Applied Clay Science 161 (2018) 215–224

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

High-efficiency extraction of Al from coal-series kaolinite and its kinetics by calcination and pressure acid leaching

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ARTICLE INFO

Keywords:
Al extraction
Coal-series kaolin
Calcination
Pressure acid leaching
Leaching kinetics

ABSTRACT

High-efficiency extraction of Al from coal-series kaolinite and its kinetics by calcination and pressure acid leaching has been studied in detail. Calcination process promoted a phase transform from crystal kaolinite to amorphous compounds. Subsequently, Al occurred in the compounds was efficiently extracted by pressure acid leaching. At optimal conditions, the extraction rate of Al reaches 98.7%. Pressure leaching process of Al was successfully described by Avrami model, and mainly controlled by chemical reaction when apparent activation energy was 16.29 kJ/mol. The complex extraction process of Al in heated acid leaching (diffusion-reaction-diffusion) was transformed into a simple chemical reaction during pressure leaching so as to realize a high-efficiency extraction of Al from coal-series kaolinite.

1. Introduction

Coal-series kaolin, as a by-product of seam deposition in coal accumulating basins, has large reserves (about 3.8 billion tonnes in China) and is rich in Al_2O_3 (Querol et al., 2008; Ji et al., 2013). Calcination (550–900 °C) is essential for further applications of coal-series kaolin in rubber and cement industries, since raw coal-series kaolin has low activity (Wang et al., 2015; Cao et al., 2016). Main reactions occurred in calcinaiton are dehydroxylation of kaolinite and formation of metakaolinite amorphous phase, AS_2 (Liu et al., 2017a). Due to special chemical activity to consume CH produced during cement hydration so as to form calcium silicate hydrates (C—S—H), calcium aluminate hydrates (C—A—H) and calcium sulfo-aluminate hydrate (C—A—S—H) gel (Murat, 1983), calcined kaolin has been widely applied in cement industry. In addition, calcined kaolin also provides a cheap and important Al source for aluminium industry (Salahudeen et al., 2015; Aliyu et al., 2016), as a substitute of bauxite.

Although extraction processes of Al from kaolin (Foo et al., 2011; Liu and Yang, 2010; Zhang et al., 2012; Liu et al., 2017b), coal fly ash (Seidel and Zimmels, 1998; Jegadeesan et al., 2008; Tong et al., 2009; Cheng-You et al., 2012; Liu et al., 2012; Shemi et al., 2015; Luo et al., 2015) and chlorite (Okada et al., 2005) by heated acid leaching have been developed, the extraction rates of Al generally range from 40% to 90% (Yu, 2002; Wu et al., 2011; Zeng and Wang, 2012; Behera, 2017). The low extraction rate not only results in waste of Al source (Wang et al., 2016; Lei et al., 2016a), but also reduces utility value of leaching residue because the high-quality leaching residue (carbon-white) can be widely applied in rubber industry (Liu et al., 2005; Brahmi et al., 2014). More importantly, the extraction rate of Al from raw kaolin by acid leaching is very limited by stable structures of Al—O—Si and Si—O—Si (Cristobal et al., 2009; Tang et al., 2010) because conventional leaching methods have little influences on destroying crystal structure of kaolinite. Crystal structure of the kaolinite can be destroyed by calcination process, but hydrated silica formed during leaching reaction would hinder a contact between leaching agent and leaching nucleus (Yu, 2002; Luo et al., 2005; Feng et al., 2010). Hence Al source could not be efficiently extracted from calcined kaolin by heated acid leaching. Unlike the heated acid leaching, pressure acid leaching can reduce resistances caused by internal diffusion of leaching agents and external diffusion of Al at the presence of hydrated silica (Tan and Ma, 2009; Cheng-You et al., 2012), and transform the complex extraction process (diffusion-reaction-diffusion) into a simple chemical reaction. How to effectively extracted Al at the same time of preparing for porous silica combining calcination with pressure acid leaching has been one of the key problems for applications of coal-series kaolin (Lin and Dong, 2011; Zhu et al., 2014; Lei et al., 2016b). Moreover, the extraction mechanism of Al from calcined coal-series kaolin at pressure acid leaching is rarely reported, which seriously hinders the development of extracting Al from kaolin.

The objective of this study is to efficiently extract Al from coal-series kaolin by calcination and pressure acid leaching. The effects of calcination temperature and calcination time on extraction rates of Al were

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https://doi.org/10.1016/j.clay.2018.04.031
Received 25 June 2017; Received in revised form 19 April 2018; Accepted 21 April 2018

investigated. The interactive effects of different factors including leaching temperature, leaching time, acid concentration, calcination temperature and calcination time on Al extraction were also studied. The phase components and structure transformations of coal-series kaolin were determined to investigate the extraction mechanism of Al. The leaching kinetics of Al about leaching temperature, acid concentration and liquid-solid ratio was carried out to research the critical law of the pressure leaching process.

2. Materials and methods

2.1. Materials

Coal-series kaolin (Liu et al., 2017a) used in this study was obtained from the Yichang region in Hubei province, China. Content of Al_2O_3 of the coal-series kaolin is about 34.18 wt%. Main gangue minerals associated in the coal-series kaolin are quartz, anatase, pyrophyllite, feldspar.

2.2. Experiment and analysis methods

The raw coal-series kaolin was ground to < 44 μm, calcined at muffle furnace (KSY-12-16-A) at given conditions, and then leached by hydrochloric acid solution at airtight reaction kettle (100 cm^3). The reaction kettle was heated to different temperatures by electric drying oven with forced convection (FN-101-2). The leaching residue was washed by deionized water for 5 times. Extracting and washing liquids were mixed for content analyses of Al. The effects of calcination temperature (600, 700, 750, 800, 850, 900 °C) and calcination time (1, 2, 3, 4, 5 h) on extraction rates of Al were investigated. Interactive effects of different factors (leaching temperature, leaching time, acid concentration, calcination temperature and calcination time) on Al extraction were discussed by an orthogonal experiment. The orthogonal table is shown in Table 1. Leaching kinetics of Al from calcined coal-series kaolin at different leaching temperatures (120, 140, 160, 180, 200 °C), acid concentrations (5, 10, 15, 20, 25 wt%) and liquid-solid ratios (5, 10, 15 cm^3/g) was studied.

Content of Al^{3+} in the mixed liquid was determined by complexometry of EDTA (Yan et al., 2010; Zheng et al., 2007). The content of Al in raw coal-series kaolin, calcined kaolin and leached kaolin (leaching residue) were analyzed by the X-ray fluorescence (XRF, Axio advanced).

The calculation for extraction rate of Al:

$$E(Al) = \frac{c(EDTA) \times (V(EDTA) - K \times V(ZnSO_4)) \times M(Al_2O_3)}{2 \times m \times 1000 \times \frac{V_2}{V_1} \times W(Al_2O_3)}$$

where c(EDTA) and c($ZnSO_4$) are concentrations of EDTA and $ZnSO_4$, 0.035 mol/dm^3; V(EDTA) and V($ZnSO_4$) are volumes of EDTA and $ZnSO_4$) consumed in titration, cm^3; K is titrimetric factor; M(Al_2O_3) is relative molecular mass of Al_2O_3; M is mass of calcined kaolin, 5 g; V_1 and V_2 are volumes of a volumetric flask and used solution; W(Al_2O_3) is mass percent of Al_2O_3 within kaolin calcined at different temperature.

X-ray fluorescence (XRF, Axio advanced) was used to quantitatively analyze chemical compositions of raw coal-series kaolin (Liu et al., 2017a), calcined kaolin and leached kaolin. The X-ray fluorescence (XRF) employed Rh radiation with power of 4 kW to analyzing element content ranging from ppm to 100% while the relative error was < 0.05%.

Phase compositions of raw coal-series kaolin (Liu et al., 2017a) and reaction products during calcination and pressure leaching were analyzed by X-ray diffraction (XRD, RU–200B/D/MAX–RB). The powder X-ray diffraction (XRD) used a rotation anode high power X–ray diffractometer (RU–200B/D/MAX–RB, Rigaku Corporation, JPN) employing CuKα radiation (λ = 0.154 nm, 40 kV, 50 mA) over scanning range 2θ = 5–70° with step width 2° min^{-1}.

Structures of calcined kaolin and leached kaolin were analyzed by Fourier transform-infrared spectroscopy (FT-IR, Nicolet 6700). The Fourier transform infrared (FT-IR) spectra of the samples were scanned on a Nicolet 6700 (Thermo Fisher Scientific, USA) using KBr diluent over 4000–500 cm^{-1}.

Table 1
Factors and levels investigated in orthogonal experiment.

Level	Leaching temperature (A, °C)	Leaching time (B, min)	Acid concentration (C, wt%)	Calcination temperature (D, °C)	Calcination time (E, h)
1	140	40	10	600	1
2	160	60	15	700	2
3	180	80	20	800	3
4	200	90	25	900	4

3. Results

3.1. Effect of calcination temperature on Al extraction

Raw coal-series kaolin samples were calcined at different temperature, and then were respectively leached by hydrochloric acid solution (15 wt%, L/S ratio of 10 cm^3/g) at 200 °C for 60 min. The influence of calcination temperature on extraction rate of Al is shown in Fig. 1. Between 600 °C and 800 °C, the extraction rate of Al increases from 53.6% to 98.6% with calcination temperature, but then suddenly decreases above 800 °C. Below 800 °C, calcination process destroyed the structure of kaolinite and promoted the leaching of Al. Above 800 °C, some secondary phases formed during calcination are supported to hinder the leaching of Al because they are more stable in acid environment (Liu et al., 2017a).

3.2. Effect of calcination time on Al extraction

The influence of calcination time on extraction rate of Al is shown in Fig. 2. Between 1 h and 3 h, the extraction rate of Al increases from 70.1% to 98.7% with calcination time, but then suddenly decreases above 3 h. It indicates that the phase transformations from kaolinite into secondary phases are also affected by calcination time. Considering of the cost and leaching efficiency, calcination for 3 h at 800 °C is propitious to leach Al from the kaolin.

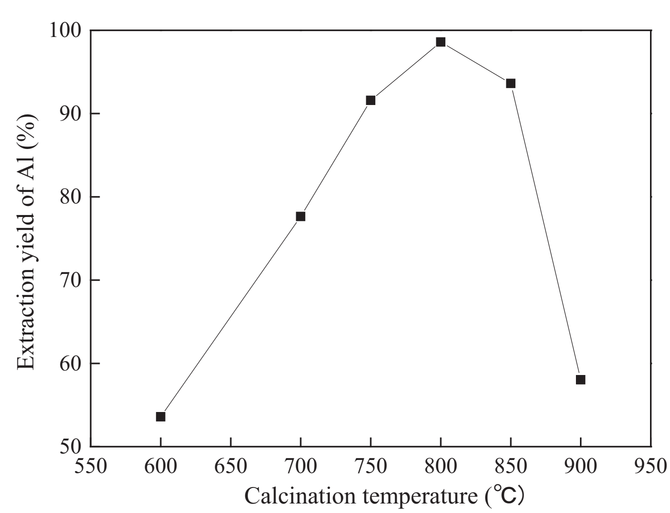

Fig. 1. The influence of calcination temperature on extraction yield of Al: calcination time (3 h), leached by hydrochloric acid solution (15 wt%, L/S ratio of 10 cm^3/g) at 200 °C for 60 min.