatures). The particle radius *R* was fixed at 0.0295 cm (262.5 mesh), the solid-to-solvent ratio was 0.02 g/mL, and the values of k, k_c, and D_e are listed in Table 1 together with the results of the statistical analysis. k, k_c, and D_e were evaluated by minimizing the *RMSE* criteria, which were expected to follow an increasing trend as the temperature increased (Bucić-Kojić et al., 2013), causing a mass transfer from the solid to the solvent. According to Geankoplis (1993), the diffusion coefficients of solid are 10^{-30}–10^{-4} m^2/s.

Figure 2 shows that the aluminum leaching recovery increased with increasing temperature as a function of time. Equation 12 was adapted to the experiment data by minimizing the difference of *RMSE*. The shape of the curve obtained from the calculation model followed the curve of the leaching experiment data. Based on Figure 2 and Table 1, this model is appropriate for estimating the leaching kinetics of aluminum from SSW, as confirmed by $c_{coef} \geq 0.995$, $RMSE \leq 0.399$ mg/g, and *E* value lower than 6.415% for all temperatures.

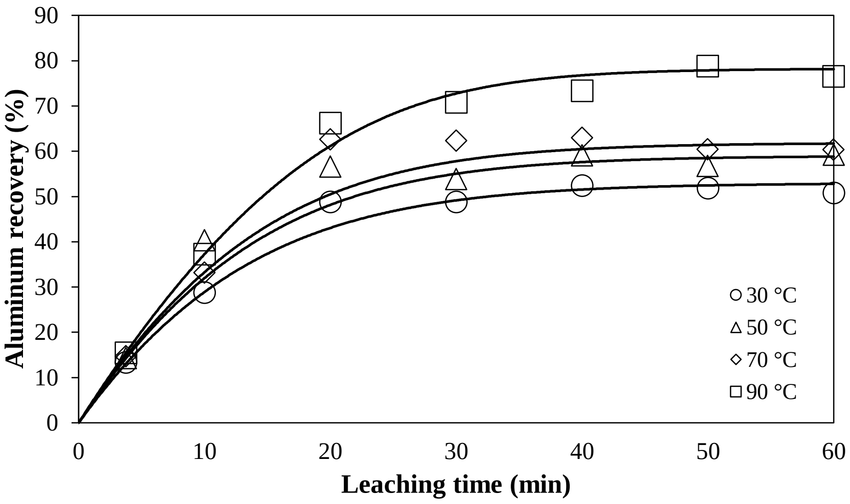

Figure 2 Aluminum leaching recovery from experimental data and model curves according to Equation 12

Table 1 Fitting model parameters (k, k_c and D_e) and statical criteria (c_{coef}, $RMSE$, E) at different leaching temperatures (T)

T (°C)	30	50	70	90
k (cm/s)	10.50	16.40	20.60	25.40
k_c (cm/s)	0.0041	0.0045	0.0047	0.0049
$D_e.10^{-5}$ (cm^2/s)	6.80	8.50	9.35	9.85
c_{coef}	0.999	0.995	0.997	0.999
$RMSE$	0.399	0.394	0.368	0.384
E (%)	2.793	6.415	4.975	2.865

The relationship among the mass transfer coefficient, the reaction rate constants, the diffusion coefficient, and the leaching temperature was characterized by the activation energy from the Arrhenius equation (Bucić-Kojić et al., 2013).

$$k = Ae^{-E_a/RT} \tag{16}$$

In the form of a logarithm, it becomes Equation 17:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{17}$$

where A is the pre-exponential factor, E_a is the activation energy (J/mol), R is the global gas constant (8.314 J/K mol), and T is the absolute temperature (K). The activation energy was calculated from Figure 3. The k value is inversely proportional to the temperature (Levenspiel, 1998). Figure 3 shows that the graph slope and intercept obtained were 1.5967 and 7.6666, respectively, using the data presented in Table 1. The activation energy can be obtained by multiplying the slope value by a global gas constant, and the result is 13.27 kJ/mol.

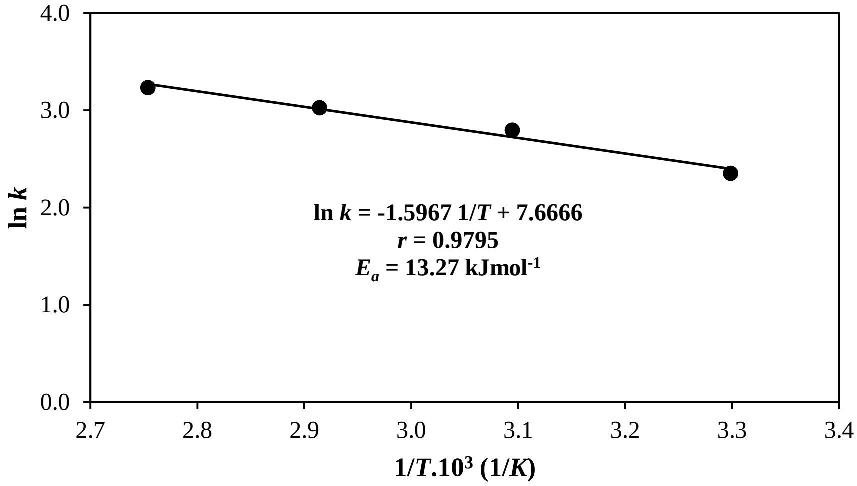

Figure 3 Arrhenius plot: *k* is the reaction rate constant, cm/s, and *T* is the absolute leaching temperature, K

4. CONCLUSION

The temperature had an influence on the leaching of aluminum recovery. The maximum recovery of aluminum after 50 minutes of agitated leaching at 90ºC was 78.8%. The reaction rate constants and the mass transfer coefficient increased with increasing temperature from 10.50 to 25.40 cm/s and from 0.0041 to 0.0049 cm/s, respectively. The effective diffusivity ranged from 6.80×10^{-5} to 9.85×10^{-5} m^2/s and also indicated a good trend with temperature.

The proposed model could describe the kinetics of aluminum leaching from the SSW DWT in accordance with test parameters. It is evidenced by the relevant statistical criteria. Consequently, valuable information on the results of this work can be given for the purposes of the development of the leaching process (simulation, optimization, scaling up, and design).

5. ACKNOWLEDGEMENT

The experimental work was financially supported by the Directorate General of Higher Education, Ministry of Education and Culture Republic of Indonesia (No. 23428/A4.2/2014).

6. NOMENCLATURE

b	stoichiometric coefficient (–)
c_{coef}	correlation coefficient (–)
$C_{exp,i}$	experimental value of aluminum recovery, particle core (%)
$C_{exp,sr}$	experimental value of aluminum recovery, solid phase (%)
$C_{pred,i}$	predicted aluminum recovery calculated with the model, particle core (%)
C_{AL}	concentration in the solvent ($kmol/m^3$)
$C_{A(R)}$	concentration of aluminum leaching ($kmol/m^3$)
D_e	effective diffusivity (m^2/s)
E	mean relative deviation modulus (–)
k	reaction rate constant (cm/s)
k_c	mass transfer coefficient (cm/s)
k_1	first partition constant (kg/m^3)
k_2	second partition constant (kg/m^3)
N	number of experimental points (–)
$\overline{q}$	average value of q, mol/m^3

q_o	initial solid-phase concentration, mol/m^3
r	radial coordinate
r_c	critical radius of core (m)
R	particle radius (m)
$RMSE$	root mean square error (–)
t	leaching time (s)
T	leaching temperature (°C)

Greek letters

ε_L	void fraction
ρ_s	sludge solid waste density (kg/m^3)
π	the ratio of a circle's (3.14159)

7. REFERENCES

Baba, A.A., Adekola, F.A., 2012. A Study of Dissolution Kinetics of a Nigerian Galena Ore in Hydrochloric Acid. *J. Saudi Chem. Soc.*, Volume 16(4), pp. 377–386

Babatunde, A.O., Zhao, Y.Q., 2007. Constructive Approaches Toward Water Treatment Works Sludge Management: An International Review of Beneficial Reuses. *Crit. Rev. Environ. Sci. Technol.*, Volume 37(2), pp. 129–164

Bucić-Kojić, A., Sovová, H., Planinić, M., Tomas, S., 2013. Temperature-dependent Kinetics of Grape Seed Phenolic Compounds Extraction: Experiment and Model. *Food Chem.*, Volume 136(3), pp. 1136–1140

Cheng, W.P., Fu, C.H., Chen, P.H., Yu, R.F., 2012. Dynamics of Aluminum Leaching from Water Purification Sludge. *J. Hazard. Mater.*, Volume 217–218, pp. 149–155

Geankoplis, C.J., 1993. *Transport Processes and Unit Operations*. PTR Prentice Hall, City, State, Country

Goto, M., Roy, B.C., Hirose, T., 1996. Shrinking-core Leaching Model for Supercritical-fluid Extraction. *J. Supercrit. Fluids*, Volume 9(2), pp. 128–133

Levenspiel, O., 1998. *Chemical Reaction Engineering, 3rd Edition*. Wiley, City, New York, USA

Nair, A.T., Ahammed, M.M., 2015. The Reuse of Water Treatment Sludge as a Coagulant for Post-treatment of UASB Reactor Treating Urban Wastewater. *J. Clean. Prod.*, Integrating Cleaner Production into Sustainability Strategies, Volume 96, pp. 272–281

Safari, V., Arzpeyma, G., Rashchi, F., Mostoufi, N., 2009. A Shrinking Particle—Shrinking Core Model for Leaching of a Zinc Ore Containing Silica. *Int. J. Miner. Process.*, Volume 93(1), pp. 79–83

Zhou, Z., Yang, Y., Li, X., Zhang, Y., Guo, X., 2015. Characterization of Drinking Water Treatment Sludge After Ultrasound Treatment, Ultrason. *Sonochem.*, Volume 24, pp. 19–26