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Kinetics of decomposition of mullite and corundum in coal fly ash under highly alkaline condition

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Abstract: Decomposition kinetics of mullite and corundum in coal fly ash with highly alkaline solution was studied. The effects of the reaction temperature and reaction time on decomposition rates of mullite and corundum and alumina extraction efficiency were investigated. The results show that increasing reaction temperature and reaction time increases the decomposition rates of mullite and corundum and alumina extraction efficiency, with the decomposition temperature of mullite lower than that of corundum. After 90 min reaction at 220 °C, more than 100 g alumina was extracted when recycling 1 L of alkaline solution. The decomposition processes of mullite and corundum corresponded with the shrinking unreacted core model, and the reaction rate was under chemical reaction control, with the activation energies of mullite and corundum being 67.46 and 161.82 kJ/mol, respectively. **Key words:** coal fly ash; mullite; corundum; decomposition kinetics; alumina

1 Introduction

Coal fly ash (CFA) is an important solid waste produced by coal-fired power plants, with its annual production in China currently exceeding 5.8×10^8 t [1]. Despite the successful applications of some of the produced CFA in metal recycling and building/functional materials production [2-5], large amounts of CFA are currently in storage, causing soil, ground water, and air pollution [6-8]. The alumina content of CFA in some parts of North-Western China, can reach as high as 40%-50% [9] and is a potential bauxite substitute for producing alumina. The annual production of high-alumina CFA is estimated to be 3×10^7 t, containing $(1.2-1.5)\times 10^7$ t of alumina [10]. The alumina in CFA is particularly important in light of the scarcity of Chinese bauxite resources, with bauxite import reaching 5.58×10⁶ t in 2015 [11]. Hence, alumina extraction from CFA has become the focus of numerous research projects.

Considerable researches have been performed on alumina extraction from CFA, mainly involving acid leaching [12,13], sintering [14–16], and hydro-chemical

extraction [17,18]. However, acid leaching inevitably causes severe equipment corrosion and generates gaseous pollutants [19,20], whereas sintering requires high reaction temperatures (1100-1300 °C), incurring high energy costs [21,22]. In contrast, hydro-chemical extraction is amenable for large-scale production due to its moderate reaction conditions and wet process. The hydro-chemical process can effectively extract alumina from CFA by transforming the silica into insoluble alumina-free NaCaHSiO4 using a mixed alkaline (NaOH + Ca(OH)₂) solution. The caustic ratio (Na₂Oto-Al₂O₃ molar ratio) of the alkaline solution must be higher than 10:1. Thus, only 30 g of alumina can be extracted when recycling 1 L of the alkaline solution, which is much lower than the 120 g that can be extracted via the traditional Bayer process [23]. The high silica content (~40%) of CFA will result in large amounts of solid residues, which cannot be used efficiently because of their high alkali content [24]. To date, the industrial extraction alumina from CFA via hydro-chemical processes has not been achieved.

Previous studies indicated that the inert mullite and corundum in CFA could be decomposed in highly alkaline solutions [25,26]. Furthermore, CFA is mainly

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composed of mullite, corundum, and amorphous silica. Approximately half of the silica in CFA exists in the form of amorphous silica and can easily be removed by the pre-desilication process [27]. Therefore, in the current study, alumina extraction from CFA was performed under highly alkaline conditions (only NaOH). Amorphous silica in the CFA was firstly removed by a pre-desilication process to increase alumina content. The pre-desilicated CFA (PCFA), which mainly contained mullite and corundum, was used as a raw material for the preparation of alumina. The effects of the reaction temperature and time on the alumina extraction efficiency were also determined. To better understand the alumina extraction mechanism, the decomposition processes of mullite and corundum were systematically investigated. In addition, the kinetic behavior of the above decomposition was evaluated and experimental data were fitted with theoretical equations to gain mechanism insights and promote the application of alumina extraction from CFA. Thus, a reference is provided for the utilization of other mullite- or corundum-containing solid wastes (e.g. aluminum dross).

2 Experimental

2.1 Materials

CFA was obtained from a thermal power plant located in Inner Mongolia, China, and dried at 100 °C for 12 h in an oven prior to analysis.

The PCFA was prepared according to the following steps. Raw CFA was milled in a Teflon resin mill chamber using zirconia balls. The milled CFA was then reacted with acid solution, and the slurry was filtered to obtain the acid-treated CFA. Finally, the acid-treated CFA reacted with an alkali solution to obtain PCFA.

All reagents were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd., China, and deionized water was used throughout the experiments.

2.2 Experimental principles

In this work, the alumina extraction from PCFA and the decomposition of mullite and corundum under highly alkaline conditions were investigated. According to previous studies [17,26], this process can be modeled by the following equations:

 $3Al_2O_3 \cdot 2SiO_2 + 10NaOH + 7H_2O = 2Na_2SiO_3 + 6NaAl(OH)_4$ (1)

 $Al_2O_3 + 2NaOH + 3H_2O = 2NaAl(OH)_4$ (2)

 $SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$ (3)

 $6NaAl(OH)_4 + 6Na_2SiO_3 = Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2 +$

$$10NaOH+4H_2O \tag{4}$$

Utilizing standard Gibbs energies taken from the

thermodynamic data manual [28], we calculated the standard Gibbs energies $(\Delta_r G^{\Theta})$ of dissolution within a temperature range of 25–325 °C, as summarized in Fig. 1. Importantly, all obtained $\Delta_r G^{\Theta}$ values were negative, indicating that the above reactions are thermodynamically feasible. However, the decomposition of corundum was less thermodynamically favorable than that of mullite, and required harsher conditions.



Fig. 1 Standard Gibbs energy change versus temperature for dissolution reactions under highly alkaline conditions

2.3 Experimental methods

Experiments were performed in a 5 L high-pressure autoclave fitted with internal cooling and external heater systems. The autoclave was protected by a pure nickel vessel from corrosion due to the highly alkali solution. An automatic proportional, integral and derivative (PID) control system was used to adjust the heating rate, agitation, and temperature of the autoclave. A sampling pipe was inserted into the bottom of the autoclave to enable real-time sampling during the reaction.

A solution of sodium aluminate (3 L) reacted with PCFA at an initial caustic ratio of 25:1, Na₂O concentration of 370 g/L, and liquid-to-solid (L/S) mass ratio of 5:1. The above solution was prepared by mixing and dissolving pure H₂O, NaOH, and Al(OH)₃. The effects of the reaction temperature and time on the decomposition of mullite and corundum were investigated. The leached slurry was filtered, and the residue was washed three times with deionized water at 80 °C and dried at 100 °C for 24 h. After drying, the liquor and residue were analyzed to determine their chemical and mineralogical compositions.

2.4 Characterization techniques

The chemical compositions of the dried solid residue and liquor were examined by inductively coupled plasma-optical emission spectroscope (ICP-OES, Optimal 5300DV, PerkinElmer Instruments, 1300 W, peristaltic pump flow 1.5 L/min, carrier gas flow 0.08 L/min). The crystalline phases and morphologies were characterized by X-ray diffractometry (XRD, X'Pert ProMPD, Panalytical, Cu K_{α} radiation, 40 kV, 100 mA) and scanning electron microscope (SEM, JSM7100F), respectively.

The extents of mullite and corundum decomposition were determined by quantitative XRD analysis [29]. The matrix-flushing method was successfully used to determine the extent of crystal phase transformations by quantitative XRD analysis [30] and fitting the experimental data with the following equation:

$$I_n/I_i = K(x_n/x_i) \tag{5}$$

where I is the intensity of a given peak, x_n is the content of mullite or corundum (depending on n) in the PCFA, subscript i refers to the internal standard, and K is a constant that can be calculated from the XRD pattern of the mullite in PCFA and the internal standard using a diffraction peak area with the same order of magnitude, or the mixture of corundum in PCFA and the internal standard using a diffraction peak area with the same order of magnitude.

Zinc oxide was chosen as the internal standard. The strongest peaks of corundum and mullite, located at 2θ values of ~25.55° and ~26.34°, respectively, were chosen for kinetic analyses, with average values of *K* being 0.084 and 3.027, respectively. The amounts of unreacted mullite and corundum in the residue and the corresponding extents of decomposition were obtained

by analyzing the XRD patterns of the homogeneous mixtures of fixed amounts of the zinc oxide and residue.

3 Results and discussion

3.1 Raw material characterization

The chemical compositions of pristine CFA are listed in Table 1 with major constituents of Al₂O₃, SiO₂, Fe₂O₃, TiO₂, and CaO. Due to the presence of amorphous silica, the mass ratio of Al₂O₃ to SiO₂ of CFA was far lower than the theoretical value of mullite (2.55:1). After pre-desilication process, amorphous silica in the CFA can be efficiently removed, and the Al2O3 content was greatly improved. In addition, the mineralogical analyses of CFA and PCFA are shown in Fig. 2. Figures 2(a) and (b) show that the CFA consists of two major crystalline phases, mullite and corundum, and a considerable amorphous silica phase. The broad diffraction peaks at $2\theta = 19^{\circ} - 25^{\circ}$ indicated that the amorphous silica in the CFA was dominated by a glass phase [31]. Meanwhile, the CFA sample is composed of many inhomogeneous small spherical particles with smooth surfaces. Figures 2(c)

Table 1 Chemical compositions of CFA and PCFA (wt.%)

Sample	Al_2O_3	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO
CFA	49.88	38.72	2.02	1.38	2.76
PCFA	72.06	20.98	0.19	1.06	0.13



Fig. 2 XRD patterns (a, c) and SEM micrographs (b, d) of CFA (a, b) and PCFA (c, d)

and (d) showed that broad diffraction peaks $(19^{\circ}-25^{\circ})$ disappeared after pre-desilication. Furthermore, the smooth surface of the raw CFA particles disappeared entirely and revealed the inner structure of the particles. It demonstrated that the phases in PCFA were mainly mullite and corundum. This necessitated further study of the decomposition mechanism of these minerals in alumina extraction process.

3.2 Phase transformations and chemical composition analysis during alumina extraction

Figure 3 shows the XRD patterns of residues obtained at different reaction temperatures, showing that at 140 °C, these residues were mainly composed of mullite, corundum, and Na₈Al₆Si₆O₂₄(OH)₂(H₂O)₂, a basic sodalite [32]. This basic sodalite is well-known as a major constituent of the Bayer process residue [33,34]. As the reaction temperature was increased to 180 °C, the diffraction peaks of mullite disappeared completely, whereas those of corundum remained unchanged, disappeared only when the reaction temperature reached 220 °C. In addition, Fig. 4 shows the XRD patterns of



Fig. 3 XRD patterns of residues obtained at different reaction temperatures for 90 min



Fig. 4 XRD patterns of residues obtained in different reaction time at 200 °C

the residues sampled in different reaction time at 200 °C, showing that at 15 min, the diffraction peaks of mullite disappeared, those of Na₈Al₆Si₆O₂₄(OH)₂(H₂O)₂ appeared, and peaks of corundum were observed at 2θ values of ~25.55° and 57.42°, respectively. The corundum peaks lost intensity with increasing reaction time, and disappeared completely after 120 min. Figures 3 and 4 qualitatively show that the mullite decomposed faster than corundum, allowing the transformation of PCFA to Na₈Al₆Si₆O₂₄(OH)₂(H₂O)₂ to be divided into two parts, i.e. the mullite and corundum decomposition.

To further clarify the decomposition mechanism, the variations of liquor composition and Al₂O₃/SiO₂ mass ratio in leached residue were analyzed and the results are shown in Tables 2 and 3. Table 2 indicates that the Al₂O₃ content of the liquor exhibited only slight changes at reaction temperatures of 140-180 °C, and rapidly increased above 180 °C. Conversely, the SiO₂ and Na₂O contents sharply decreased with increasing the reaction temperature from 140 to 180 °C, and showed only slight changes above 180 °C. According to the XRD analysis (Fig. 3), the formation of $Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2$ reduced the SiO₂ and Na₂O contents of the liquor with increasing the reaction temperature from 140 to 180 °C, despite the concomitant dissolution of mullite. In addition, at reaction temperatures above 180 °C, the complete decomposition of mullite and decreased SiO₂ content of the liquor inhibited further formation of $Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2$, whereas the Al_2O_3 content of the liquor rapidly increased due to corundum decomposition. These observations confirmed that the mullite decomposed and transformed into Na₈Al₆Si₆O₂₄(OH)₂(H₂O)₂ under the highly alkaline conditions at reaction temperatures below 180 °C, whereas the decomposition of corundum only occurred at higher temperatures.

Table 3 shows that the Al_2O_3 content of the liquor gradually increased with increasing reaction time from 15 to 90 min, exhibiting only slight changes after 90 min, whereas those of SiO₂ and Na₂O decreased slightly with increasing reaction time. These results indicated that

 Table 2 Main liquor components and Al₂O₃/SiO₂ mass ratios of

 leached residue at different reaction temperatures for 90 min

			1	
Tommomotumo/9C	$ ho/(ext{g} \cdot ext{L}^{-1})$			Al ₂ O ₃ /SiO ₂
Temperature/ C	Al_2O_3	SiO_2	Na ₂ O	mass ratio
140	83.01	4.56	353.64	2.06
160	90.33	2.02	344.32	1.95
180	96.15	1.47	340.70	1.82
200	132.47	1.23	339.58	1.07
220	134.17	1.12	338.28	0.95

Table 3 Main liquor components and Al_2O_3/SiO_2 mass ratios of leached residue at 200 °C for different reaction time

Time	$ ho/(ext{g} \cdot ext{L}^{-1})$			Al ₂ O ₃ /SiO ₂
1 Ime/mm	Al_2O_3	SiO ₂	Na ₂ O	mass ratio
15	105.35	1.77	343.52	1.64
30	119.79	1.68	341.28	1.38
60	128.43	1.54	340.61	1.12
90	132.47	1.23	339.78	1.07
120	133.09	1.16	339.04	1.02

mullite decomposed rapidly and increasing reaction time allowed for the decomposition of corundum at 200 °C. The SiO₂ content in the leached liquor was very low, which is beneficial to the precipitation of sodium aluminate, similar to the Bayer process for alumina preparation.

Table 4 and Fig. 5 show the chemical composition and SEM image, respectively, of the leached residue obtained after reaction at 220 °C for 90 min. The residue is mainly composed of SiO₂, Al₂O₃, and Na₂O. This result agrees well with the XRD analysis. The residue exhibited a uniform size distribution and well-developed polyhedral crystals, and a similar morphology was observed in previous studies [35,36]. Furthermore, the extracted alumina was more than 100 g when recycling 1 L of the alkaline solution.

Table 4 Chemical composition of leached residue obtainedafter reaction at 220 °C for 90 min (wt.%)

Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	Na ₂ O
29.85	31.42	0.38	2.61	0.31	20.72



Fig. 5 SEM image of residue after reaction at 220 °C for 90 min

3.3 Decomposition kinetics of mullite and corundum

Since the alumina extraction efficiency is closely related to the decomposition of mullite and corundum,

the decomposition kinetics of these minerals was investigated. Figure 3 shows that the diffraction peaks of mullite and corundum disappeared after reaction at 180 and 220 °C for 90 min, respectively. Therefore, the decomposition kinetics of mullite was investigated at 120–180 °C in 20 °C interval and the decomposition kinetics of corundum was evaluated at 190–220 °C in 10 °C interval.

Figure 6 shows that the extent of mullite decomposition increased with increasing reaction temperature and time, with 49.87% of the mullite dissolved after reaction at 120 °C for 90 min, whereas the extent of decomposition increased to 76.13% after reaction at 160 °C for 45 min, and almost complete decomposition (95.38%) was observed after reaction at 180 °C for 30 min. Therefore, high reaction temperatures favored mullite decomposition. Similarly, Fig. 7 shows that the extent of corundum decomposition increased with increasing reaction temperature and time, reaching 95.61% after reaction at 220 °C for only 15 min, demonstrating that the reaction temperature significantly affected the decomposition of the PCFA constituents.



Fig. 6 Effect of reaction time and temperature on extent of mullite decomposition



Fig. 7 Effect of reaction time and temperature on extent of corundum decomposition

To determine the kinetic parameters and rate controlling step of the decomposition of mullite and corundum in the highly alkaline solution, the shrinking unreacted core model was applied to experimental data. According to this model, the rate of reaction between the solid particle and leaching reagent is controlled by one of the following steps: external diffusion, product layer diffusion, or chemical reaction. Furthermore, the reaction rate equations for the shrinking unreacted core model were previously determined [37].

When the reaction is under external diffusion control, we have

$$x = kt \tag{6}$$

When the reaction is under product layer diffusion control, we have

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = kt \tag{7}$$

When the reaction is under chemical reaction control, we have

$$1 - (1 - x)^{1/3} = kt \tag{8}$$

where x is the extent of reaction, k is the apparent reaction rate constant, and t is the reaction time. The fitting coefficients (R^2) for the mullite and corundum decomposition are listed in Tables 5 and 6, respectively. Through the comparison and analysis, the decomposition of mullite and corundum was best fit using the chemical reaction control model. Additionally, the linear relationships between $1-(1-x)^{1/3}$ and reaction time for

Table 5 Fitting coefficients R^2 of mullite decomposition data at 120–180 °C

	Fitting coefficient, R^2			
Temperature/ °C	External diffusion control	Product layer diffusion control	Chemical reaction control	
120	0.9284	0.9502	0.9969	
140	0.9163	0.9618	0.9971	
160	0.9429	0.9405	0.9925	
180	0.9310	0.9546	0.9897	

Table 6 Fitting coefficients R^2 of corundum decomposition data at 190–220 °C

_	Fitting coefficient, R^2			
Temperature/ °C	External diffusion control	Product layer diffusion control	Chemical reaction control	
190	0.9540	0.9490	0.9919	
200	0.9489	0.9573	0.9927	
210	0.9223	0.9612	0.9973	
220	0.9352	0.9378	0.9901	

the decomposition of mullite and corundum at different reaction temperatures are plotted in Figs. 8 and 9, respectively. The results indicated that the kinetics of the decomposition reaction of mullite and corundum agreed well with the shrinking unreacted core model.



Fig. 8 Plots of $1-(1-x)^{1/3}$ as function of reaction time at different reaction temperatures for mullite decomposition in highly alkaline solution



Fig. 9 Plots of $1-(1-x)^{1/3}$ as function of reaction time at different reaction temperatures for corundum decomposition in highly alkaline solution

Using the data in Tables 5 and 6, the apparent activation energies of mullite and corundum were calculated using the Arrhenius equation, and the kinetics data are plotted in Figs. 10 and 11 using the natural logarithm of the reaction rate as a function of 1/*T*. The apparent activation energy of mullite, which is equal to the slope of the straight line, was determined to be 67.46 kJ/mol, whereas the apparent activation energy of corundum was 161.82 kJ/mol. This indicates that corundum is more difficult to decompose than mullite under identical reaction conditions. In addition, the activation energy values (>40 kJ/mol) of mullite and corundum demonstrated that the decomposition process was controlled by chemical reactions [37].



Fig. 10 Arrhenius plot of mullite decomposition data at 120-180 °C



Fig. 11 Arrhenius plot of corundum decomposition data at 190–220 °C

4 Conclusions

(1) The alumina extraction efficiency and decomposition of mullite and corundum in CFA in a highly alkaline medium were investigated. The mullite decomposition rate reached 95.38% after reaction at 180 °C for 30 min, and that of corundum decomposition reached 95.61% after reaction at 220 °C for 15 min.

(2) The decomposition temperature of mullite was significantly lower than that of corundum. When recycling 1 L of the alkaline solution, more than 100 g of alumina was extracted after reaction at 220 °C for 90 min.

(3) The decomposition of mullite and corundum was best fit with the shrinking unreacted core model and the reaction rate was under chemical reaction control, with activation energies of dissolution determined to be 67.46 and 161.82 kJ/mol for the mullite and corundum, respectively.

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粉煤灰中莫来石及刚玉高碱溶液分解动力学

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摘 要: 对粉煤灰中莫来石和刚玉在高碱溶液分解动力学进行研究。考察反应温度和反应时间对莫来石和刚玉分 解率及氧化铝回收效率的影响。结果表明,升高反应温度及延长反应时间有利于莫来石、刚玉分解和氧化铝回收, 且莫来石的分解温度低于刚玉的分解温度。当在 220 °C 条件下反应 90 min 后,1L 循环碱液可回收多于 100 g 氧 化铝。莫来石和刚玉的分解过程符合收缩核模型,且反应速率受化学反应控制,二者的反应活化能分别为 67.46 和 161.82 kJ/mol。

关键词:粉煤灰;莫来石;刚玉;分解动力学;氧化铝

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