International Journal of Mineral Processing 153 (2016) 109–117

Contents lists available at ScienceDirect

International Journal of Mineral Processing

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

Mineral phase transition of desilicated high alumina fly ash with alumina extraction in mixed alkali solution

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ARTICLE INFO

Article history:
Received 16 June 2015
Received in revised form 9 May 2016
Accepted 11 May 2016
Available online 16 May 2016

Keywords:
Desilicated high alumina fly ash
Mixed alkali solution
Mineral phase transition
Alumina extraction
$NaCaHSiO_4$

ABSTRACT

High alumina fly ash (HAFA), a main industrial solid waste produced in increasing amounts in western China, is a type of alumina-rich resource that can replace bauxite in the preparation of alumina. A new process of alumina extraction from HAFA is proposed in this paper. This method involved the raw HAFA being treated first by a low concentration alkali solution to form desilicated HAFA and then alumina was effectively extracted from desilicated HAFA in mixed alkali solution ($NaOH + Ca(OH)_2$). The effects of the reaction conditions on alumina leaching from desilicated HAFA were investigated. The extraction efficiency of alumina could reach 92.0% under the following optimal conditions: alkali to ash ratio of 6, calcium to silicate ratio of 1.0, and reaction temperature of 280 °C. After alumina extracted from desilicated HAFA, the solid residues were collected and characterized to better understand the mechanism of mineral phase transition of desilicated HAFA with alumina extraction in mixed alkali solution. By changing the calcium to silica ratio or alkali to ash ratio, the mineral phases could be transformed from $1.2Na_2O{\cdot}0.8CaO{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}H_2O$ to $NaCaHSiO_4$. A relatively high alkali to ash ratio or calcium to silicate ratio was preferred for the extraction of alumina from desilicated HAFA.

1. Introduction

Coal fly ash (CFA) is an industrial residue produced after the combustion of pulverized coal in coal-fired power stations. About 750 million tons of CFA are generated on a global basis each year; in China, the CFA output amounted to 375 million tons in 2009, and it has been increasing annually according to economic growth (Blissett and Rowson, 2012). However, the global average utilization efficiency of CFA is estimated to be close to 25% only (Wang, 2008). For China, this average rate has reached 69% in 2013, but there is still excess CFA untreated to stockpile open in National Development and Reform Commission (2014). Mass CFA, which is produced by coal combustion power plants, is polluting the environment and wasting resources; moreover, heavy metals in CFA worsen the pollution problem (Nowak et al., 2013). High alumina fly ash (HAFA) is unique because it has a high concentration of alumina (Al_2O_3wt.% > 50%), which mainly comes from the thermal power plants in Inner Mongolia and Shanxi Province in China (Bai et al., 2011; Qi and Yuan, 2011). HAFA is considered as a potential substitute product for the preparation of alumina, because alumina content in it is much higher than that of normal architectural material (Yao et al., 2014).

There are some extraction processes of alumina from HAFA, mainly involving sintering process, acid leaching process and other technical innovation by auxiliary means such as microwaves (Fernandez et al., 1998; Ren and Zhang, 2010; Tang and Chen, 2009; Wu et al., 2012). However, alumina extraction from HAFA is costly and a mass of red mud is generated as a new pollution residue during sintering because of the high reaction temperature and lime addition (Li et al., 2011; Tang and Chen, 2009). In addition, several other metal elements (such as Fe, Ca, and Mg) exist in HAFA; these metals should be removed via leaching of alumina in acid leaching methods, thereby increasing the process cost (Matjie et al., 2005; Wu et al., 2012). Given the high silica content and main aluminum-rich phase of mullite in HAFA, the traditional Bayer process for the recovery of alumina from bauxite (low in silica) is not suitable for extracting alumina from HAFA. Nowadays, pressure leaching with alkaline solutions for extracting alumina from HAFA has been extensively studied; this process can effectively dissolve silica and alumina from HAFA. And for reducing the reaction pressure, concentrated NaOH solution has been employed to extract of aluminum from diasporic bauxite and red mud (Cao et al., 2009; Zhong et al., 2009).

In our previous paper, we proposed a mild hydro-chemical process of alumina extraction from HAFA by a mixed alkali ($NaOH + Ca(OH)_2$) solution under low pressure and temperature (Li et al., 2014; Rayzman et al., 1997). Using HAFA as raw material, the alumina extraction efficiency can reach 91.3% under optimal conditions, while almost all of the silica in HAFA is converted into insoluble sodium

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http://dx.doi.org/10.1016/j.minpro.2016.05.004
0301-7516/

calcium silicate ($NaCaHSiO_4$). As it is known that about half of silica with the form of amorphous glass phase exits in HAFA, and it is easy to be digested in low concentration alkali solution at low temperature (Bai et al., 2010). That amorphous silica has the potential application of producing high value-added white carbon black, calcium silicate whisker and so on. Therefore, it is better to separate amorphous silica before extraction of alumina from HAFA in this mixed alkali solution with less solid residue production.

In the present study, extraction of alumina from desilicated HAFA was investigated. Amorphous silica in HAFA was digested in dilute alkali solution first. The formed desilicated HAFA was employed as a raw material for the effective extraction of alumina in mixed alkali solution ($NaOH + Ca(OH)_2$). Three key factors in alumina leaching process were studied, including reaction temperature, alkali to desilicated HAFA mass ratio, and calcium hydroxide to silica mole ratio. To better understand the reaction mechanism of alumina extraction from HAFA in mixed alkali solution, the mineral phase transition of desilicated HAFA was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and SEM–energy-dispersive X-ray spectroscopy (EDS) characterization.

2. Experimental

2.1. Materials

Raw HAFA was obtained from pulverized coal-fired boilers of thermal power plants located in Inner Mongolia, China. It was dried at 105 °C for 8 h before the experiments. Desilicated HAFA was prepared according to the following steps. Desilication was carried out in a 2000 mL stirred autoclave using diluted NaOH solution. Raw HAFA (400 g) was mixed with 1200 mL of 15 wt.% NaOH solution in a 2000 mL breaker. The reaction mixture was transferred to a stirred autoclave and heated to react at 120 °C for 2 h. The stirring speed was 300 r min^{-1}. After being cooled to about 50 °C, the mixture was filtered using a vacuum pump. The filtered cake was washed twice using deionized water. The remaining solid residue, which was desilicated HAFA, was dried at 105 °C for 12 h in the oven after washing. The chemical composition, morphology, and crystalline of both raw HAFA and desilicated HAFA were analyzed by inductively coupled plasma (ICP), SEM, and XRD, respectively.

2.2. Experimental methods

Leaching reaction of alumina from desilicated HAFA was conducted in six 300 mL Hastelloy homogeneous reactors. Concentrated NaOH solution (150 mL), with mass fraction of 50% and mixed with calcium hydroxide and desilicated HAFA, was charged into six Hastelloy homogeneous reactors. The extraction of alumina from desilicated HAFA was carried out with different alkali to ash ratios (2–20) and calcium to silicon ratios (0–1.5) at 220 °C–300 °C for 2 h. Leached residues were then separated by filtration with a vacuum pump, washed with deionized water, dried at 105 °C for 12 h, ground, and characterized.

Raw HAFA, desilicated HAFA, and leached residues were analyzed by XRD (X'Pert Pro MPD, Panalytical Company, 40 kV, 40 mA, Cu Kα radiation) to identify the crystalline phases. Morphological and chemical analyses of raw HAFA, desilicated HAFA, and leached residues were performed via SEM with EDS (JSM-6701F, JEOL, Ltd., Japan). The chemical components of the leaching liquor were analyzed by ICP-OES (Optimal 5300 DV, Perkin Elmer instruments, 1300 W, carrier gas flow of 0.08 L/min, and peristaltic pump flow of 1.5 L/min).

The following formula was used to calculate the extraction efficiency of Al_2O_3:

$$\text{Extraction efficiency of } Al_2O_3(\omega t.\%) = V \times C/(M \times W) \times 100\%$$

where V is the volume of digested liquid [L], C is the concentration of Al_2O_3 in digested liquid [g/L], M is the mass of desilicated HAFA [g], and W is the content of Al_2O_3 in desilicated HAFA [g/g].

3. Results and discussion

3.1. Raw material characterization

Based on XRD analysis, the chemical compositions of raw and desilicated HAFA are shown in Table 1. Raw HAFA was mainly composed of Al_2O_3, SiO_2, Fe_2O_3, CaO, TiO_2, and MgO with A/S of 1.14, and the sum of the composition of Al_2O_3 and SiO_2 exceeded 90 wt.%. In the XRD pattern in Fig. 1, the identified mineral phases in HAFA were mainly 42.61 wt.% mullite, 26.80 wt.% amorphous silica alumina glass, 23.05 wt.% amorphous silica glass, and 7.54 wt.% corundum. Compared with raw HAFA, the SiO_2 content in desilicated HAFA declined and A/S increased from 1.14 to 1.74. Meanwhile, the Na content was fixed at 10.35 wt.%. The XRD pattern of desilicated HAFA in Fig. 2 indicated that the main mineral phases of desilicated HAFA were mullite, sodium aluminum silicate hydrate ($Na_8(AlSiO_4)_6(OH)_2 \cdot 4H_2O$), and corundum, while the amorphous silicate could not be found. It can be concluded that the amorphous silica alumina glass has been converted into sodium aluminum silicate hydrate, while the amorphous silica glass is removed from the HAFA during desilicated process. Therefore, the solid residue produced after alumina extracted from the desilicated HAFA will be reduced, which is in favor of treating HAFA with lower secondary pollution.

Fig. 3 shows the SEM micrographs of raw and desilicated HAFA. Raw HAFA contains distinctive spherical particles with smooth surfaces, whereas desilicated HAFA is composed primarily of different glassy spheres with a rough surface. These findings indicated that some new mineral phases formed in desilicated HAFA. In agreement with the findings of XRD analysis, the newly formed sodium aluminum silicate hydrate could easily adhere to the surface of relatively stable mullite.

3.2. Effect of reaction conditions on alumina leaching from desilicated HAFA

Before studying the mechanism of mineral phase transition, the reaction conditions affecting alumina leaching from desilicated HAFA were investigated. Based on our previous research on alumina extraction from HAFA in mixed alkaline (Li et al., 2014), we found that three key factors (i.e., reaction temperature, calcium to silicon ratio, and alkali to ash ratio) greatly affected the alumina extraction efficiency and caustic ratio (Na_2O-to-Al_2O_3 molar ratio). For the extraction of alumina from desilicated HAFA, the same three key factors were also studied.

Fig. 4 displays the effects of the reaction temperature on the alumina extraction efficiency and caustic ratio. The extraction efficiency of alumina increased with the reaction temperature (from 220 °C to 280 °C), and changed slightly when the reaction temperature continuously increased to 300 °C. The alumina extraction efficiency reached the highest value of 92.0% at a reaction temperature of 280 °C or above, whereas the obtained alumina extraction efficiency was 85.4% at 260 °C. The caustic ratio of the leaching solution decreased rapidly as the reaction temperature increased from 220 °C to 280 °C, but changed slightly from 280 °C to 300 °C. The lowest caustic ratio was 11.6 at a reaction temperature of 280 °C or above. The reaction temperature of 280 °C was selected for other experiments. However, this result slightly differed from the extraction of alumina from raw HAFA. The reason for this difference remains unknown, but other conditions, such as reaction time and alkali concentration, may result in a high alumina extraction efficiency at different reaction temperatures.

Table 1
Chemical composition of raw HAFA and desilicated HAFA.

Content (wt.%)	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2	MgO	Na_2O	A/S[a]
Raw HAFA	48.61	42.50	1.51	2.83	1.37	0.80	–	1.14
Desilicated HAFA	50.73	29.16	1.71	4.11	2.94	0.21	10.35	1.74

[a] A/S is the Al_2O_3-to-SiO_2 mass ratio.