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Alumina Extraction from Coal Fly Ash via Low-Temperature Potassium Bisulfate Calcination

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Abstract: Owing to the depletion of bauxite and increasing demand for alumina, calcination methods for extracting alumina from coal fly ash (CFA) were developed. However, these methods have disadvantages such as the need for high temperatures and the emission of toxic gases. Hence, in this study, Al_2O_3 was extracted from CFA via low-temperature potassium bisulfate calcination technology. Effects of the potassium bisulfate amount, calcination temperature, and calcination time on the alumina extraction efficiency were investigated using X-ray diffraction, thermal gravimetry, scanning electron microscopy, differential scanning calorimetry, and energy-dispersive spectroscopy. It was found that this technique could recover alumina efficiently, and potassium bisulfate significantly contributed to the degradation of mullite and corundum phases. Al_2O_3 in CFA was converted into soluble $\text{K}_3\text{Al}(\text{SO}_4)_3$. With a $\text{KHSO}_4/\text{Al}_2\text{O}_3$ molar ratio of 7:1, calcining temperature of 230 °C, and calcining time of 3 h, the alumina extraction efficiency reached a maximum of 92.8%. The Avrami–Erofeev equation showed the best fit with the kinetic data for the low-temperature calcination of CFA with KHSO_4 . The activation energy was 28.36 kJ/mol.

Keywords: coal fly ash; potassium bisulfate; low-temperature calcination; alumina extraction

1. Introduction

The discharged amount of coal fly ash (CFA) from high-temperature coal-burning power plants is expected to be 560 to 610 Mt/year based on the China Electric Power Federation forecast from 2016 to 2019 [1]; it will exceed three billion tons by 2020 in China and is behind only the tailings found in industrial solid waste [2]. Uncontrolled aggregation and discharge make CFA a main potential source of dangerous chemicals that could be released into the environment [3,4]. To enhance its utilization effectiveness, researchers made considerable efforts to study the potential of using CFA as a raw material for soil modification, production of glass/ceramics, zeolites or geopolymers, and metal extraction [5–7]. In particular, the CFA discharged in Shanxi and Inner Mongolia contains more alumina (40–50%) than the boundary bauxite in China and is a non-bauxite aluminum resource with high development and utilization potential [8]. The alumina industry of China imported more than 60 million tons of bauxite in 2017 [9]. Therefore, the depletion of bauxite reserves and increases in the alumina demand promoted studies on alumina extraction from high-alumina CFA in China [10].

CFA is generated at very high temperatures and consists of mullite, quartz, and some amorphous phases. Specifically, mullite is a major inactive source of Al in CFA [11]. Several processes for extracting alumina from CFA were reported and can be broadly classified into acid [12–15], alkali [16–19],

and sintering processes [20]. Acid processes can effectively achieve the separation of silica and alumina in CFA [21,22]. However, acid processes inevitably cause serious equipment corrosion and, thus, require expensive acid-resistant equipment. In addition, impurities such as iron oxide and calcium oxide are difficult to remove from the leaching solution [23]. Alkali processes can achieve high alumina extraction efficiency, but the alkali solutions with high concentrations used in these processes cause a high caustic ratio in the final solution. Sintering processes are considered to have significant potential for industrial use as they are similar to the major extraction technologies currently used in the Al_2O_3 plants [24]. However, the use of calcination is limited by the formation of more toxic gases and the reduced activation effectiveness at high temperatures. Nevertheless, the use of additives (e.g., lime and ammonium sulfate) during heating can lower the calcination temperature and promote Al_2O_3 extraction [25,26]. One of the advantages of these additives is that they are widely available at low costs. There are some limitations of these processes. Alumina extraction from CFA through sintering is costly, and the residual red mud generated because of the high reaction temperature and lime addition is a new pollutant. As reported earlier, adding low amounts of lime to CFA increases the alumina dissolution to 94.5% during calcination at 1050 °C and leaching in an alkaline solution [27]. High-purity alumina was produced through sintering, leaching, $\text{NH}_4\text{Al}(\text{SO}_4)_2$ precipitation, and calcination of fly ash and ammonium sulfate. With this method, the Al extraction rate under optimized conditions was 90.11% [28]. Van der Merwe et al. [29] used either ammonium sulfate or ammonium bisulfate or a mixture of the two salts as an extracting agent for recovering aluminum from ultrafine CFA during a 2-h thermal treatment process at different processing temperatures.

Although thermal activation improves alumina extraction, problems such as the need for high calcination temperatures and release of toxic gases like NH_3 still exist. Therefore, to facilitate Al_2O_3 extraction from CFA via thermal treatment, researchers have to develop efficient methods that can decrease the calcination temperature, as well as the release of poisonous gases.

Hence, in this study, a novel thermal activation method based on potassium bisulfate (KHSO_4) was established for alumina extraction from high-alumina CFA; this method was aimed at inhibiting the formation of toxic gases and reducing the calcination temperature in comparison to conventional NH_4HSO_4 sintering. The thermal behavior, phase conversion, and alumina extraction rates under different conditions were studied. Next, the reaction kinetics were calculated and fitted with a theoretical model. Finally, the mechanisms of CFA activation and alumina extraction were explored.

2. Experimental

2.1. Materials

CFA was collected from the Jungar Power Plant in Inner Mongolia, China, and its chemical composition is given in Table 1. Clearly, over 85 wt.% of the CFA is composed of Al_2O_3 and SiO_2 . Al_2O_3 accounts for up to 51.7 wt.% of CFA, which makes CFA a possible non-bauxite resource for Al_2O_3 generation. It also contains traces of CaO , TiO_2 , Fe_2O_3 , K_2O , FeO , MgO , and Na_2O .

Table 1. Composition of the coal fly ash (CFA) (wt.%).

Component	Al_2O_3	SiO_2	CaO	TiO_2	Fe_2O_3	K_2O	FeO	MgO	Na_2O	LOI ^a
Content	51.70	36.30	2.68	1.75	1.28	0.34	0.30	0.24	0.09	2.21

^a Loss on ignition.

Analytical-grade KHSO_4 was purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). All the substances were also of analytical grade.

2.2. Procedures

The new method is schematically illustrated in Figure 1. Each time, CFA (10 g) was blended fully with KHSO_4 , followed by thermal treatment. The $\text{KHSO}_4/\text{Al}_2\text{O}_3$ molar ratio was 4, 5, 6, 7, or 8.

Then, the mixtures placed in quartz crucibles were heated at 5 °C/min in a KY-R-ST80 muffle furnace to different target temperatures ranging from 190 to 250 °C. Once the desired temperatures were reached, the corresponding crucibles were left for calcination from 1–4 h. Subsequently, the crucibles were cooled naturally. After that, the product was suspended in distilled water at a concentration of 1 g/3 mL in a beaker, which was heated to 100 °C and mixed for 30 min. The beaker was then cooled naturally. The beaker contents were filtered and rinsed with deionized water repeatedly. Then, alumina level in the leachate was detected by ethylenediamine tetraacetic acid–potassium fluoride (EDTA–KF) titrimetry [30].

Figure 1. Flow diagram of the new calcination method for alumina extraction from coal fly ash (CFA).

2.3. Characterization

The alumina level in the filtrate obtained after washing the contents in the beaker with deionized water was detected via ethylenediamine tetraacetic acid–potassium fluoride (EDTA–KF) titrimetry [30]. The chemical compositions of the CFA, calcined products, and residue were measured via X-ray fluorescence analysis (XRF, Axios, PANalytical, Almelo, The Netherlands).

Crystalline phases of the CFA and calcined products were investigated via X-ray diffraction (XRD, 6100, Shimadzu, Kyoto, Japan) using Cu K α radiation with the following parameters: acceleration voltage = 40 kV, current = 30 mA, scanning angles ranging from 5° to 60°, and scanning speed of 2°/min.

Thermal gravimetry–differential scanning calorimetry (TG–DSC) was conducted using an STA449C integrated instrument (Netzsch, Selb, Germany) under N₂ flow; samples weighing 10 mg were heated from 25 to 700 °C at a heating rate of 5 °C/min.

Morphologies of the CFA, calcined products, and residue were characterized via scanning electron microscopy (SEM, 7500F, JEOL, Tokyo, Japan), and chemical compositions were analyzed via energy-dispersive spectroscopy (EDS).

The Al concentration in the filtrates was detected using EDTA–KF titrimetry with alumina as the standard. The alumina extraction rate ($\omega(\text{Al}_2\text{O}_3)$) was computed as follows:

$$\omega(\text{Al}_2\text{O}_3) = \frac{m_F(\text{Al}_2\text{O}_3)}{m_{FA}(\text{Al}_2\text{O}_3)}, \quad (1)$$

where $m_{FA}(\text{Al}_2\text{O}_3)$ is the Al_2O_3 mass in the fly ash, and $m_F(\text{Al}_2\text{O}_3)$ is that in the filtrate. Each experiment was carried out thrice, and the mean was calculated. The uncertainty for alumina was set at $\pm 2\%$.

3. Results and Discussion

3.1. TG–DSC Results

Figure 2 presents the weight loss and heat flow data of pure KHSO_4 and that of the fly ash with KHSO_4 . The DSC curve of pure KHSO_4 showed several exothermic and endothermic peaks in the range of 100–750 °C (Figure 2a). The peaks at 199 °C and 217 °C correspond to the melting and phase conversion of KHSO_4 to $\text{K}_2\text{S}_2\text{O}_7$ with a mass loss of approximately 6.35%. From 350 °C to 550 °C, KHSO_4 or $\text{K}_2\text{S}_2\text{O}_7$ slowly transformed to K_2SO_4 with a mass loss of approximately 6.98%. The rapid degradation when the temperature reached approximately 590 °C indicates the completion of the phase transition.

Figure 2. Thermal gravimetry–differential scanning calorimetry (TG–DSC) curves: (a) pure KHSO₄ and (b) CFA blended with KHSO₄.

The DSC curve of the fly ash with KHSO₄ showed endothermic peaks from 71 to 226 °C (Figure 2b). The first peak at 71 °C indicates a mass loss of 0.4% owing to the elimination of physically adsorbed water. The second peak at 180–270 °C indicates a mass loss of 3.15% and coexists with two peaks at 206 and 226 °C, which correspond to the melting of KHSO₄ and transformation of minor KHSO₄ into K₂S₂O₇ and active reaction of KHSO₄ with CFA, respectively [31]; the reaction is shown in Equation (2). The third mass loss of 6.37% at 400–570 °C, together with another peak, corresponds to the burning of unburnt carbon in CFA [32,33]. The exothermic and endothermic peaks from 350 °C to 550 °C are not present in Figure 2b, suggesting that KHSO₄ completely reacted with CFA.

3.2. Effects of Calcination Parameters on Alumina Extraction Efficiency

Figures 3–5 show the effects of the calcination temperature, KHSO₄/Al₂O₃ molar ratio, and calcination time on the efficiency of alumina extraction from CFA, respectively. The error bar represents the standard error of the mean when comparing all values. As the temperature increased, the extraction efficiency improved gradually, reached a maximum of 92.8% at 230 °C, and then increased gently. At KHSO₄/Al₂O₃ molar ratios < 6, increasing KHSO₄ dosage most significantly improved the alumina extraction efficiency, which reached 88.3% at a molar ratio of six. The alumina extraction efficiency increased up to 92.8% at a ratio of seven, but slightly reduced to 92.7% when the molar ratio further increased to eight. Moreover, the alumina extraction efficiency nearly reached its maximum value after 3 h of reaction (Figure 5) but did not significantly improve with further prolonging of the reaction time.

Figure 3. Effects of calcination temperature on alumina extraction from CFA at a reaction time of 3 h and KHSO₄/Al₂O₃ molar ratio of seven.

Figure 4. Effects of KHSO₄/Al₂O₃ molar ratio on alumina extraction from CFA at a calcination temperature of 230 °C and time of 3 h.

Figure 5. Effects of calcination time on alumina extraction from CFA at 230 °C and a KHSO₄/Al₂O₃ molar ratio of seven.

3.3. Decomposition Mechanism

To explore how KHSO₄ addition activated CFA and the underlying mechanism, we investigated the crystallographic structures of the CFA, calcined products, and residue via XRD.

As shown in Figure 6, the main crystal phase in the calcined products was K₃Al(SO₄)₃, without mullite or corundum. This result suggests that KHSO₄ actively reacted with the CFA, which considerably accelerated the degradation of mullite and corundum. The low-temperature thermal decomposition of CFA by KHSO₄ can be understood through the following reactions:

As shown in Figure 7, the dominant crystal phases of CFA were mullite and corundum, which correspond to peaks at $2\theta = 16.5^\circ, 25.9^\circ, 26.2^\circ, 35.2^\circ$, and 40.8° and at $25.6^\circ, 37.8^\circ, 43.4^\circ$, and 64.5° , respectively. The evident bulge at $2\theta = 22^\circ$ corresponds to tridymite and cristobalite [34]. After calcination at 190 °C, the mullite ($16.5^\circ, 25.9^\circ, 26.2^\circ, 35.2^\circ$, and 40.8°) and corundum peaks ($25.6^\circ, 37.8^\circ, 43.4^\circ$, and 64.5°) gradually weakened in intensity, while the slight peaks of amorphous silicon

oxide from 18° to 24° became stronger. This was because the mullite and corundum in CFA containing KHSO_4 degraded under these conditions. These results are consistent with the alumina extraction rate of 54.7% given in Figure 3. Furthermore, at 210°C , the corundum (25.6° , 37.8° , 43.4° , and 64.5°) peaks disappeared, indicating the nearly complete decomposition of corundum. Nevertheless, some mullite peaks remained. Accordingly, the Al_2O_3 extraction rate at 340°C improved to 80.6%. At 230°C , amorphous quartz also showed peaks from 18° to 24° , suggesting that mullite also fully degraded, and the alumina extraction efficiency increased to 92.8%. At 250°C , 93.1% of alumina was extracted from CFA, suggesting that the diffraction peaks of the residue changed little compared to those at 230°C .

Figure 6. X-ray diffraction (XRD) patterns of products calcined at 230°C with a $\text{KHSO}_4/\text{Al}_2\text{O}_3$ molar ratio of seven for 3 h.

Figure 7. XRD spectra of CFA and residue changing with calcination temperatures.

At a $\text{KHSO}_4/\text{Al}_2\text{O}_3$ molar ratio of four, the typical peaks of mullite and corundum weakened in intensity (Figure 8). When the ratio increased to five, these characteristic peaks weakened further. Moreover, the peaks of mullite at $2\theta = 26.2^\circ$ and those of corundum at 25.6° and 37.8° were hardly visible. Additionally, the alumina extraction rates were below 70%, indicating the incomplete reactions of KHSO_4 with mullite and corundum. At a molar ratio of six, the main peaks of mullite at $2\theta = 16.5^\circ$ and 25.9° and those of corundum disappeared; however, the peaks of mullite at 26.2° , 35.2° , and 40.8° reduced in intensity, and the alumina extraction efficiency nearly reached a maximum of 88.3%. At $\text{KHSO}_4/\text{Al}_2\text{O}_3$ molar ratios > 7 , neither the mullite nor the corundum peaks could be found,

and the alumina extraction efficiency slightly increased, implying that the NaHSO_4 dosage could be excessive. Therefore, 7:1 was considered the optimal $\text{KHSO}_4/\text{Al}_2\text{O}_3$ molar ratio.

Figure 8. XRD spectra of CFA and residue at different $\text{KHSO}_4/\text{Al}_2\text{O}_3$ molar ratios.

As shown in Figure 9, after 1 h of calcination, the peaks of mullite (16.5° , 25.9° , 26.2° , 35.2° , and 40.8°) and corundum (43.4° and 64.5°) gradually reduced in intensity, while the peaks of corundum at 25.6° and 37.8° disappeared. After 2 h of calcination, the characteristic peaks of mullite (26.2° , 35.2° , and 40.8°) and corundum (43.4° and 64.5°) weakened in intensity, while the other mullite peaks (16.5° and 25.9°) disappeared. As the calcination time increased to 3 h, the characteristic peaks of neither mullite nor corundum could be found in the spectra. Considering the results presented in Figures 5 and 9, it was concluded that the mineral phases of mullite and corundum in CFA were almost fully degraded by KHSO_4 during low-temperature calcination. After 4 h of calcination, the characteristic peaks did not significantly change in terms of their intensity, suggesting the reaction between CFA and KHSO_4 was not completed until 3 h. Thus, 3 h was considered the optimal calcination time for ensuring the complete reaction.

Figure 9. XRD spectra of CFA and residue at different time periods of calcination.

3.4. Analysis of Reaction Kinetics Using Kinetic Model

Chemical reactions involving solid reactants occur at the reactant interface to form compounds [35]. The reactions do not continue without the diffusion of products and will proceed at the interface of one or both reactants. As the mechanisms of these reactions depend on the test conditions and on the properties of the solids, the overall process rate may be controlled by chemical kinetics or transport processes.

The kinetic models considered in recent studies are listed in Table 2 [36]. Considering the reaction data obtained in this study, models (1)–(5) were considered highly suitable for describing these reactions, with a correlation coefficient higher than 0.98. This implies that the reaction is limited by the diffusion of reactants through the product layer. It is also obvious that the kinetic data show the best fit with the Avrami–Erofeev equation at all temperatures.

Table 2. Fitting results obtained using several kinetic models.

Limiting Step	Equation	R^2		
		190 °C	210 °C	230 °C
1. Deformation of Avrami–Erofeev equation	$\ln[-\ln(1-\alpha)] = n \ln t + n \ln k$	0.99573	0.99644	0.99755
2. Diffusion through the product layer (sp)	$1 - 3(1-\alpha)^{2/3} + 2(1-\alpha) = kt$	0.98859	0.98359	0.98212
3. Diffusion through the product layer (pp)	$\alpha^2 = kt$	0.98500	0.98859	0.98627
4. Diffusion through the product layer (cp)	$\alpha + (1-\alpha) \ln(1-\alpha) = kt$	0.99010	0.98909	0.98975
5. Diffusion through the liquid film (sp)	$\alpha^2 = kt$	0.89787	0.90375	0.89545
6. Surface chemical reactions (cp)	$\alpha + (1-\alpha)^{1/2} = kt$	0.95330	0.96554	0.97435
7. Surface chemical reactions (sp)	$\alpha + (1-\alpha)^{1/3} = kt$	0.96794	0.97994	0.99006
8. New shrinking core model	$1/3 \ln(1-\alpha) + [(1-\alpha)^{-1/3} - 1] = kt$	0.94335	0.89564	0.84721

sp—spherical particles, pp—plate particles, cp—cylindrical particles, k —a chemical constant, α —the degree of alumina extraction efficiency, and t —the leaching time.

The Avrami–Erofeev equation based on the concept of nucleation and nuclei growth [37] can successfully explain the leaching kinetics of various solid–liquid reactions [38,39]. In this study, the kinetics of the reaction between CFA and KHSO_4 were analyzed using the Avrami–Erofeev equation, given as follows:

$$-\ln(1-\alpha) = (kt)^n, \quad (7)$$

where α , k , and t are the alumina extraction efficiency, rate constant, and time of the reaction, respectively, and n is the mechanism-specific Avrami exponent. Equation (7) can be linearly converted to Equation (8).

$$\ln[-\ln(1-\alpha)] = n \ln t + n \ln k. \quad (8)$$

The reaction kinetics were analyzed using the data acquired at 210, 220, and 230 °C, and the results are presented in Table 3. The exponent n is equal to the slope of the straight line in the plot of $\ln[-\ln(1-\alpha)]$ versus $\ln(t)$, and the rate constant k can be calculated from the intercepts, as shown in Figure 10.

The apparent activation energy was calculated using the Arrhenius equation based on the results presented in Table 2. The values of R^2 suggest that this equation reasonably fits with the experimental data. The apparent activation energy, equal to the slope of the straight line in the plot of the natural logarithm of the reaction rate versus $1000/T$ (Figure 11), was 28.36 kJ/mol with R^2 equal to 0.98666. These kinetic calculation results will be highly valuable for performing parameter adjustments and scaling up alumina production.

Table 3. Reaction kinetics calculated using data acquired at 210, 220, and 230 °C.

Temperature (°C)	Order, n	Rate Constant, k	R^2 , Linear Regression Fit
210	0.8716	0.010106649	0.99573
220	0.94872	0.011215829	0.99644
230	1.08314	0.013399652	0.99755

Figure 10. Kinetic plots obtained using the Avrami–Erofeev equation at 210, 220, and 230 °C.

Figure 11. Plots of $-\ln(k) \cdot R$ versus $1000/T$ to determine activation energy.

3.5. SEM and EDS Results

The SEM and EDS images of CFA and the residue are shown in Figures 12 and 13, respectively. The raw CFA comprised size-variable spherical bodies, having a smooth surface, composed of mullite or aluminosilicate glass resulting from the reactions between alumina and SiO_2 during coal combustion (Figure 12). These results agree with those reported in earlier studies [40,41]. EDS analysis showed that the major elements in the CFA were Si, Al, Ca, and O constituting different compounds in CFA. Al was mainly related with Si. The particle diameter of the residue was approximately 2–5 μm (Figure 13). The general structure of CFA was damaged, and the mullite on the spherical surface was fully degraded during low-temperature calcination. EDS showed that the proportions of major elements in these particles differed significantly from those presented in Figure 12. EDS mapping showed the major component was amorphous silica, which is in accordance with the XRD images. Table 4 presents the chemical composition of the residue after alumina extraction. Compared to the chemical composition of CFA in given Table 1, the Al_2O_3 content was reduced from 51.70% to 13.88%, and SiO_2 content increased from 36.30% to 70.32%. This shows that most of the aluminum components in CFA were extracted, while the silica components were retained in the residue. This eliminates the separation process of silica and aluminum that is required in alkali processes and reduces slag production compared to the alkali or alkali lime calcination processes; therefore, the discharge of solid waste and the resulting environmental pollution are reduced. The SiO_2 content in the residue is high, and its activity is high as well. It can be used as a raw material to prepare silicon-based products, such as zeolite, tobermorite, xonotlite, and geopolymers [5,42–44].

Figure 12. SEM and energy-dispersive spectroscopy (EDS) images of CFA.

Figure 13. SEM and EDS images of residue.

Table 4. Composition of the residue (wt.%).

Component	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	Fe ₂ O ₃	K ₂ O	FeO	MgO	Na ₂ O	LOI ^a
Content	13.88	70.32	1.93	2.12	1.15	1.18	0.18	0.22	0.19	7.32

^a Loss on ignition.

Figure 14 shows the SEM images of CFA and the residue after calcination at 230 °C at different durations. After 1 h of calcination, the structure of CFA was eroded by KHSO₄, showing holes and depressions to different degrees, as well as rough spherical surfaces (Figure 14); thus, the activation of KHSO₄ started to destroy the surface structure of CFA. When the reaction proceeded for 2 h, the spherical particles were eroded further, and they started to break. The entrapped globules were exposed and released, and they continued to react with KHSO₄. At a calcination time of 3 h, the spherical particles were completely destroyed, and the entrapped globules were all released. The Si–O–Al bonds in mullite were broken so that alumina could be extracted.

Figure 14. SEM images of CFA and residue after calcination at 230 °C for different durations: (a) CFA; (b) 1 h; (c) 2 h; (d) 3 h.

4. Conclusions

(1) A new method for Al₂O₃ extraction from CFA was proposed by adding KHSO₄ at low calcination temperatures. This method offers the following advantages: low energy consumption, no emission of toxic gases, high extraction efficiency, economical, and environmentally friendly.

(2) The reaction between CFA and KHSO₄ formed soluble K₃Al(SO₄)₃. The calcination temperature, KHSO₄/Al₂O₃ molar ratio, and duration of calcination considerably impacted the Al₂O₃ extraction rate. The extraction efficiency of alumina from CFA reached up to 92.8% with a KHSO₄/Al₂O₃ molar ratio of 7:1 when calcination was carried out at 230 °C for 3 h.

(3) The Avrami–Erofeev equation showed the best fit with the kinetic data for low-temperature calcination of CFA with KHSO₄. The activation energy was 28.36 kJ/mol.

(4) XRD results showed that the mullite and corundum in CFA almost decomposed under the abovementioned optimum conditions, and the residue was mainly composed of SiO₂. SEM results showed that the spherical CFA particles decomposed completely during low-temperature calcination, and EDS mapping also showed that the residue was primarily composed of SiO₂.

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