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Leaching Kinetics of Yttrium Extraction from Coal Fly Ash using Sulfuric Acid

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Abstract

Leaching kinetics for extracting yttrium from the coal fly ash was investigated in the presence of sulfuric acid during extraction. The leaching kinetics of yttrium were conducted at reactant densities of 5~1,000 g coal fly ash per L of 1.0~10.0 N H_2SO_4, agitation speed of 250 rpm and temperature ranging from 30 to 90°C. As a result, the leaching kinetic model was determined in a two-step model based on the shrinking core model with spherical particles. The first step was proceeded by chemical reaction at ash surface, and the second step was proceeded by ash layer diffusion because the leaching conversion of yttrium by the first chemical reaction increases with increased the time irrelevant to the temperature whereas it increases with increased the leaching temperature. The activation energy of the first chemical leaching step was determined to be 1.163 kJmol^{-1}. After the first chemical reaction, the activation energy of ash layer diffusion leaching was derived to be 41.540 kJmol^{-1}. The optimum conditions for leaching the yttrium metal of 60 % were found to be the slurry density of 250 g fly ash per L of H_2SO_4, solvent concentration of 2.0 N H_2SO_4, second step leaching of temperatures of 30°C for 3 hours and then 90°C for 3 hours at agitation rate of 250 rpm.

Keywords: Fly Ash, Leaching, REM (Rare Earth Metal), Yttrium, Recovery, Sulfuric Acid

I. INTRODUCTION

Rare earth metals (REM) are a family of lanthanides ranging from lanthanum to lutetium, plus scandium and yttrium, unlike the name, cerium is the 26 th most abundant element. Coal has been used as main fuel for power plants around the world due to its abundant reserves, relatively low price, stable supply and etc. As of December 2015, coal-fired power plants using anthracite and bituminous coal have taken about 46 % (203,765,391 MWh) of the gross generation (442,914,458 MWh) of Korea Electric Power Corporation (KEPCO)'s subsidiary companies [1]. In Korea, it's expected new coal-fired power plants (10,500 MW) will be constructed by 2027 based on the 5th (1999~2015) and the 6th (2013~2027) basic plan for electricity supply and demand, and the importance of coal-fired power generation has been growing. The production of ashes from coal fired thermal power plants is about 8.56 million tons a year, and it is increased to more than 16.3 million tons in 2020 [2]. At present only 82 % of fly ash produced is being used for the production of cement clinker, and as an additive of mortar and concrete mixtures with remaining 18 % being disposed as a waste. Also, the ash ponds of coal-fired power plants are filled with about 57.08 million tons of coal ashes and most of them are high carbon ashes which contain more than 5 % of LOI (Loss On Ignition). Meanwhile, coal ashes were found to contain important REMs such as Yttrium (Y) and Neodymium (Nd), which was in the range of 23 - 75 mg/kg. However, it still requires developing effective recovery and separation methods in order to utilize REMs in ash. Recovery of valuable elements (Y and Nd) from various and extensive ash sources can provide the existing power plants with additional profit; therefore, it can significantly improve economics of the power plants [3]. Among the REM in ashes, yttrium has been the highest concentration and broadly used in various fields that require phosphors with high light emitting properties, such as BLU (Back Light Unit), CCFL (Cold Cathode Fluorescent Lamp), CRT(Cathode Ray Tube), IPS (In PanelSwitching), LCD (Liquid Crystal Display), LED (Light Emitting Diode), OLED (Organic Light Emitting Diode) and PDP(Plasma Display Panel) [4][5]. The CAGR (Compound Annual Growth Rate) in the light market has been increased to 30 % due to the increase in world demand every year. Therefore, KEPCO Research Institute has started projects for investigating the extraction and recovering of REMs in ash by sulfuric acid. This paper was only discussed the leaching kinetics of yttrium containing the highest REMs concentration from coal fly ash by sulfuric acid.

II. THEORY

The leaching mechanism of yttrium from REM fly ash is explained using a shrinking core model having a constant size, and a two step reaction between a chemical reaction of ash surface and the diffusion layer reaction inside ash because REM fly ash is oxidized through the combustion in coal fired boiler with temperature ranges from 1,200 to 1,400°C. Accordingly, the leaching mechanism assumes that the H_2SO_4 solution diffuses into ash layers remaining after the first chemical reaction. Finally, after the completion of leaching, REM fly ash only remains ash layers as shown in the leaching behavior diagram of Fig. 1. The Y_2O_3 existing in the REM fly ash is converted into $Y_2(SO_4)_3$ phase under H_2SO_2 solution as in the following Eq. 1.

$$3H_2SO_4(A) \quad + \quad Y_2O_3(B) \quad \rightarrow \quad Y_2(SO_4)_3 \quad + \quad 3H_2O \qquad (1)$$

Reaction order is assumed a first-order chemical reaction based on the shrinking core model [5]-[9] with the same particle

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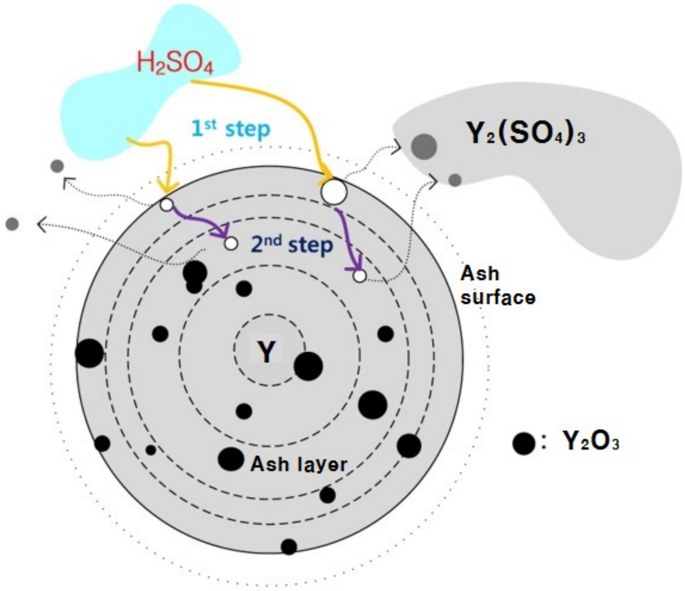


Fig. 1. Schematic diagram for the leaching behavior of yttrium from coal fly ash.

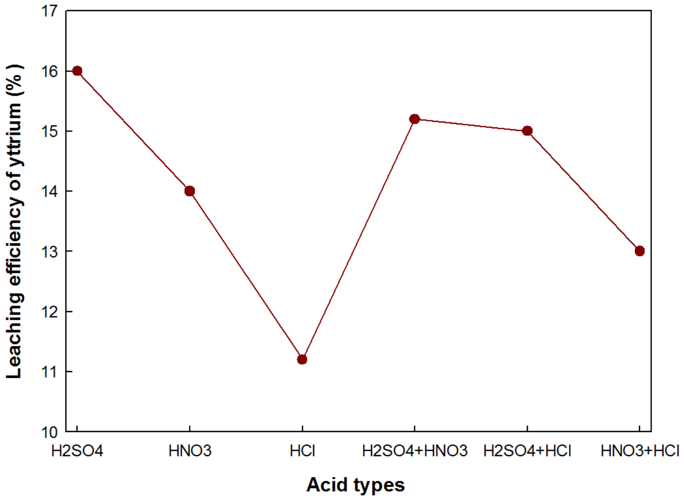


Fig. 2. Leaching efficiency of yttrium from coal fly ash at various acids.

size before and after the leaching that has a spherical shape, the chemical leaching reaction of yttrium at ash surface may be explained by Eq. 2.

$$-\frac{1}{Sex}\frac{dN_B}{dt} = -\frac{\frac{1}{3}}{4\pi r_c^2}\frac{dN_A}{dt} = -\rho_B\frac{dr_c}{dt} = \frac{1}{3}k_S C_A \tag{2}$$

where, S_{ex} is the external surface area [m^2], N_B is moles of REM fly ash reactant [mol], and t, N_A, r_c, ρ_B, k_s and C_A are time [s], moles of H_2SO_4 reactant [mol], radius of unreacted fly ash [m], molar density of yttrium component included in fly ash [molL^{-1}], first-order rate constant for the chemical reaction [s^{-1}] and concentration of H_2SO_4 reactant [molL^{-1}], respectively.

However, the variation of sulfuric acid concentration can be neglected during the chemical leaching reaction because the H_2SO_4 is excessively existed in the reactor than the stoichiometric ratio. Since it can be considered as a constant in Eq. 2, this chemical reaction model is simplified as conversion fraction of yttrium as follows:

$$1 - (1-X_B)^{\frac{1}{3}} = k_{c,chem}t \tag{3}$$

$k_{c,chem}$ is apparent rate constant for chemical reaction [s^{-1}], and X_B is fraction of converted yttrium in REM fly ash. The variation of H_2SO_4 conversion fraction (X_A) can be also ignored because it is excessively added. $k_{c,chem}$ is defined by the rate constant for chemical leaching reaction as an inverse of the time necessary to complete the leaching conversion of yttrium from ash surface at r_c=0.

$$k_{c,chem} = \frac{C_{A0}k_S}{3\rho_B R} \tag{4}$$

R is the radius of initial REM fly ash particle. C_{A0} is initial concentration of H_2SO_4. ρ_B is the molar density of yttrium in REM fly ash and ks is the rate constant for the chemical leaching at first-order reaction. During the chemical reaction at surface of REM ash, the yttrium oxide existing on the surface of REM fly ash is first leached out. The ash layer remaining after the initial chemical reaction becomes thinner and acts as a resistance and wall against the leaching reaction from the surface to inside core whereas the pore plays as a tunnel for leaching reaction of yttrium inside ash . Therefore, the ash layer diffusion can be considered as a second stage for the rate-determining step. In the ash layer diffusion model, there are many kinetic equations [6]-[10], but the reaction rate for the leaching of yttrium inside ash can be explained by the diffusion controlled rate of H_2SO_4 through the ash layers as follows:

$$1-(1-X_B)^{\frac{2}{3}} + 2(1-X_B) = k_{c,ash}t \tag{5}$$

$k_{c,ash}$ is defined by the rate constant for the leaching reaction of yttrium inside ash layer as an inverse of the time necessary to complete the leaching conversion at r_c=0.

$$k_{c,ash} = \frac{2D_eC_{AO}}{\rho_B R^2} \tag{6}$$

D_e is the effective diffusion coefficient of H_2SO_4 in the ash layer.

III. EXPERIMENTAL METHOD

Sulfuric acid of various concentrations of 1.0 ~ 10.0 N was used as leaching reagents for leaching experiments. The fly ash sample was added to a 1 L Pyrex beaker containing the acid solution. To investigate the effect of leaching temperatures, the sample was inserted to a double-insulated Pyrex vessel after the temperature increased to the goal temperature. The solution temperature was maintained by heating mantle and the mixture of ash and sulfuric acid was agitated to 250 rpm by an impeller-type stirrer. The samples for measuring the leaching efficiency were collected at target times, and then filtered by 0.45 μm cellulose acetate filter. The filtrate after removed the residues was diluted

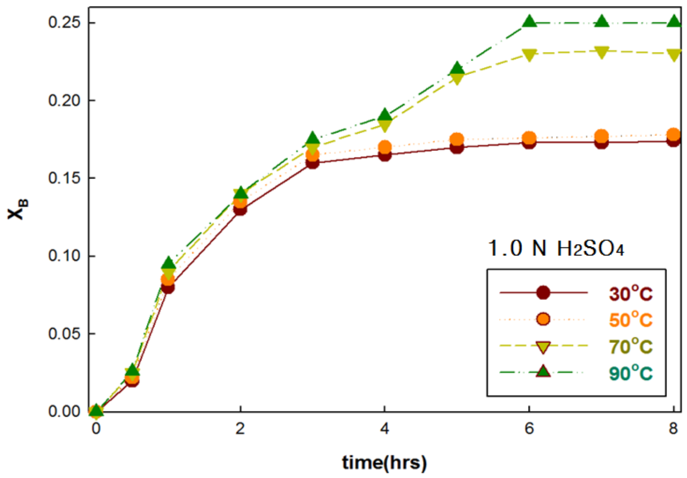


Fig.3. Leaching conversion of yttrium from coal fly ash at various heating temperatures and times.

Table 1. Chemical composition and rare earth metals concentration of REM fly ash

Chemical compositions (%)								Rare earth metals (mg/kg)				
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_2	Y	Nd	Eu	Tb	Dy
50.89	30.60	3.75	5.54	3.19	2.00	0.78	1.14	70.6	56.3	2.5	2.1	12

Table 2. Parameters obtained from the regression for chemical reaction determining step of ash surface

Temperatures	30°C	50°C	70°C	90°C
a (slope)	$9.8399e^{-4}$	$1.0133e^{-3}$	$1.0404e^{-3}$	$1.0612e^{-3}$
b (y-intercept)	-1.9952	-1.9938	-1.9919	-1.9912
R^2	0.9576	0.9536	0.9504	0.9496

Table 3. Parameter searching data obtained from the regression for ash layer diffusion determining step

Temperature	30°C	50°C	70°C	90°C
a (slope)	$8.4872e^{-6}$	$6.5365e^{-6}$	$6.0502e^{-5}$	$8.6465e^{-5}$
b (y-intercept)	$7.8159e^{-3}$	$8.9603e^{-3}$	$-1.7236e^{-3}$	$-7.7124e^{-3}$
R^2	0.9815	0.8728	0.9751	0.9978

about 10 times by added 1.0 M HCl, and analyzed by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry, X-series X5, Thermo Elemental, UK) analysis. Also, tests of leaching efficiency of yttrium was performed by hydrochloric, nitric and those mixing acids as well as sulfuric acid as a leaching acid to determine the optimum leaching solvent prior to this study [11]. Leaching tests were conducted out under the low slurry density of 5~1,000 g coal fly ash per L of 1.0~10.0 N H_2SO_4 with the different temperatures : 30, 50, 70 and 90°C to investigate the temperature effect on leaching. Rare earth metal concentration in the REM fly ash was also analyzed by ICP-MS with high sensitivity for rare earth metal ions. The physical properties of coal fly ash samples were measured as follows. The chemical compositions of ash raw sample and the residues after the leaching were analyzed by XRF (X-ray fluorescence equipment, EMAX-3770, Horiba Corp.). Particle morphologies and crystal components of ash and residues were analyzed by SEM-EDS (scanning electron microscopy-energy dispersive spectroscopy, 5200-1AE, JEOL Ltd). Adsorption and desorption isotherms of nitrogen on the samples were measured for BET surfaces at 77 K using an air permeability apparatus (ASAP 2010, Micromertics Corp.). Before the measurements, the samples were degassed 150°C at for 2 hours in the adsortion vaccum port prior to exposure to nitrogen gas.

IV. RESULT AND DISCUSSION

The raw material was fly ash containing yttrium and collected from Tean thermal power plant in Korea. Table 1 is an elemental composition of REM fly. Fly ash is primarily composed of rare earth composite oxide. Most fly ash minerals have the high SiO_2 and Al_2O_3 content whereas existed as minor minerals such as Fe_2O_3, CaO, K_2O, MgO and Na_2O. The yttrium metal in REMs contained 70.6 mg/kg, and then was highly distributed to 56.3 mg/kg Nd with the other minor constituents such as Eu, Tb, and Dy.

Fig. 2 shows the changes in leaching efficiency under a slurry density of 50 g fly ash per L of various acids of 1.0 N, with agitation speed of 250 rpm at a room temperature of 30°C. In case of sulfuric acid, leaching efficiency was the highest than other single acid and those mixing acids. This means that the reactive selectivity of sulfuric acids on yttrium leaching was the highest than any acids, and, in case of mixing acids, the mixing acid of HNO_3 and H_2SO_4 was higher than the mixing acid of HNO_3 and HCl. Therefore, sulfuric acid may be suitable for this fly ash as leaching . The yttrium was leached under a slurry density of 50 g fly ash per L of 1.0 N H_2SO_4, with agitation of 250 rpm at a temperature range of 30 to 90°C. If metal components exist as the forms of the simple metal (Y), the stoichiometric ratio of H_2SO_4 (Samchun chemicals, d.1.84, 97 %, 0.97×1840 g/ℓ×1.0 mole/98.08g × 2 eq/1mole=36.34 eq/ℓ, 36.34 N) required to convert into sulfate forms is about 0.00004 N, but other REMs are simultaneously leached out in H_2SO_2 solution during the leaching period. Therefore, we added sulfuric acid of 1.0 N with the high concentration over the stoichiometric ratio reacting with all REMs in the fly ash, and kept the solution at a strong acidic condition of less than pH of 0.4. Fig. 3 represents the fractional conversion of yttrium during the leaching. As shown in Fig. 3, Y_2O_3 of 25 % existing in the REM fly ash was leached out to $Y_2(SO_4)_3$ solution after the reaction of 6 hours at the condition of 90ºC and 1.0 N H_2SO_4. This study was applied to a two-stage model because the conversion rate of REM fly ash was divided into two steps, the first chemical reaction and the second ash layer diffusion on the basis of reaction time of 3 hour. Y_2O_3 existing in the ash surface was completely leached out to $Y_2(SO_4)_3$ solution after 3 h under the condition of slurry density of 50 g ash/L, 1.0 N H_2SO_4 irrelevant to leaching temperatures.

Generally, most chemical reaction rates increase with increased the reaction temperature. However, initial leaching reaction was fast accomplished within 3 hours at all leaching temperature. Fist chemical leaching of yttrium at ash surface was not affected to leaching temperature whereas was controlled by leaching times. After that time, the leaching below temperature of 50°C was rarely accompolished. Therefore, this leaching reaction was suggested as a two-step model. The conversion rate of yttrium ash could be divided into two steps on the basis of reaction time of 3 hours: a rapid chemical reaction at ash surface and a slow reaction stage inside ash.On the basis of the amount of REM components existing initially in the REM fly ash, the concentration of H_2SO_4 was added 1.0 N. Therefore, it was assumed that C_A is constant during the leaching. On the basis of Eq. 3, the apparent rate constant ($k_{c,chem}$) can be calculated by the least square method at various reaction temperatures as shown in

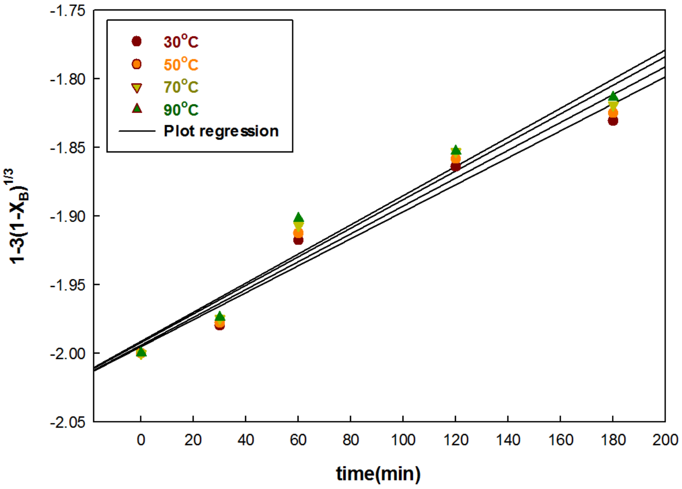


Fig. 4. Relationship between $1-3(1-X_B)^{1/3}$ and leaching times.

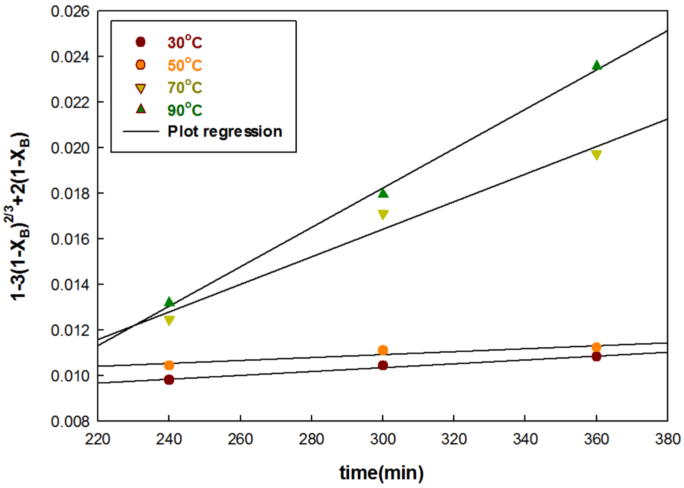


Fig. 6. Relationship between leaching conversion and reaction time during the ash layer leaching.

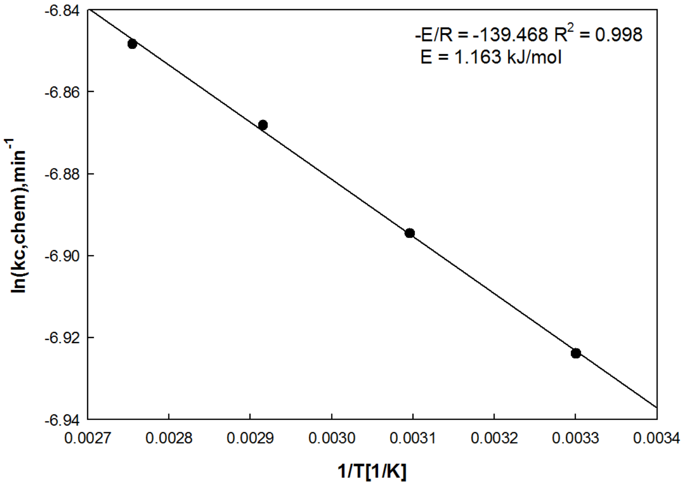


Fig. 5. Arrhenius plot of chemical leaching reaction.

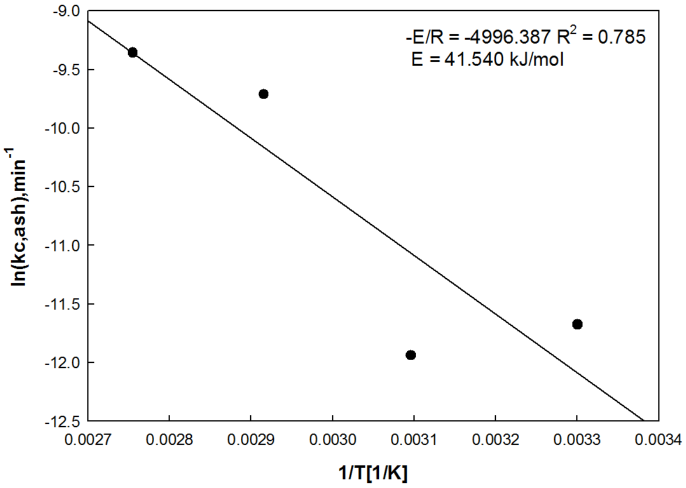


Fig. 7. Arrhenius plot of ash layer diffusion leaching inside fly ash.

Fig. 4. To examine the effect of reaction temperatures, the apparent activation energy was calculated from rate constants according to the temperatures as shown in Table 2. In the case of the chemical reaction control, the intercept and slope were -6.46299 and -139.468, respectively, as shown in Fig. 5.

The activation energy for the chemical leaching reaction of yttrium at ash surface was determined to be 1.163 $\mathrm{kJmol^{-1}}$ in the range of 30 to 90°C. The small activation energy value on leaching of yttrium at ash surface shows that this leaching reaction is insensitive to temperature change for the leaching of yttrium. The chemical reaction is a rate determining step until 3 hours. The fly ash surface becomes rough after the chemical reaction and only the ash layers remain.

These ash layers will act as the resistance for H_2SO_4 to go into inner layers for the leaching. Accordingly, the ash layer diffusion was assumed as a second stage after the chemical reaction. On the basis of Eq. 5, the apparent rate constant ($k_{c,ash}$) is calculated using the least square method at various reaction temperatures as shown in Fig. 6. To investigate the effect of leaching temperatures, the apparent activation energy was calculated from rate constants shown in Table 3. In the ash layer diffusion stage, the slope and intercept were -4.996×10^3 and 4.40141, respectively, as shown in Fig. 7. Finally, the apparent activation energy was derived to be 41.540 $\mathrm{kJmol^{-1}}$ in the temperature range of 30 to 90°C. This estimated activation energy is different from those values was higher than the other industrial by-products with 1.0~9.977 $\mathrm{kJmol^{-1}}$ [9][10]. The difference in activation energies is probably due to the existence of yttrium crystal combined with quartz and mullite crystals in the raw material. In this combustion of coal minerals at coal fired power plant, silica and alumina was melts, reacts and then condensed as a quartz, and mullite. As a result, the rare earth yttrium combined with quartz and mullite cystals as a complex polymetal oxide compounds. These crystal compounds were induced as a resistance and wall of leaching of yttrium during the leaching behaviors inside complex compounds. To maximum leach yttrium in the fly ash, a suitable slurry density must be considered. At low slurry density, yttrium in fly ash cannot be leached enough. On the contrary, various impurities such as sillicon, aluminium, and calcium ions can simultaneously be leached with target materials at high slurry density concentration, which can cause undesired effects. Thus, before leaching, the optimum leaching slurry density (ash to sulfuric acid) to maximize the yttrium leaching has to be determined with thermodynamic data. Leaching experiments were performed at various slurry densities

Table 4. Pore properties of fly ash samples before and after leaching.

Leaching	Pore Volume (cm³/g)			Pore Size (Å)			Surface area (m²/g)		
	Total pores	BJH Adsorption	BJH Desorption	Average pore	BJH Adsorption	BJH Desorption	BET surface	BJH Adsorption	BJH Desorption
Before	0.002943	0.002535	0.002394	74.3232	165.3710	137.4600	1.5838	0.6130	0.6967
After	0.013716	0.009553	0.009313	32.7520	51.5810	52.7840	16.7508	7.4080	7.0576

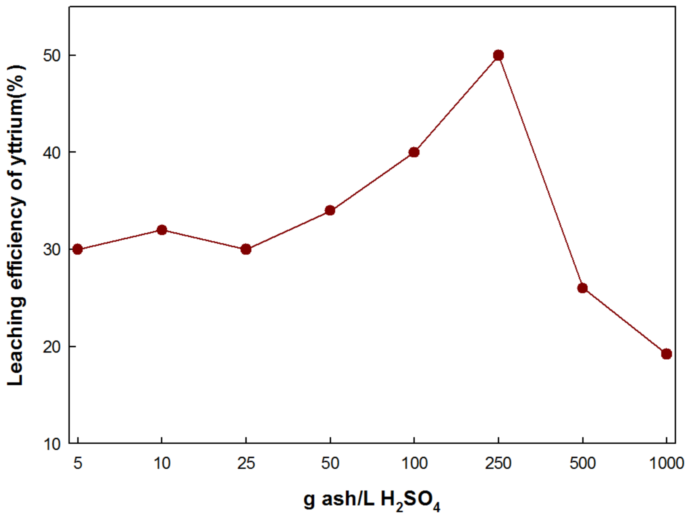


Fig. 8. Leaching efficiency of yttrium from coal fly ash at various solid loading.

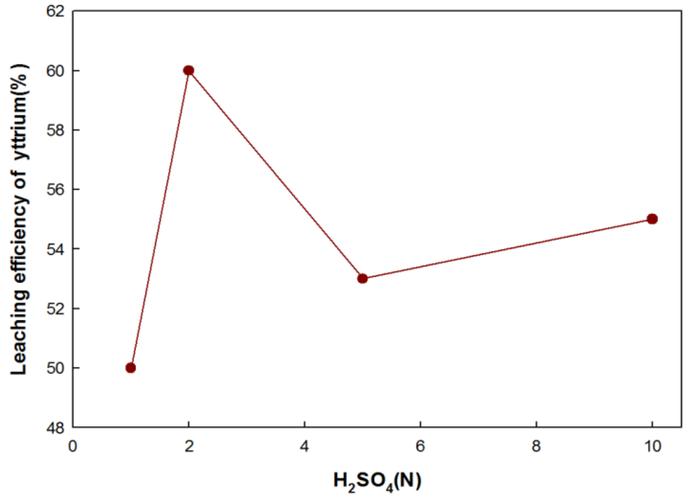
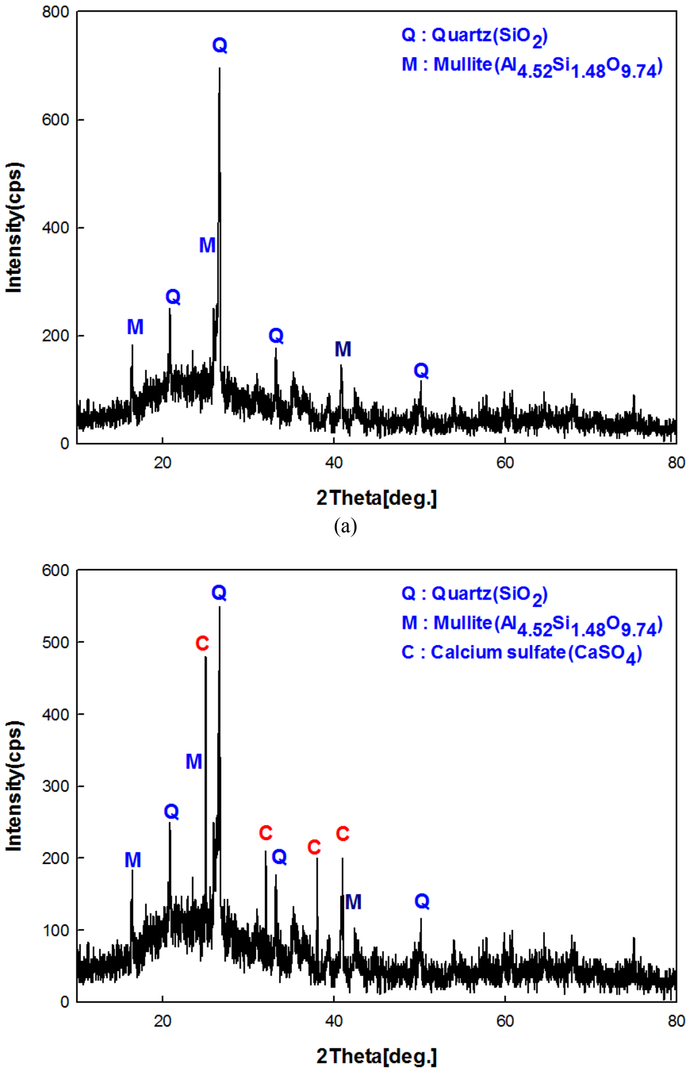


Fig. 9. Leaching efficiency of yttrium from coal fly ash at different sulfuric acid concentrations.

to find optimum slurry density for leaching yttrium the ash. Fig. 8 shows the changes in leaching efficiency for various slurry densities of 5~1,000 g ash per L of 1.0 N sulfuric acid at two steps temperature of 30°C (3 hours) and 90°C (3 hours). When the slurry density was less than 30 g ash per L of 1.0 N sulfuric acid, the leaching levels were below 35 %. The leaching level increased with increased slurry density to 250 g ash per L of 1.0 N sulfuric acid, but did not go beyond 50 % even. This may be from the decrease of the ash surface to react the sulfuric acid during the yttrium leaching above 250 g ash per L of 1.0 N sulfuric acid. Therefore, slurry density of 250 g ash per L of 1.0 N sulfuric acid may be suitable for coal fly ash as leaching is limited at 1.0 N sulfuric acid.

Fig. 9 shows the changes in leaching efficiency at two step temperature of 30°C (3 hours) and then 90°C (3 hours), slurry density of 250 g ash per L of various sulfuric acid. As the sulfuric acid concentration as a optimal solvent was about less than 1.0 N, the leaching efficiency of ytrrium from fly ash was below 50 %. Fig. 8 shows the results that when various concentrations of sulfuric acid at two step temperature of 30°C (3 hours) and 90°C (3 hours), slurry density of 250 g ash per L of H_2SO_4 was used, the maximum leaching efficiency was about 60 % and increased with increased the sulfuric acid below 2.0 N H_2SO_4 whereas it was decreased with increased sulfuric acid at above 3.0 N H_2SO_4. This is probably due to the precipitation of SO_4^{2-} as calcium sulfate as shown in Fig. 10. As previously study [12], this may be from the consume of SO_4^{2-} to precipitate the calcium sulfate during the high sulfuric acid leaching. The XRD analysis of the residue after the leaching shows the peaks of $CaSO_4$ crystals (as in Fig. 10(b)) formed by combined calcium cation and sulfate anion. Therefore, sulfuric acid with more than 3.0 N may not be suitable for this REM fly ash due to formation of precipitates such



(a)

(b)

Fig. 10. Crystals of ash samples (a) before and (b) after the yttrium leaching.

as calcium sulfates.

Particle size of ash raw material had a range of 1~10 μm and it kept the same size approximately after the leaching reaction as shown in Fig. 11. From the result, we could know that the ash has unreacted layers and these layers act as a resistance and wall over leaching reaction. As a result of N_2 adsorption and desorption, BET surface area had a value of 1.5838 m^2/g before the leaching but 7.4080 m^2/g after the leaching at two step temperature of 30°C for 3 hours and then 90°C for 3 hours as shown in Table 4. In the case of initial REM fly ash, pore volumes was very low because REM fly ash has no microstructure. On the other hand, in the case of REM fly ash after the leaching, it was converted from initial nonporous state to last porous state because all the REMs soluble in H_2SO_4 solution were leached out during the leaching. Average pore size and pore volume before and after the leaching of fly ash were calculated by BJH method. Pore size distribution were newly shown by pore formation during the leaching, and the average pore size was decreased from 74.3232 to 32.7520 Å and pore volume increased from 0.002943 to 0.013716 cm^3/g. This result conforms with the SEM result that REM fly ash is converted from nonporous state to micro porous state through the leaching.

V. CONCLUSION

This study was carried out using Taean fly ash. Leaching reaction mechanism was proposed by a two-steps shrinking core model as a leaching mechanism of yttrium oxide in the H2SO4 from REM fly ash. The first reaction was proceeded by chemical reaction at ash surface, and the second reaction was proceeded by ash layer diffusion inside fly ash.

1. REM fly ash was converted from initial nonporous state of 1.5838 m^2/g, 0.002943 cm^3/g to final porous state of 16.7508 m^2/g, 0.013716 cm^3/g after the leaching because all soluble materials were dissolved out during the leaching. Thus effective leaching was performed by second step at first leaching at room temperatures, and then second step at temperature of 90°C.

2. The first reaction was leached out by chemical reaction at the room temperature of 30°C for 3 hours. The reaction rate and yield increased with increasing times irrelevant to leaching temperatures. In the first chemical reaction step, the activation energy was derived to be 1.163 $kJmol^{-1}$. The postulated reaction was well conformed both by the linear relationship of the rate constant and the apparent activation energy.

3. In the second ash layer diffusion step at temperature of 90°C, the apparent activation energy was determined to be 41.540 $kJmol^{-1}$, which is very larger than the chemical reaction. Therefore, temperature dependence in the ash layer diffusion step was more sensitive than the chemical reaction stage irrelevant to leaching temperatures.

4. The optimum conditions for leaching the yttrium metal of 60 % were performed to be the slurry density of 250 g fly ash per L of H_2SO_4, solvent concentration of 2.0 N H_2SO_4, second step heating of temperatures of 30°C for 3 hours, and then 90°C for 3 hours at agitation rate of 250 rpm.

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REFERENCES

[1] Korea Electric Power Corporation, "Statistics of Electric Power in Korea (2015)", 2016.

[2] Kim, J. K., Park, S. U. and Lee, H. D., "Database of Rare Valuable Metal Distribution and Physicochemical Properties of Fly Ash Generated at Coal Fired Power Plants of KEPCO's Subsidiary Companies," KEPCO Research Institute, Technical Report No.TM. 9337.M2016.0209, 2016, Korea, pp.19-39.

[3] Park, S. U., Kim, J. K., Seo, Y. S., Hong, J. S., and Lee, H. D., "Review on Evaluation of Rare Earth Metals and Rare Valuable Metals Contained in Coal Ash of Coal Fired Power Plants in Korea," KEPCO Journal on Electric Power and Energy, Vol.1, No.1, 2015, pp.121-125.

[4] Merit Stock Security Co., LTD., "2015-2020 Prospect of Light Market of LED," http://blog.naver.com/postView.nhn?blogId=top-1000&blogNo=220773696280

[5] Kang, L. S., Shin, D. Y., Lee, J.U., Ahn, J.W., and Hong, H.S., "Current Technology Trends Analysis on the Recovery of Rare Earth Elements from Fluorescent Substance in the Cold Cathode Fluorescent Lamps of Waste Flat Panel Displays," J. Korean Powder Metall. Inst., Vol.22, No.1, 2015,pp.27-31.

[6] Fogler, H. S., "Elements of Chemical Reaction Engineering Engineering:11.5 The Shrinking Core Model," Prentice Hall International Series, Third Edition, A Simon & Schuster Company, New Jersey, pp.719-724.

[7] Souza, A.D., Pin, P.S., Lim, E.V.O., Silva, C.A., Lea, V.A., "Kinetics of Sulphuric Acid Leaching of a Zinc Silicate Calcine," Hydrometallurgy, Vol.89, 2007, pp.337-345

[8] Yoon, H.S., Kim,C.J., Chung, K.W., Lee, J.Y., Shin, S.M., Lee, S. J.,Joe, A.R., Lee, S.I., and Yoo, S.J., "Leaching Kinetics of Neodymium in Sulfuric Acid of Rare Earth Elements (REM) Slag Concentrated by Pyrometallurgy from Magnetite Ore," Korean J. Chem. Eng., Vol.31, No.10, 2014, pp.1766-1772.

[9] Kim, C. J., Yoon, H.S., Chung, K.W, Lee, J.Y., Kim, S.D., Shin, S.M., Lee, S.J.,Joe, J.R., Lee, S.I.,Yoo, S.J, Kim, S.H., "Leaching Kinetics of Lanthanum in Sulfuric Acid from Rare Earth Element (REM) slag," Hydrometallurgy Vol.146, 2014, pp.133–137.

[10] Kim, C. J., Yoon, H.S., Chung, K.W, Lee, J.Y., Kim, S.D., Shin, S.M., Lee, S.J.,Joe, J.R., Lee, S.I.,Yoo, S.J, Kim, S.H., Cho, J.T., Kim, J.H., Lee, E.J., Lee, S.I., and Yoo, S.J., "Leaching Kinetics of Praseodymium in Sulfuric Acid of Rare Earth Elements (REM) Slag Concentrated by Pyrometallurgy from Magnetite Ore," Korean Chem. Eng. Res., Vol.53, No.1, 2015, pp.46-52.

[11] Kim, J. K., Park, S. U. and Lee, H. D., "Design of Optimal Extraction Process of Rare Earth Metals from Coal Fly Ash using the Leachung Kinetic Experiments," Korea Electric Power Corporation's Research Institute, Technical Report No.TM.9337. M2016.0490, 2016, Korea, pp.38-54.

[12] Kim, R. N., "Study of Acid Leaching of Rare Earth Elements Ore from Mushgai Khudag Area, Mongolia," Soeul National University's Graduate School of Engineering, Master Degree Paper, 2014, pp.43-45.