



Research article

A novel process to enrich alumina and prepare silica nanoparticles from high-alumina fly ash

Chun-li Liu^{a,b}, Shi-li Zheng^a, Shu-hua Ma^{a,*}, Yang Luo^a, Jian Ding^a, Xiao-hui Wang^a, Yi Zhang^a^a CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China^b University of Chinese Academy of Science, Beijing 100049, PR China

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ABSTRACT

Extraction of alumina from high-alumina fly ash (HAFA) enhances the value-added utilization of HAFA. However, this industrial application has been restricted by the high silica content of HAFA. Thus, alumina enrichment via the separation of silica is a key technique for HAFA utilization. In this study, a novel method of alumina enrichment by ammonium fluoride activation was proposed. The influence of the ammonium fluoride to silica in HAFA molar ratio (F/Si), the calcination temperature, and calcination time on the alumina to silica mass ratio (Al/Si) of the calcined product were investigated. The results showed that the Al/Si ratio reached 8.83 when HAFA with a F/Si ratio of 5.0 was calcined at 850 °C for 60 min. Silica in HAFA was transformed into gaseous ammonium fluosilicate, which was separated from the calcined product by condensation, thereby increasing the Al/Si ratio. However, impurities in HAFA inhibited further improvement of the Al/Si ratio. Subsequently, dissolution of ammonium fluosilicate with a surfactant produced silica nanoparticles with a surface area of 454.2 m²/g and a recyclable ammonium fluoride solution through an ammonification process. Thus, this work provides a novel strategy for the high-value utilization of HAFA.

1. Introduction

High-alumina fly ash (HAFA) is produced mainly by coal-fired power plants in the northern Shanxi province and the central & western regions of Inner Mongolia, China. The alumina content in HAFA can reach 40–50 wt%, which is far higher than that of normal fly ash (20–30 wt%) and close to that of middle-grade bauxite (50–60 wt%) [1,2]. The annual production of HAFA is estimated to be 50 million tonnes, which contains approximately 20–25 million tonnes of alumina, making it an ideal substitute for bauxite [3]. In recent years, a number of processes for recovering alumina from HAFA have been reported, and some of them have passed intermediate levels of testing in China [4–6]. However, successful commercial application of these processes has not been realized. The high silica content (~50%) of HAFA is the main factor restricting the further development of these processes. The large amount of silica slag produced during the alumina extraction process has a complex composition, making it difficult to use. The high silica content also necessitates the use of more energy and other raw materials, resulting in higher production costs. For example, in the lime-soda sintering process, the silica in HAFA transforms into dicalcium silicate (2CaO·SiO₂) during alumina extraction at temperatures > 1200 °C, and it has been roughly calculated that 2–3 t of

calcium silicate residue is generated in the recovery of 1 t of alumina [7]. Therefore, enrichment of alumina in HAFA by removing silica seems to be the logical choice. Furthermore, when the Al₂O₃ to SiO₂ mass ratio (Al/Si) of HAFA is above 8, alumina can be directly extracted via the Bayer process [8]. Thus, alumina enrichment will be beneficial to industrial production.

Considerable work has been carried out on alumina enrichment of HAFA [9,10]. However, previous results suggest that the Al/Si ratio can only be increased to ~2.6. This is because HAFA is formed at very high temperatures and is mainly composed of mullite, corundum, and amorphous silica [11]. In previous studies, the removal of amorphous silica has been the main method for improving the Al/Si ratio, whereas mullite as another major source of silica in HAFA has been considered nonreactive owing to the stability of Al–O–Si bonds [12]. Thus, to significantly enhance the Al/Si ratio of HAFA, it is necessary to also remove silica from stable mullite in HAFA. However, this process has not been investigated.

F-containing substances, such as ammonium fluoride, ammonium bifluoride, and sodium fluoride, have good chemical reactivity [13–15]. They are often used as fluxing agents for aluminosilicate minerals or ashes to extract valuable elements. In 1931, Shead and Frederick-Smith [16] verified that ammonium fluoride is an efficient fluorinating agent

* Corresponding author.

E-mail address: shma@ipe.ac.cn (S.-h. Ma).

for the decomposition of silicates and rocks. Thereafter, Kolikova et al. [17] examined interactions between ammonium fluoride and silicate minerals (albite, biotite, orthoclase, and labradorite) by stirring solid ammonium fluoride with powdered mineral samples at ambient temperatures, which resulted in the partial decomposition of the silicates. Recently, Zhang et al. [18] developed an efficient and simplified digestion technique using ammonium bifluoride in a screw-top Teflon vial (open-vessel digestion) for the multi-element analysis of various rock samples. These previous studies proved that ammonium fluoride and ammonium bifluoride can be used as activators to separate and recover both alumina and silica from aluminosilicates. However, to date, few studies have focused on F-containing substances as activators for alumina enrichment of HAFA. In addition, because of their many outstanding properties, including good stability, high surface area, good dispersibility, and ease of modification, silica nanoparticles have many important applications [19,20]. If alumina and silica nanoparticles can be obtained from HAFA simultaneously, the industrial application of alumina recovery from HAFA will be greatly promoted.

Therefore, in the current work, a novel and straightforward approach was proposed for alumina enrichment and silica nanoparticle preparation from HAFA using ammonium fluoride as an activator. The mechanism for the reaction of HAFA and ammonium fluoride was comprehensively examined, with a focus on the effects of ammonium fluoride dosage, calcination temperature, and calcination time. Subsequent dissolution of the byproduct obtained from the calcination process of HAFA and ammonium fluoride using a surfactant resulted in the production of silica nanoparticles and a recyclable ammonium fluoride solution through an ammonification process [21,22]. Owing to the high separation efficiency of alumina and silica, this approach could be used for both large-scale utilization of HAFA and high-value production of silica nanoparticles.

2. Materials and methods

2.1. Materials

The HAFA sample was collected from a pulverized coal boiler located in Inner Mongolia, China. Commercially available analytical reagents ammonium fluoride (Sinopharm Group, > 99 wt%) and sodium dodecyl sulfate (Sinopharm Group, > 99 wt%) were used as additives.

2.2. Equipment

A modified tubular furnace with a temperature-controlling system, able to maintain a desired temperature with an error of ± 1 °C, was used for heating specimens. Fig. 1 shows a schematic of the experimental setup. The setup consists of universal reactor 1 for calcination of the raw starting material and condenser 2 for trapping and collecting the byproduct generated by the calcination process. The working zones of reactor 1 and condenser 2 were made from nickel of NP-2 grade. The gaseous substance emitted during the calcination process was condensed into the byproduct and the tail gas was absorbed in a Teflon

device filled with an aqueous solution. In order to collect all the byproduct and absorb all the tail gas, it was necessary to blow out reactor 1 and condenser 2 with N_2 .

2.3. Experimental procedure

The experimental procedure had two major steps, as detailed in Fig. 2. HAFA was calcined in the presence of ammonium fluoride to generate a calcined product with a high Al/Si ratio, a gaseous byproduct, and tail gas in a closed environment. The byproduct was collected by condensation, and the tail gas was absorbed by an aqueous solution to obtain an absorption liquid. The byproduct and absorption liquid were used to produce silica nanoparticles by adding a certain quantity of sodium dodecyl sulfate and ammonia, and ammonium fluoride could be recycled by crystallization.

The calcination process was conducted in the reactor 1 shown in Fig. 1. HAFA (5.0 g) was mixed with ammonium fluoride in a 250 mL agate mortar, and then the mixture was moved into a 50 mL corundum crucible in the tubular furnace. To investigate the influence of ammonium fluoride dosage, the molar ratio of ammonium fluoride to silica in HAFA (F/Si) was varied at 2.5–5.5. To investigate the influence of reaction conditions, the reaction was performed at a temperature of 700 °C–900 °C for 15 min–90 min.

Silica nanoparticles were prepared from the byproduct generated during the calcination process in a 150 mL Teflon reactor. To investigate the influence of surfactant on the surface of the silica product, 20 g of byproduct was mixed with sodium dodecyl sulfate (0, 0.002, 0.004, 0.006, 0.008, or 0.010 g) in 100 mL of the absorption liquid. After using 15% ammonia to adjust the pH to 9, the mixture was stirred (300 rpm) at room temperature for 1.5 h, aged for 1 h, and then the precipitate was recovered by filtration, washing, and drying at 105 °C for 2 h.

2.4. Characterization

The dried samples were analyzed by X-ray diffraction (XRD; X'Pert Pro MPD, Panalytical Company; 40 kV, 30 mA, $2\theta = 5^\circ\text{--}90^\circ$, Cu-K α X-ray source) to identify the crystalline phases. The chemical compositions of the samples were examined by X-ray fluorescence spectroscopy (AXIOS-MAX, 50 kV, 60 mA, integration time of 40 s). The morphologies and chemical compositions of HAFA and the calcined product were examined via scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS; JSM-6701F, JEOL Ltd.). The morphology of the silica nanoparticles was characterized by field emission transmission electron microscopy (TEM, JEOL-2100F, Japan). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific) was used to examine the chemical state of the silica nanoparticles.

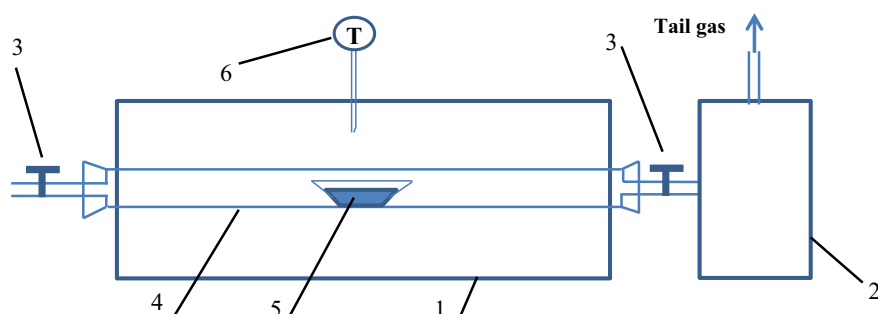


Fig. 1. Experimental setup for treating HAFA using ammonium fluoride: 1, reactor for heat treatment; 2, condenser for trapping and collecting the byproduct; 3, valves; 4, nickel alloy tube; 5, corundum crucible with sample; and 6, thermometer.

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