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Kinetics of aluminium leaching from coal fly ash by sulphuric acid

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The extraction of aluminium from coal fly ash (CFA) is an important industrial process and has produced commercial interest. However, the leaching kinetics of aluminium has received little attention. This work, therefore, addresses the leaching kinetics of aluminium from fly ash in sulphuric acid. A shrinking core model has been used to investigate aluminium extraction kinetics and its results are presented. The effects of leaching time, solid to liquid ratios and reaction temperature on aluminium extraction rate are studied. The process optimization reveals that the extraction rate can reach up to 68.68% when the fly ash reacts with sulphuric acid at a 1:3 solid to liquid ratios of fly ash / H_2SO_4 (100 g / 300 mL) at 220°C for 4 hour reaction time. The sulphuric acid concentration was maintained constant at 18 M. The leaching rate increases with increasing temperature and solid to liquid ratios. The leaching kinetics indicates that chemical reaction at the surface of the particles is the rate-controlling process during the reaction. The shrinking core model enabled the determination of activation energy of about 60.85 kJ/mol, which is likely to be a consequence of the chemical reaction at the surface of the particles.

Keywords: Coal fly ash, Leaching kinetics, Mechanism, Aluminium, Sulphuric acid**.**

Coal fly ash typically contains 26-31% alumina whereas Bauxite, a naturally occurring alumina ore, contains about 30-60% alumina[1] and is the main source of aluminium metal in the world. Based on its amphoteric properties, alumina is capable of dissolution in either acidic or alkaline media and is therefore recoverable by chemical and hydro-metallurgical means[2]. However, the crystalline mullite phase present in fly ash is acid-insoluble and aluminium in this phase cannot easily be recovered while the non-crystalline amorphous phase is acid-soluble and aluminium can thus easily be recovered by direct acid leaching[3,4,2]. The direct acid leaching method, though low on aluminium extraction efficiencies, has advantages of low cost, mild process conditions and low energy demand[2]. This study was primarily concerned with the extraction of aluminium metal by direct acid leaching of coal fly ash. Sulphuric acid is often used as the leachant in leaching processes for recovery of metals from fly ash because of its stability, ease of use, low cost and ability to allow for good solubilization of alumina[5,3]. But, the insoluble sulphates such as $CaSO_4$ that are formed during leaching with sulphuric acid can hinder the leaching by coating the coal fly ash particles with precipitates of low permeability. Roy *et al*. and Talbot *et al*. applied chemical equilibria models in order to elucidate a number of chemical mechanisms that take place when coal fly ash comes in contact with water. Their approach is also applicable for leaching systems of metals, where coal fly ash is brought in contact with sulfuric acid[6-8].

The leaching of fly ash in sulphuric acid is a heterogeneous reaction system consisting of solid particles and fluid reactant. The major models developed for these reactions include the first order, shrinking core, shrinking particle, homogeneous and grain models, among which the shrinking core model has been widely accepted in hydrometallurgy for the dissolution kinetics of fluid-solid systems[9-12]. So the current study can be described in the framework of heterogeneous non-catalytic reactions in conjunction with the shrinking core model. Many studies have been carried out on aluminium dissolution kinetics from coal fly ash, kaolin and clay with shrinking core model[13-15]. The acid leaching process of coal fly ash roasted with KF as assistant was modeled[9], indicating that the aluminium dissolution rate was controlled by chemical reaction and its dissolution percentage reached 92.46%. However, fluoride ions were easily introduced in the following acid leaching process, which has negative effect on the environment. Seidel and Zimmels investigated aluminium leaching mechanism and kinetics for coal fly ash using sulfuric acid, which confirmed that the leaching process followed the shrinking core model. During sulfuric acid leaching process, calcium sulfate formed and precipitated within the pores and on the particle surface, resulting in a self inhibition effect on mass transfer at the leaching sites[15]. Iron leaching kinetics was also studied. Lee et al. used oxalic acid to dissolve iron oxides from a clay material and found that the dissolution rate increased with oxalate concentrations in the optimum *p*H range (2.5-3.0). Dissolution of fine pure hematite (105-140 µm) followed a diffusion-controlled shrinking core model[16]. Leaching kinetics for the removal of iron from low grade gibbsite bauxite with HCl was studied. The dissolution of iron followed the first order equation $-\ln(1-\alpha) = kt$, with an apparent activation energy of 81.0 $kJ \cdot mol^{-1}$. Removal of more than 98% iron from hematite was achieved with about 10% aluminium loss from gibbsite phases of the ore by using 4 $mol \cdot L^{-1}$ acid[17]. Similarly aluminium and iron dissolution kinetics from coal mining waste by hydrochloric acid was studied by Cui et al. and found that the aluminium leaching reaction is controlled by surface reaction at low temperatures (40-80°C) and by diffusion process at higher temperatures (90-106°C). The iron dissolution process is dominated by surface reaction at 40-100°C[12]. The kinetic analysis of alumina extraction from fly ash using an ammonium hydrogen sulfate roasting method indicates that the roasting process follows shrinking unreacted core model and inner diffusion through product layer is the rate controlling step[18]. As a large and prospective aluminium source, the study on fly ash leaching mechanism and kinetics is insufficient. Dissolution kinetics of aluminium from coal fly ash is rarely found, which is needed to optimize aluminium leaching process and purify aluminium products.

In the present work the mechanism and kinetics of the aluminium extraction from VAL fly ash by leaching process were studied and modelled. The process conditions studied include solid to liquid ratios (g/mL), temperature, and time. The influence of solid to liquid ratios and leaching temperature on dissolution kinetics are investigated. A kinetic model was developed to predict dissolution of fly ash. It is shown that in the VAL fly ash - sulphuric acid leaching system, leaching variables such as temperature and solid to liquid ratios has a major role in determining the kinetics of the process, via a mechanism that involves a build-up of resistance to mass transfer.

Experimental Section

Materials

The fly ash sample is collected from the electrostatic precipitator of captive power plant of Vedanta Aluminium Limited (VAL) at Jharsuguda, Odisha. The as-received sample with no further grinding and size classification are characterized chemically and mineralogically. The elemental compositions of the VAL fly ash was determined by ICP-OES (Perkin Elmer Optima 2100 DV) which showed the presence of Al_2O_3 (27.64%), SiO_2 (65.12%), CaO (1.35%), Fe_2O_3 (4.69%), TiO_2 (0.81%), K_2O (0.12%), MgO (0.61%), Na_2O (0.16%) and LOI (0.98%)[19].

Leaching process

To determine the kinetics of dissolving aluminium, the change in the rate of extraction was observed, at three different temperatures, by monitoring the variation of aluminium extraction with time. A set of experiments was carried out by treating fly ash samples (100 g) with 300 mL of 18 M H_2SO_4 at varying time (2h, 3h, 4h) to investigate the extent of aluminium extraction from coal fly ash, without any further size reduction. The mixture was taken in a one-litre flask and boiled on constant stirring to its boiling temperature i.e. 220°C with the evolution of white fumes. Boiling was continued up to 2, 3 and 4 hr with time-to-time addition of appropriate amount of H_2SO_4 in order to retain the desired solid to liquid ratio. Then similar experiments were carried out by treating same fly ash samples with 18 M H_2SO_4 at varying temperatures (180, 200, 220°C) and solid to liquid ratio (1:2, 1:3 and 1:4). The leaching time was maintained constant at four hours. The mixture usually became slurry due to loss of water and further solidified at its boiling point. Then the mixture was extracted with 500 mL hot distilled water, filtered through a G3 Buchner funnel, followed by repeated washing with hot water. The leach liquor and washings were mixed and evaporated to a known volume before analysis for aluminium by ICP-OES. Residues obtained during the leaching experiments were washed several times till neutral, dried at 110°C and are subjected to various physico-chemical analysis such as X-ray diffraction and Scanning electron microscopy. The leaching conditions for the kinetics experiments are given in Table 1. The sulphuric acid concentration was maintained constant at 18 M for all the leaching experiments.

Table 1 — Sulphuric acid leaching condition for the kinetics experiments

Experiment Run	Leaching condition			
	Leaching temperature (°C)	Leaching times (hr)	Acid concentration (M)	Solid to Liquid ratio (g/mL)
Run 1	180	2, 3, 4	18	1:3
Run 2	200	2, 3, 4	18	1:3
Run 3	220	2, 3, 4	18	1:3

Shrinking core model

The shrinking core model assumes that the reaction products, and/or inert matter that remain in the solid phase, form a layer of 'ash' that encapsulates the unreacted core[8,20,15]. The model considers that a reaction first occurs at the surface of the particle and moves towards the center. As the reaction proceeds, the unreacted core of the particle is reduced in size whereas more products are formed. For a reaction of this kind, the following steps are considered to occur in series: (1) Diffusion of the fluid reactants from the bulk liquid phase through the liquid film to the solid surface. (2) Reaction between the fluid reactants and the solid particle. (3) Diffusion of the reaction products from the solid surface back into the bulk liquid phase (fly ash). It is considered that the slowest of the above steps is the rate-controlling step. The above steps can be integrated and written as follows[21-23]:

Film diffusion control: $X = K_1 t$ … (1)

Chemical reaction control: $1-(1-X)^{1/3} = K_r t$ … (2)

Product layer diffusion: $1-3(1-X)^{\frac{2}{3}} + 2(1-X) = K_d t$ … (3)

where X is the cumulative leaching fraction, t is the leaching time in hour, K_1 is the film diffusion rate constant, K_r is the surface chemical reaction rate constant and K_d is the product layer diffusion rate constant.

So leaching rate is generally controlled by one of the above steps. The experimental data were analyzed on the basis of shrinking core model in order to determine the rate-controlling step. The film diffusion control is not considered as a rate-limiting step for this case because the fluid reactant is liquid and therefore offers minimal resistance for transport of reactants to the surface of the particle[15,23]. For a rate-controlling step of diffusion through this ash, Cussler (1984) specifies the following characteristics: weak temperature variation and independence of flow rate[20]. The process of aluminium leaching from coal fly ash by sulfuric acid is considered elsewhere by Seidel[24]. According to Siedel, the degree of aluminium recovery was found to decrease with an increase in the content of coal fly ash in the leaching medium. This intriguing phenomenon could not be reconciled by the mass action law of the dissolution reactions, but rather by mass transfer considerations. It was shown that the leaching process involves a self-inhibition mechanism owing to precipitation of calcium sulphate on the surface, and within pores, of the coal fly ash particles[15].

Statistical analysis was carried out using the Origin version 6.0 software. This determined both the activation energy and regression coefficients for a 95% confidence interval.

The cumulative leaching fraction or conversion factor was evaluated as

$$X = \frac{\text{Percentage of aluminium extracted}}{100}$$

The experimental data from different reaction variables were analyzed using equations 2 and 3. Multiple regression coefficients and leaching rate constants were obtained from the integral rate expressions. This was done by plotting the left sides of equations 2 and 3 with the reaction time.

Results and Discussion

Effect of leaching variables on aluminium extraction

The effect of different concentrations of sulphuric acid on aluminium extraction has already been studied at the temperature of 220°C in our previous work, where it has been observed that there is a steady increase in extraction efficiency of aluminium with increasing concentration of sulphuric acid from 1.5 M to 18 M (3 N to 36 N)[19]. So sulphuric acid concentration of 36 N (18 M) has been optimized for kinetic study and all the leaching experiments are conducted using 18 M H_2SO_4.

Effect of residence time

The effect of time (2, 3, 4 hrs) on aluminium extraction with sulphuric acid leaching at three different temperatures such as 180, 200, 220°C is shown in Fig. 1. An aluminium extraction efficiency of 31.68% after 2 h, 47.76% after 3 hr, 68.68% after 4 hr of reaction was obtained. The figure illustrates

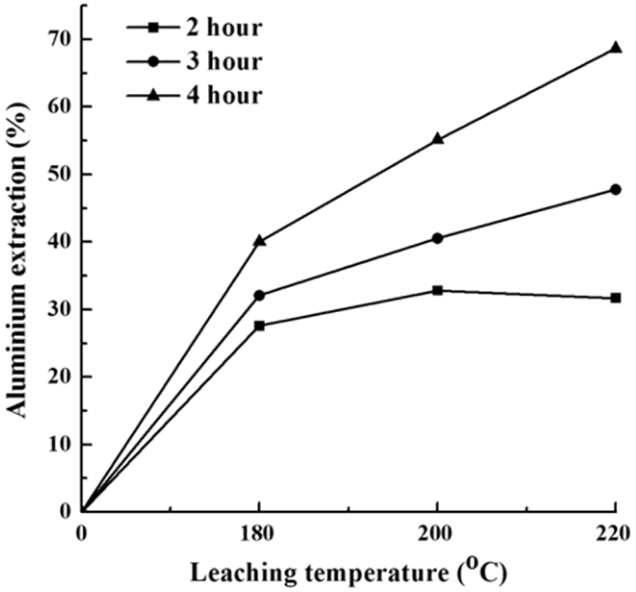


Fig. 1 — Effect of time on aluminium extraction at different temperatures (18 M H_2SO_4, 1:3 fly ash (g) : sulphuric acid (mL)

that extraction efficiency increased with increase in leaching time from 2 hr to 4 hr i.e. higher aluminium extraction was achieved with longer leaching time. The increased extraction with longer leaching time signifies the fact that adequate leaching time is necessary to overcome resistance to mass transfer of reactants and products caused by calcium sulphate precipitate formations in and around the fly ash particle[2,15,25]. Therefore, 4 hr was adopted as the appropriate leaching time for kinetic study.

Effect of temperature

The effect of temperature on aluminium extraction from fly ash at different time interval is presented in Fig. 2. The figure illustrates that extraction efficiency increased with temperature up to 220°C. The maximum extraction efficiency of 68.68% for Al was obtained at 220°C. For this reason, leaching temperature was optimized to 220°C for the kinetic analysis. Higher aluminium extractions at higher temperatures were attributed to the fact that molecules at higher temperatures have more thermal energy required for effective reaction or the proportion of reactant molecules with sufficient energy to react is significantly higher[2].

Effect of solid to liquid ratio

The effect of solid to liquid ratio on aluminium extraction at different time interval is presented in Fig. 3. The figure shows 59.92% at 1:2, 68.68% at 1:3 and 68.61% of aluminium extraction at 1:4 solid to liquid ratios was observed. From the result, it is being observed that higher aluminium extraction was obtained at the higher solid to liquid ratio of 1:3. The solid to liquid ratio is a representation of the ratio of weight of solids to volume of acid. The higher aluminium extraction at the higher solid to liquid ratio is ascribed to a possible attrition effect among ash particles due to a higher slurry mixture density. The attrition may have prevented any build-up of calcium sulphate precipitate layer on the ash particles hence allowing high mass transfer rates of reactants and products. Lower aluminium extraction at the lower

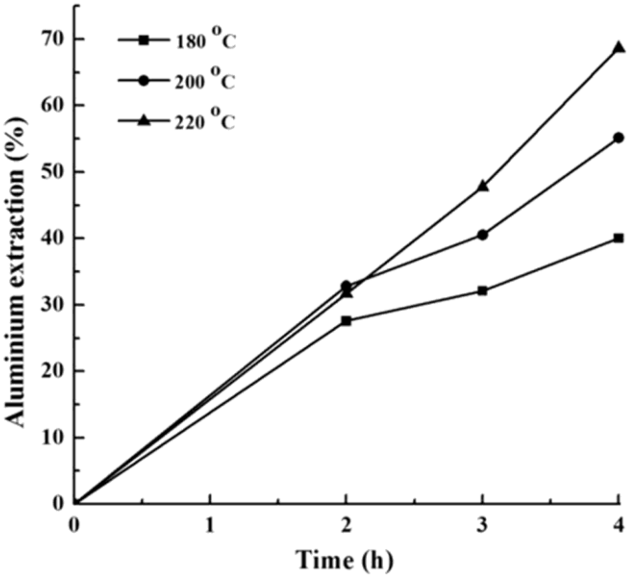


Fig. 2 — Effect of temperatures on aluminium extraction (18 M H_2SO_4, 1:3 fly ash (g) : sulphuric acid (mL))

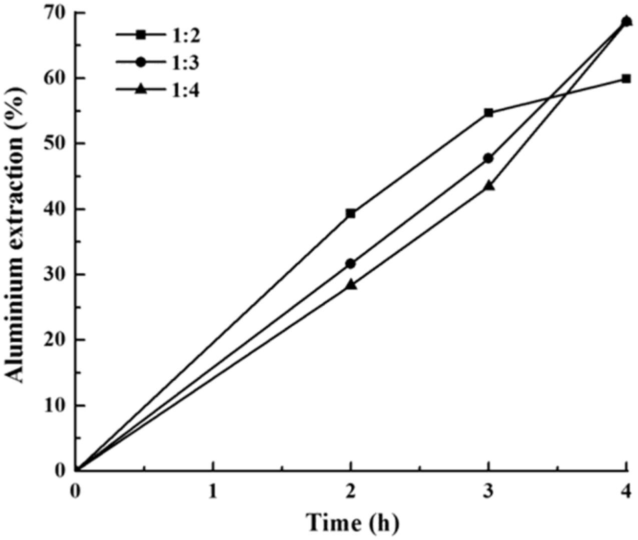


Fig. 3 — Effect of solid to liquid ratios on aluminium extraction (18 M H_2SO_4, 220°C temperature)

solid to liquid ratio may be attributed to increased sulphate ions due to increased acid volume hence promoting intensified formation of calcium sulphate precipitates. The precipitates obstruct mass transfer across the fly ash particle thus hindering alumina dissolution[2]. The decreased aluminium extraction for the solid to liquid ratio greater than 1:3 was probably due to low mass transfer rates of reactants and products caused by the increased density of the fly ash reaction mixture. This may have caused the particles not to be suspended efficiently in the solution as the stirring rate was kept constant. Based on this information, 1:3 was therefore adopted as the appropriate solid to liquid ratio for kinetic study.

X-ray Diffraction analysis

The phase compositions of fly ash as received and after 4 hrs leaching period are illustrated in Fig. 4. The XRD pattern shows the presence of quartz, mullite, hematite and magnetite as the dominant phases. It is being noticed that the quartz, mullite, magnetite and hematite peaks observed in pre leached fly ash at 2θ values of 26.73 (d=3.33), 26.07 (d= 3.41), 33.28 (d= 2.68) and 35.34 (d= 2.53) respectively are differing from each other in post leached fly ash[19]. The fly ash leached after 4 hour shows the presence of quartz peaks at 2θ values of 20.59, 26.56 and 39.71, mullite peaks at 2θ values of 16.51, 34.74 and 39.71 and then magnetite and silimanite peaks are observed at 34.74. The effect of leaching on the fly ash is observed mainly on mullite peak. There is a reduction of the mullite peaks in the samples after leaching. However leaching had least effect on quartz peak appearing at 2θ = 26.73°. So the fly ash leached at 4 hrs had the lowest diffraction peaks for mullite. This indicates that aluminium ions were extracted into solution and may react with sulphate ions to form products with increased surface area.

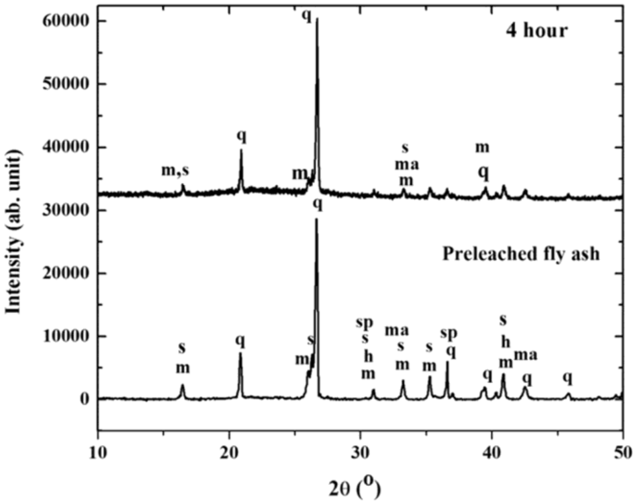


Fig. 4 — XRD patterns for pre leached fly ash and after 4 hours leaching period (18 M H_2SO_4, 220°C, 1:3 solid to liquid ratio)

q = Quartz; m = Mullite; ma = Magnetite; sp = Spinel; s = Silimanite; h = Hematite.

Scanning Electron Microscope (SEM) analysis

The morphological structures of the samples studied at different leaching periods are represented in Fig. 5. It is evident that the studied fly ash is composed of smooth surface with collection of hollow spherical particles of different sizes as well as particles of irregular shape which are known as silica embedded in the surfaces[19]. Due to presence of hollow spheres, a considerable amount of alumina was enclosed inside these spheres (Fig. 5a). The surface morphology of the samples after leaching (Fig. 5b, 5c, 5d) varies significantly. It reveals particles with deformed shapes that are rough, pitted and corroded relative to the raw fly ash. This is attributed to the leaching of alumina out of the particle surface due to the acid attack on the smooth surface during leaching[23]. This was also evident in XRD analysis where mullite peaks diminished with prolonged leaching periods.

Kinetic analysis

Mechanism for leaching of fly ash

The dissolution of aluminium from coal fly ash particles is assumed to follow a mechanism of irreversible heterogeneous non-catalytic reaction[15]. The H^+ ions from the acid react with solid aluminium compounds that are progressively exposed on the surface and within pores of the coal fly ash particles. The relevant chemical reactions that lead to dissolution of compounds of major elements in the coal fly ash, including aluminium and iron, can be described schematically as follows[15]:

$$H_2SO_4 \leftrightarrow 2H^+ + SO_4^{2-} \quad \text{… (4)}$$

$$MO + 2H^+ \leftrightarrow M^{2+} + H_2O \quad \text{… (5)}$$

(Where M = Ca, Mg,…………)

$$J_2O + 2H^+ \leftrightarrow 2J^+ + H_2O \quad \text{… (6)}$$

(Where J = Na, K, ……..)

$$Al_2O_3 + 6H^+ \leftrightarrow 2Al^{3+} + 3H_2O \quad \text{… (7)}$$

$$2Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3\downarrow + 3H^+ \quad \text{… (8)}$$

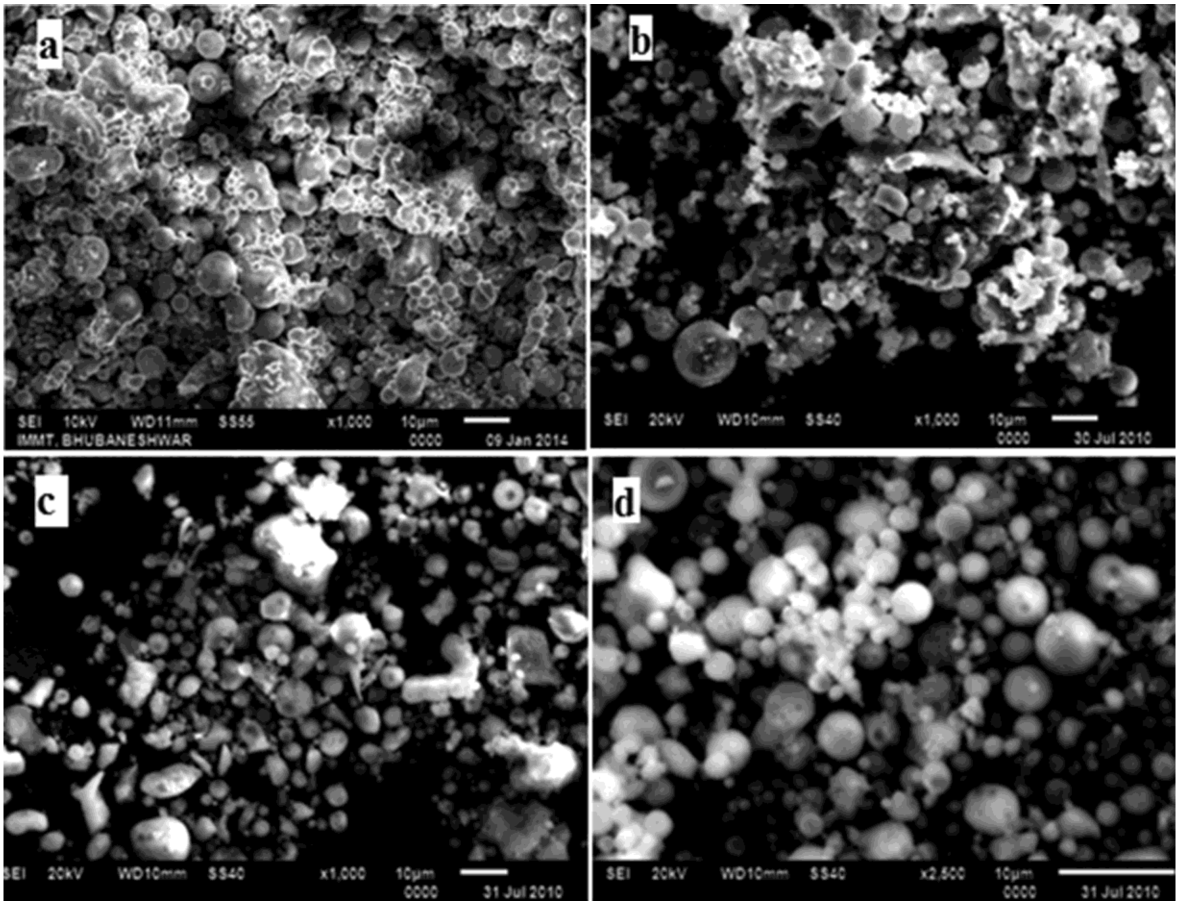


Fig. 5 — SEM micrographs of fly ash at different leaching stages a) original coal fly ash b) fly ash after 2 hr leaching c) fly ash after 3 hr leaching d) fly ash after 4 hr leaching by 18 M sulphuric acid (220°C, 1:3 solid to liquid ratios)

$$Fe_2O_3 + 6H^+ \leftrightarrow 2Fe^{3+} + 6H_2O \quad \ldots (9)$$

$$2Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3\downarrow + 3H^+ \quad \ldots (10)$$

$$Ca^{2+} + SO_4^{2-} \leftrightarrow CaSO_4 \quad \ldots (11)$$

Lai-shi et al.[26] also studied the similar reaction mechanisms involved in the H_2SO_4 leaching with metal oxides present in fly ash and are given in Eqs (12) and (13).

$$Al_2O_3 + 3H_2SO_4 \leftrightarrow Al_2(SO_4)_3 + 3H_2O \quad \ldots (12)$$

$$Fe_2O_3 + 3H_2SO_4 \leftrightarrow Fe_2(SO_4)_3 + 3H_2O \quad \ldots (13)$$

Rate controlling mechanisms

From the above study, the optimized conditions for aluminium leaching obtained is 220°C temperature, 1:3 solid to liquid ratios (100 g/ 300 mL), 4 hr of leaching time and the acid concentration of H_2SO_4 is maintained constant at 18 M for all the leaching experiments. As explained earlier, the dissolution rates of coal fly ash were analyzed here on the basis of the shrinking extraction type core model under the assumption that the material consists of homogeneous spherical solid particles that react isothermally with the fluid media[9,15].

To determine the rate controlling regime, experimental results at different temperatures were plotted in terms of the standard equations of the shrinking core model. The reaction kinetic models are represented by linear kinetic equations as given below:

$X = K_1t$, for film diffusion control with film diffusion rate constant $K_1 = 3bk_g C_o/ \rho r_o$

$1-(1-X)^{1/3} = K_rt$, for chemical reaction control with chemical reaction rate constant $K_r = kC^n_oM/ \rho r_o$

$1-3(1-X)^{2/3} + 2(1-X) = K_dt$, for product layer (ash) diffusion control with product diffusion rate constant $K_d = 6MDC_o/b\rho r_o^2$

where X is the cumulative leaching fraction (%), t is the leaching time in hour, k_g = fluid mass transfer coefficient (m.hour^{-1}), D is the diffusion coefficient (cm^2.hour^{-1}), C_o is the initial concentration of H_2SO_4 (mol·L^{-1}), k is the chemical reaction rate constant (cm.hour^{-1}), M is the molecular weight of mineral, r_o

is the initial average radius of particles (cm), ρ is the density of fly ash (kg.m^{-3}) and b is the stoichiometric coefficient.

All the kinetics experiments were conducted at a temperature range of 180°C to 220°C using 18 M H_2SO_4 at 1:3 solid to liquid ratio and 2, 3, 4 hr of leaching time. The leaching time in kinetics experiments was extended to 4 hours in order to allow for as much extraction as possible. The sulphuric acid leaching conditions along with percentage of Al extraction for the kinetic study are presented in Table 2.

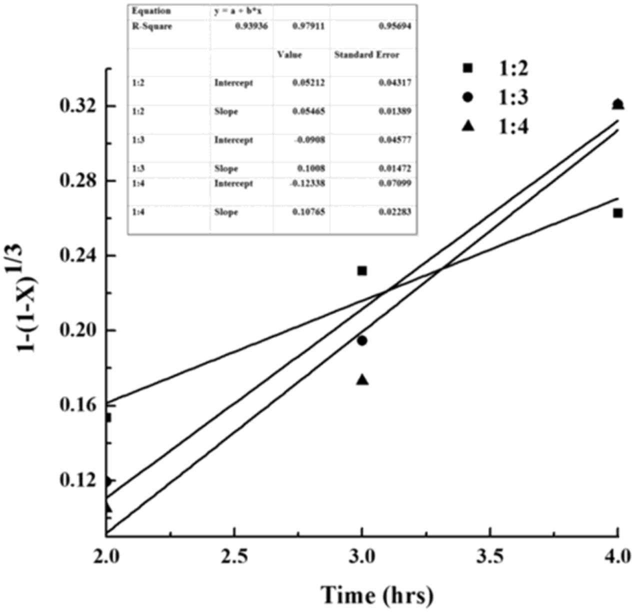
Effect of solid to liquid ratio on leaching kinetics

The leaching experiments provide reliable data for a reaction kinetic model. The kinetic equations such as (2) and (3) as functions of time at solid to liquid ratio of 1:2, 1:3 and 1:4 were plotted and are presented in Figs. 6 and 7 while the concentration of H_2SO_4 and temperature are maintained at 18 M and 220°C respectively. The apparent rate constants are calculated from Eqs. (2) and (3).

The effect of solid to liquid ratio on the rate constant was found to be significant. This was studied by performing different experiments at 1:2, 1:3 and 1:4 (g/mL) solid to liquid ratios. The temperature and acid concentration were maintained at 220°C and 18 M respectively. Table 3 shows the rate constants at different solid to liquid ratios for the surface chemical reaction models and product layer diffusion models with their respective regression coefficients. Based on the experimental data in Fig. 3, a plot of 1-(1-X) $^{1/3}$ versus time and 1-3(1-X)$^{2/3}$+ 2(1-X) versus time for aluminium extraction is presented in Figs. 6 and 7. The film diffusion control (X = K_1t) is not considered as a rate-limiting step here because the fluid media used for this study is liquid in nature and it is therefore considered that mass transfer across the

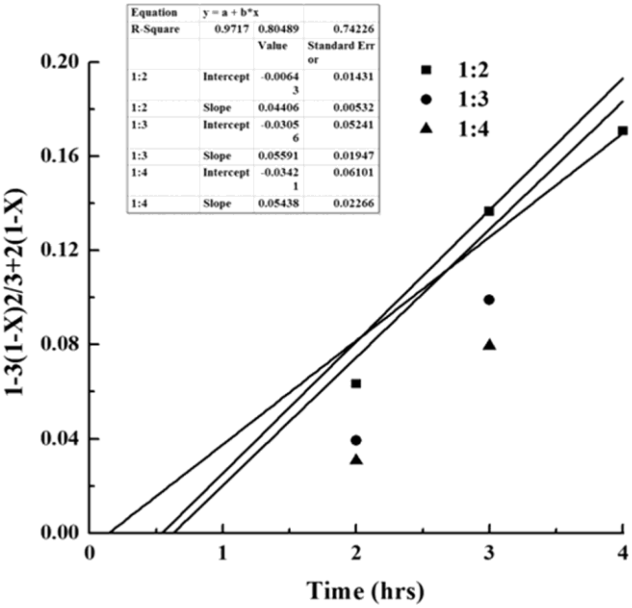
Table 2 — Al extraction (%) at different time interval of particular temperatures

H_2SO_4 conc.	Fly Ash (g) : 18 M H_2SO_4 (mL)	Temperature (°C)	Time (hr)	Al (%)
18 M	1:3	180	2	27.55
			3	32.09
			4	40.04
18 M	1:3	200	2	32.80
			3	40.55
			4	55.14
18 M	1:3	220	2	31.68
			3	47.76
			4	68.68



Equation	y = a + b*x		
R-Square	0.93936	0.97911	0.95694
		Value	Standard Error
1:2	Intercept	0.05212	0.04317
1:2	Slope	0.05465	0.01389
1:3	Intercept	-0.0908	0.04577
1:3	Slope	0.1008	0.01472
1:4	Intercept	-0.12338	0.07099
1:4	Slope	0.10765	0.02283

Fig. 6 — Plot of 1-(1-X)$^{1/3}$ versus time at various solid to liquid ratios (18 M H_2SO_4, 220°C)



Equation	y = a + b*x		
R-Square	0.9717	0.80489	0.74226
		Value	Standard Error
1:2	Intercept	-0.00643	0.01431
1:2	Slope	0.04406	0.00532
1:3	Intercept	-0.03056	0.05241
1:3	Slope	0.05591	0.01947
1:4	Intercept	-0.03421	0.06101
1:4	Slope	0.05438	0.02266

Fig. 7 — Plot of 1-3(1-X)$^{2/3}$+2(1-X) versus time at various solid to liquid ratios (18 M H_2SO_4, 220°C)

Table 3 — Regression coefficients and apparent rate constants

	Surface chemical reaction		Product layer diffusion	
Process variable	K_r/h $^{-1}$	R^2	K_d/h $^{-1}$	R^2
Temperature/°C				
180	0.0274	0.9705	0.0185	0.9529
200	0.0551	0.9575	0.0483	0.9308
220	0.1008	0.9792	0.1017	0.9459
Solid to liquid ratios (Fly ash/g : Acid/mL)				
1:2	0.0546	0.9393	0.0537	0.9579
1:3	0.1008	0.9791	0.1017	0.9458
1:4	0.1076	0.9569	0.1057	0.9119

fluid film will have least effect on the system[15,23,27,28]. Low correlation coefficients were obtained for the diffusion through the product layer model, indicating that this model could not represent the rate controlling step. A good linear relationship of $1-(1-X)^{1/3}$ versus time suggests that the extraction rate of aluminium is dominated by surface chemical reaction process under these condition from 1:2 to 1:4 solid to liquid ratios at 220°C using 18 M H_2SO_4. It is also observed that the rate constant increased appreciably with increased solid to liquid ratios from 1:2 to 1:4. So the surface chemical reaction (i.e. reaction at the surface of the core of the unreacted particle) was strongly dependent on the solid to liquid ratio giving a rate constant of 0.0546 hour^{-1} at 1:2 and 0.1076 hour^{-1} at 1:4 solid to liquid ratio.

Effect of temperature on leaching kinetics

The temperature is a factor of great importance for the leaching kinetics. The effect of reaction temperature was examined from 180°C to 220°C under the conditions of 18 M H_2SO_4 and 1:3 solid to liquid ratio (g/ml) from 2 to 4 hour. In order to determine the kinetic parameters and rate controlling step, the experimental data as shown in Fig. 2 and Table 2 was analyzed on the basis of kinetic Eqs (2) and (3) (shrinking core model) and the experimental data validity was tested by statistical and graphical methods and then the multiple regression coefficient obtained for the integral rate expression were calculated and are presented in Table 3.

Based on the experimental data in Fig. 2, plot of $1-(1-X)^{1/3}$ versus time and $1-3(1-X)^{2/3}+2(1-X)$ versus time for aluminium extraction is presented in Fig. 8 and 9 in a temperature range from 180°C to 220°C. As already mentioned, film diffusion control ($X= K_1t$) will not be considered as a rate limiting step here as the fluid media used for this study is liquid in nature.

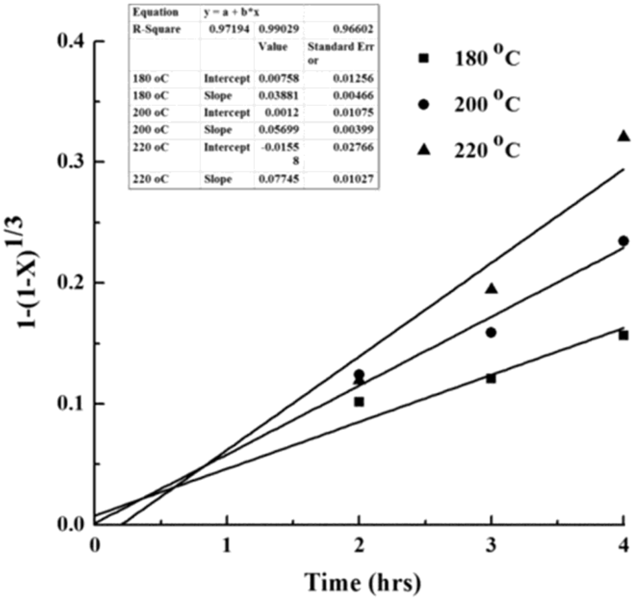


Fig. 8 — Plot of $1-(1-X)^{1/3}$ versus time for the acid leaching of fly ash at 180°C, 200°C & 220°C (18 M H_2SO_4, 1:3 solid to liquid ratios)

Examination of the kinetic equation plots as functions of time at 180°C give perfectly fitting straight lines. However, from the two kinetic equation plots, a good linear relationship of $1-(1-X)^{1/3}$ versus time with a linear regression coefficient of 97.05% (Fig. 9, Table 3) suggests that the extraction rate of aluminium is dominated by surface chemical reaction at 180°C. On the other hand, from the analysis of two kinetic equation plots as functions of time at 200°C, the plot of $1-(1-X)^{1/3}$ versus time with a linear regression coefficient of 95.75% (Fig. 6) shows a better fitting straight line. This indicates that the aluminium dissolution rate at 200°C was better modelled by the reaction kinetic model represented by kinetic equation $1-(1-X)^{1/3}= K_rt$, for surface chemical reaction control. Similarly, from the two kinetic equation plots as

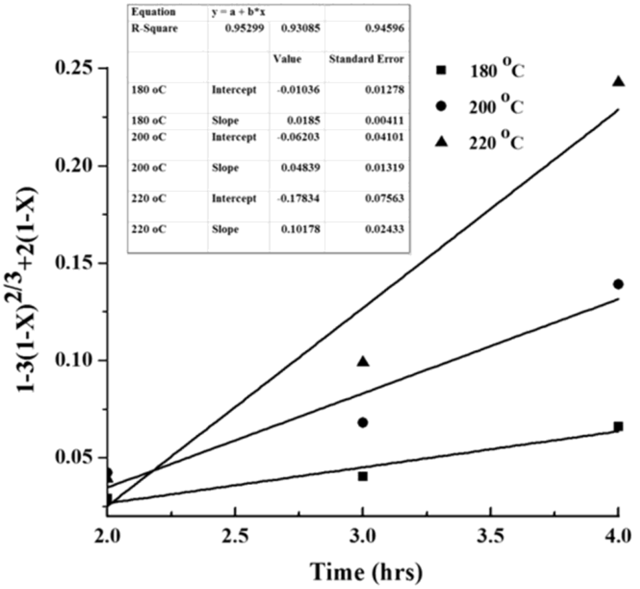


Fig. 9 — Plot of 1-$(1\text{-X})^{2/3}$+ 2(1-X) versus time for the acid leaching of fly ash at 180°C, 200°C & 220°C (18 M H_2SO_4, 1:3 solid to liquid ratios)

functions of time at 220°C, a good linear relationship of 1-$(1\text{-X})^{1/3}$ versus time with a linear regression coefficient of 97.92% (Fig. 8, Table 3) suggests that the extraction rate of aluminium is dominated by surface chemical reaction at 220°C.

So from the overall study, a good linear relationship of 1-$(1\text{-X})^{1/3}$ versus time with zero point intercept suggests that the extraction rate of aluminium from fly ash is dominated by chemical reaction at the particle surface under these condition from 180°C to 220°C at 1:3 solid to liquid ratios using 18 M H_2SO_4. The coupling of particle size distribution to the shrinking core model was not done in this study. Much as the coal fly ash particle size may not have had much influence on the extent of aluminium extraction, not coupling the particle size distribution with the shrinking core model may have caused erroneous shifts in the control regime. Therefore, in order to accurately predict the control regime in the leaching of coal fly ash, the use of a model that takes into account the coupling of particle size distribution to the shrinking core model may be required. From Table 3, the values of rate constant at different temperatures increased with increase in temperature. This is because with increase in temperature, the extraction rate of aluminium increases[2,23]. At a temperature of 180°C, the rate constant was 0.0274 hour^{-1}, and then it increased to 0.1008 hour^{-1} at a temperature of 220°C. There was a significant gap between the values obtained at 180, 200 and 220°C. This is because high temperatures affect the kinetic characteristics of the leaching process and this leads to high reactivity[23, 29].

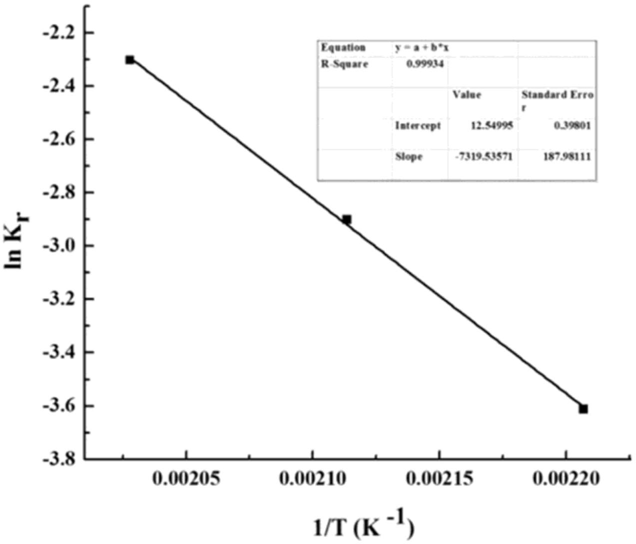


Fig. 10 — Arrhenius plot for Al extraction from fly ash at leaching temperatures from 180°C to 220°C and [H_2SO_4] = 18 M

Determination of Activation Energy

The apparent activation energy can be calculated using the Arrhenius equation,

$$K_r = A\, e^{-E_a/RT} \qquad \ldots (14)$$

where, A is the frequency factor or pre-exponential constant, E_a is the activation energy, T is the absolute temperature in Kelvin and R is the gas constant i.e. 8.314×10^{-3} $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Taking natural logarithms on both sides, Eq. (12) becomes:

$$\ln K_r = \ln A - E_a/RT \qquad \ldots (15)$$

K_r values are being obtained from the slope of the lines given in Fig. 8 at corresponding temperatures. The plot of $\ln K_r$ versus 1/T is shown in Fig. 10 for aluminium extraction. According to Eq. (15), the apparent activation energy can be calculated from the slope of the straight line.

A higher activation energy implies that a surface reaction (~62 kJ/mol) dominates the dissolution kinetics, while a lower activation energy suggests that diffusion (~20 kJ/mol) is the rate controlling step[30, 12]. In the present study, aluminium extraction from fly ash is interface-limited and the activation energy of the overall reaction is calculated as about 60.85 kJ/mol (14.54 kcal/mol). This activation energy is near the values of activation energy of 45.9 kJ/mol calculated for sodium hydroxide leaching of a gibbsitic bauxite[31], 48.15 kJ/mol calculated for oxidative ammonia leaching of sphalerite[32], 34 kJ/mol calculated for oxidative sodium hydroxide leaching of mechanically activated low-grade wolframite concentrate[33] and 41.1 kJ/mol calculated for sulphuric acid leaching of spent nickel oxide catalyst[34]. The activation energy in a heterogeneous reaction system can also be used to distinguish between transport-controlled reactions, surface chemical reactions, or mixed reactions. In general the activation energy of a diffusion-controlled process is characterized as being 1 to 3 kcal/mol[35], 2 to 5 kcal/mol[36] or 3 to 6 kcal/mol[37]. In addition, the activation energy for a chemically controlled process is usually greater than 10 kcal/mol[35] or more specifically falls between 10 to 20 kcal/mol[36]. The activation energy calculated using the Arrhenius equation further confirms the rate controlling step and it shows that the leaching of fly ash in sulphuric acid is a surface chemical reaction controlled process.

The kinetic model for the leaching process of aluminium from fly ash is represented as

$$1-(1-X)^{1/3} = 2.82 \times 10^5 e^{\frac{-60.85}{RT}} t \qquad \dots (16)$$

where $2.82*10^5$ is the pre exponential factor A in hour^{-1}, R is the universal gas constant, T is the temperature in Kelvin, t is time in hour and 60.85 kJ/mol is the activation energy (E_a).

Conclusion

In the present study, the shrinking core model was used to study aluminium extraction kinetics from coal fly ash using H_2SO_4 as a leaching medium. The effect of solid to liquid ratios and temperature on leaching of aluminium from coal fly ash was investigated. Results indicated that the extraction rate of aluminium increased significantly with temperature and solid to liquid ratios. Extraction efficiency of about 68.68% of the aluminium present in the coal fly ash was achieved under the following conditions: temperature 220°C, reaction time 4 hour, sulphuric acid concentration 18 M and solid to liquid ratio 1:3 (Fly ash (g) / sulphuric acid (mL)). The kinetic study indicated that leaching of aluminium was the surface chemical reaction controlled process for all leaching times, and the reaction rate increased with temperature giving a leaching rate constant of 0.0274 hour^{-1} at 180°C and then it increased to 0.1008 hour^{-1} at a temperature of 220°C. Also the results showed that the effect of solid to liquid ratio on the leaching rate was significant, presenting a leaching rate constant of 0.0546 hour^{-1} at 1:2 and 0.1076 hour^{-1} at 1:4 solid to liquid ratio. The activation energy was calculated as about 60.85 kJ/mol (14.54 kcal/mol) which is consistent with values of activation energies reported for surface controlled reactions.

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