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Extraction of alumina from coal fly ash by mixed-alkaline hydrothermal method

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ABSTRACT

Alumina was leached from coal fly ash using a mixed alkali (NaOH + $Ca(OH)_2$) through the hydrothermal method. The effects of leaching conditions on the alumina were studied, and the results showed that the alumina extraction ratio increased with increased reaction temperature, calcium–silicon ratio, and liquid–solid ratio. By optimising the leaching conditions, the alumina extraction ratio could reach 91.3%. The obtained leaching residues were analysed by X-ray diffraction (XRD) and scanning electron microscope (SEM) + energy dispersive spectrometer (EDS), and the reaction mechanism was also discussed. Results showed that amorphous silica and mullite were first dissolved and transformed into hydro-sodalite at relatively low temperatures. Hydro-sodalite reacted with calcium hydroxide to form sodium calcium silicate ($NaCaHSiO_4$), which was the major component of the leaching residue. Zeolite was the equilibrium product, which accounted for most of the alumina leaching loss. The addition of $Ca(OH)_2$ effectively inhibited the silicon leaching into the solution.

1. Introduction

Coal fly ash (CFA) refers to the fine particles collected from coal-fired power plants. The fine particles and heavy metals in the CFA can cause serious environmental pollution (Izquierdo and Querol, 2006). CFA has been successfully used for many years in a wide range of applications, including building material applications, concrete pavements, soil stabilisation and mine reclamation (Huang et al., 2011). The CFA in parts of Inner Mongolia, China, contains 40%–50% of alumina (Zhang, 2007) and is a potential resource for extracting alumina. An estimated 12 million tons of high-alumina CFA is produced in Inner Mongolia every year and approximately 100 million tons of high-alumina CFA has accumulated over the years. Large areas of land occupied by CFA do not only carry a significant contamination risk for local areas but also prevent the resource from being used effectively. Meanwhile, the amount of bauxite that has been imported by China has reached 4.48 million tons in 2011 (National Bureau of Statistics of China, 2012). Hence, alumina extraction from high-alumina CFA has become the focus of research.

The main form of alumina in CFA is mullite, and the alumina–silica ratio (mass ratio of alumina to silica) is approximately 1–1.5. With the low alumina–silica ratio and the stable mineral phase of mullite (Dai et al., 2010), a traditional Bayer Process is not suitable for the extraction of alumina from CFA (Bi and Yu, 2006). Alumina can be extracted from CFA using the acid method (Bai et al., 2011; Shemi et al., 2012) or the alkali method (Tang and Chen, 2008). By using the acid method, alumina is dissolved in acids at high temperature. However, the acid method has not been used in industry because acid-resistant equipment is expensive and iron oxide has to be separated from the alumina prior to treatment. In the alkali method, fly ash is calcined with soda and lime at 1200 °C, and the silica is converted into stable calcium silicate ($2CaO{\cdot}SiO_2$), thus separating the silica from the alumina (Bai et al., 2010; Sun and Chen, 2013). The alkali method is a relatively mature process, but the high sintering temperature consumes vast amounts of energy. The alkaline hydrothermal process treats alumina-containing minerals at moderate conditions and is considered as a more promising method. The alkaline hydrothermal method has been used to recover alumina from alumina-containing materials, including red mud (Cresswell and Milne, 1982) and nepheline (Ablamoff and Qian, 1988). Sun (Sun et al., 2008) investigated the recovery of alumina from red mud with sub-molten NaOH. Zhang (Zhang et al., 2011) studied the recovery of alumina and alkali in red mud by the NaOH hydrothermal process. In addition, some studies have been conducted on the alumina extraction of coal fly ash using the alkali method. Wang (Wang et al., 2001) studied the digestion of mullite in dilute alkaline solution. Su (Su et al., 2011) prepared ultrafine aluminium hydroxide from fly ash using a two-step alkaline (NaOH) dissolution process. In which, NaOH was added into the alkaline hydrothermal reaction system as a liquid reactant to extract silica, then NaOH and CaO were used to treat the desiliconized fly ash. As NaOH reacts with the SiO_2 present in CFA, the consumption rate of the NaOH becomes relatively high, and the alumina

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also needs to be separated from the silica in the solution before the precipitation of sodium aluminate.

In this study, $Ca(OH)_2$ was introduced into the hydrothermal reaction system with NaOH to form alumina-free minerals, such as calcium silicate ($2CaO{\cdot}SiO_2$) and calcium metasilicate ($CaO{\cdot}SiO_2$). The addition of $Ca(OH)_2$ may reduce the usage rate of NaOH, immobilise the SiO_2 and improve the extraction ratio of alumina. The effects of leaching process conditions on the alumina extraction are investigated and the relative mechanism is also discussed.

2. Material and methods

2.1. Raw materials

The CFA used in this study was obtained from pulverised coal-fired boilers of thermal power plants located in Inner Mongolia, China. CFA was dried at 105 °C for 8 h before the experiments. The chemical composition and the crystal form of the CFA were analysed by ICP and X-ray diffraction (XRD), respectively. Fig. 1 shows that the main crystallised mineral phases of CFA are mullite ($3Al_2O_3{\cdot}2SiO_2$) and corundum (Al_2O_3). As seen in Table 1, the alumina content in CFA was approximately 48.8% and the Al_2O_3/SiO_2 was approximately 1.2. Combined with XRD analysis, in which there was no obvious diffraction peak of silica, the existence of amorphous silica can be confirmed. The CFA before extraction of alumina is composed of many small spherical particles, as demonstrated by SEM (Fig. 2). In the experiments, all chemicals used were of analytical grade and deionised water was used.

2.2. Experimental procedure

The effects of reaction temperature, C/S ratio and L/S ratio on alumina extraction from CFA were investigated according to designed experiments.

The experiments were carried out in a 1-litre stirred high temperature autoclave fitted with an external heater and an internal cooling system. The autoclave is protected by a nickel vessel from corrosion when a highly concentrated alkali solution is used. An automatic proportional, integral and derivative control system managed the heating rate, agitation and temperature of the autoclave. CFA, $Ca(OH)_2$ and 40% NaOH were added into the autoclave, and the mixture was then digested at 230–280 °C at different residence times. After the reaction, the reaction residues were filtered and washed with deionised water.

The CFA and leached residues were analysed with XRD (X'Pert Pro MPD of PANalytical Company, 40 kV 40 mA, Cu Kα radiation) for the identification of the crystalline phases. Morphological and chemical analyses of CFA and leached residues were performed via SEM with EDS (JSM-6701F, JEOL Ltd., Japan). The chemical components of the leaching liquor were analysed by ICP-OES (Optimal 5300DV of PerkinElmer instruments, 1300 W, carrier gas flow 0.08 L/min, peristaltic pump flow 1.5 L/min).

Table 1
Main chemical composition of the CFA (mass fraction, wt.%).

Al_2O_3	SiO_2	CaO	TFe	TiO_2	LOI
48.8	40.6	3.8	1.7	1.8	1.5

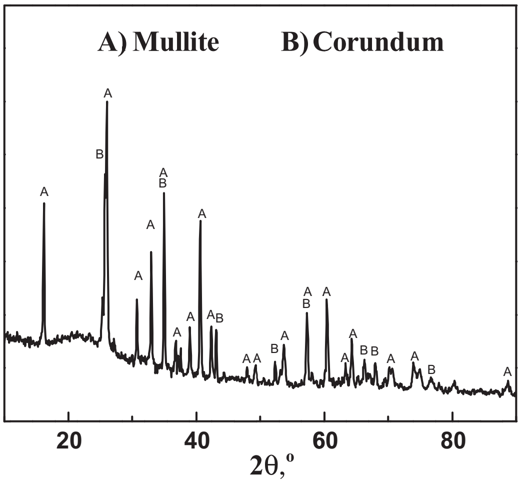

Fig. 1. XRD pattern of raw CFA.

3. Results and discussion

3.1. Effect of reaction temperature

The effects of the reaction temperature on the alumina extraction ratio ($\alpha_{Al_2O_3}$) and the caustic ratio (Na_2O-to-Al_2O_3 molar ratio, α_K) are shown in Fig. 3. The extraction ratio of alumina was increased with increased reaction temperature. The alumina extraction ratio reached 91.3% at 260 °C and was maintained even at higher temperatures. Meanwhile, the caustic ratio of the solution decreased rapidly as the reaction temperature increased from 230 to 260 °C, and changed slightly from 260 to 280 °C. Hence, an optimal reaction temperature of 260 °C was selected for other experiments.

The XRD patterns of the residues after extraction at various temperatures are shown in Fig. 4. The residue consists mainly of mullite, $Ca(OH)_2$ and hydro-sodalite ($Na_8Al_6Si_6O_{24}(OH)_2{\cdot}2H_2O$) at 146 °C. With an increased reaction temperature, the diffraction intensity of hydro-sodalite was enhanced at 190 °C and then gradually weakened. After 20 min of reaction at 260 °C, the characteristic diffraction peaks ($2\theta = 5^\circ$ and 15°) of hydro-sodalite disappeared. The diffraction intensity of $Ca(OH)_2$ was very strong at 146 °C and decreased gradually with increased temperature. The characteristic diffraction peaks of $NaCaHSiO_4$ and zeolite ($1.33Na_2O{\cdot}0.67CaO{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}H_2O$) were emerged at 228 °C and were enhanced with increased reaction temperature.

3.2. Effect of C/S ratio

Calcium hydroxide was added into the reaction to react with the silicon for immobilising the silicon in solid phase, which can then help with the separation of Si from Al. As shown in Fig. 5, the alumina extraction ratio increased by increasing the C/S to 1.0, and then remained nearly constant at approximately 91% with higher C/S ratios. Similarly,

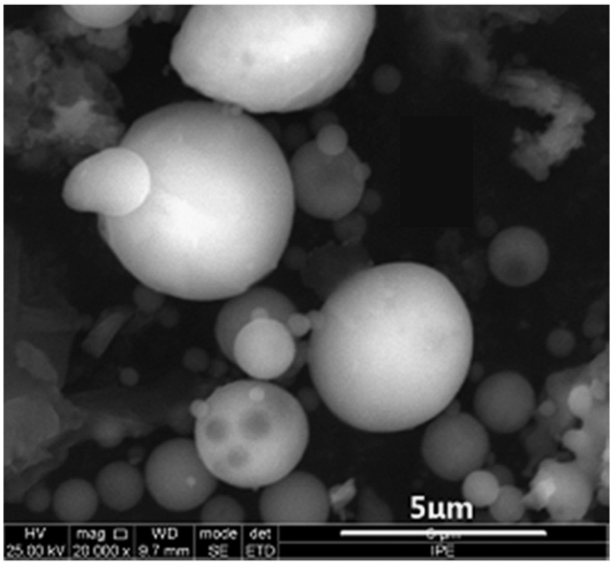

Fig. 2. SEM images of raw CFA.