Preparation of Ultrafine $\alpha$-Al$_2$O$_3$ Powder from Fly Ash by Ammonium Sulfate Roasting Technology

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Abstract. (NH$_4$)$_2$SO$_4$ roasting technology was used for extracting alumina from fly ash which located in Shandong Zibo power plant. The roasting temperature, the mole ratio of Al$_2$O$_3$ to (NH$_4$)$_2$SO$_4$ and roasting time on the effect of the extraction rate of alumina was studied. The optimal roasting technology condition is 380°C for 120min with mole ratio of Al$_2$O$_3$ to (NH$_4$)$_2$SO$_4$ of 1:6. Under the optimal roasting condition, the extraction rate of Al$_2$O$_3$ can reached 82% and a new phase NH$_4$Al(SO$_4$)$_2$ was formed in clinker. NH$_4$Al(SO$_4$)$_2$ in clinker was dissolved by distilled water and then separated from silicon-rich residue by filtration. Iron in NH$_4$Al(SO$_4$)$_2$ solution was removed by goethite process, and then, NH$_4$Al(OH)$_2$CO$_3$ was synthesized by adding (NH$_4$)$_2$CO$_3$ in NH$_4$Al(SO$_4$)$_2$ solution. Ultrafine $\alpha$-Al$_2$O$_3$ powder was prepared by calcining NH$_4$Al(OH)$_2$CO$_3$ in 1200°C for 120min, which was characterized by XRD and SEM.

Introduction

Fly ash is generated during high temperature combustion of coal in coal-fired power plants [1-2]. Currently, about 800 million tons of coal fly ash has been generated in the world [3-4]. Since coal is still the major energy resource in China, the output of fly ash has increased continuously over the past several years, reaching 480 million tons in 2010 [5]. The annual fly ash discharge is more than 4×10$^8$ tons in China [6-7]. Presently, fly ash is consumed on a large scale in cement and concrete fillers as well as roadway and pavement utilization [8-11]. However, despite these positive uses, the production rate of fly ash is much greater than its consumption. There is still a proportion which is disposed of in ponds or landfill, so fly ash has become the main waste of power plant [12].

Fly ash contains significant amounts of alumina, typically about 20-50%, which presents an exciting new alternative source of alumina other than bauxite. Thus, extraction of aluminum from coal fly ash is environmentally and scientifically significant for disposing and utilizing waste materials and exploring new aluminum source, and has attracted extensive attention recently [13].

The Bayer process is the dominating method of refining alumina from bauxite ores throughout the world. The Bayer process mainly involves the bauxite digestion, solid-liquid separation, gibbsite precipitation and calcination [14]. In fly ash, the main form of alumina 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, a traditional Bayer Process is not suitable for the extraction of alumina from fly ash [15-18]. 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 had has to be separated from the alumina prior to treatment [19]. In the alkali method, fly ash is calcined with soda and lime at 1200°C, and the silica is converted into stable calcium silicate, thus separating the silica from the alumina. The alkali method is a relatively mature process, but the high sintering temperature consumes vast amounts of energy [17].
Recently, a new process for extracting alumina from coal fly ash has been established; where ammonium sulfate is used to roasting with coal fly ash [20]. Compared with acidic methods and alkali methods, this process results in fewer residues and less corrosive to equipment because ammonium sulfate as a raw material.

Ultrafine $\alpha$-$\text{Al}_2\text{O}_3$ powder has received increasing attention due to its wide applications in transparent and electronic ceramics, single crystals, abrasives and catalysts [21]. Presently, the traditional methods for preparing $\alpha$-$\text{Al}_2\text{O}_3$ powder are thermal decomposition of ammonium aluminum carbonate hydroxide (AACH) or ammonium aluminum sulfate hydroxide, Bayer process [22].

This research is therefore focused on the preparation of ultrafine $\alpha$-$\text{Al}_2\text{O}_3$ powder from fly ash by ammonium sulfate roasting technology. The technology includes the extraction of $\text{Al}_2\text{O}_3$ from fly ash by roasted with (NH$_4$)$_2$SO$_4$, Fe removal of solution, the synthesis of AACH and the preparation of ultrafine $\alpha$-$\text{Al}_2\text{O}_3$. The effects of roasting process conditions on the extraction rate of $\text{Al}_2\text{O}_3$ were investigated and the product was characterized.

**Experimental**

**Material**

The fly ash was taken from thermal power plants in Shandong Zibo power plant, China. The chemical composition and the crystallized mineral phases of fly ash were analyzed by X-ray fluorescence analysis and X-ray diffraction, respectively.

![Figure 1. XRD pattern of fly ash.](image)

**Table 1. Chemical composition of fly ash.**

| Component | SiO$_2$ | $\text{Al}_2\text{O}_3$ | TFe |
|-----------|---------|-----------------|-----|
| Contents (wt.%) | 51.37 | 39.60 | 2.42 |

According to the result of chemical composition analysis, listed in Table 1, the contents of $\text{Al}_2\text{O}_3$ and SiO$_2$ in fly ash were 39.60% and 51.37% respectively, and $\text{Al}_2\text{O}_3$/ SiO$_2$ of fly ash was approximately 0.77. As seen in Figure 1, the main crystallized mineral phases of fly ash were mullite and quartz.

Ammonium sulfate and all the other chemicals used in this study were of analytical grade and purchased from National Pharmaceutical Group, China.

**Experimental Procedure**

The whole technological flowsheet of preparation of ultrafine $\alpha$-$\text{Al}_2\text{O}_3$ powder from fly ash is shown in Figure 3.
Results and Discussion

The Extraction of Al₂O₃ from Fly Ash

To determine the effect of temperature on the extraction rate of aluminium, experiments were performed with roasting time 150 min and mole ratio (Al₂O₃/(NH₄)₂SO₄) of 1:8. The effect of temperature on the extraction rate of aluminum was presented in Figure 5. The figure shows an increase in aluminum extraction with increase in temperature. An extraction of 13% was obtained at 250 °C, 60% at 300 °C, 77% at 350 °C and 82% at 380°C. The figure further illustrates that roasting temperature beyond 380 °C showed a decline in extraction rate of Al₂O₃.

To determine the effect of mole ratio (Al₂O₃/(NH₄)₂SO₄) on the extraction rate of Al₂O₃, experiments were performed with roasting temperature 380°C and roasting time 150min. The effect of mole ratio (Al₂O₃/(NH₄)₂SO₄) on the extraction rate of Al₂O₃ was presented in Figure 6. The figure shows 60% aluminium extraction was obtained at mole ratio of 1:4, 81% aluminium extraction at mole ratio of 1:6, 82% aluminium extraction at mole ratio of 1:8 and same at mole ratio of 1:10. The figure further illustrates that aluminium extraction increase with increase in mole ratio of (NH₄)₂SO₄ and tended to stable when the mole ratio exceeded 1:6.

The experiments investigating the effect of the roasting time on the extraction rate of Al₂O₃ were carried out at a temperature of 380°C and mole ratio (Al₂O₃/(NH₄)₂SO₄) of 1:8. The effect of roasting time on the extraction rate of Al₂O₃ was presented in Figure 7. The figure shows an increase in aluminium extraction with increase in roasting time. An extraction of 68% was obtained at 60min, 79% at 90min, 82% at 120min and 82% at 150min. The figure shows that extraction rate of Al₂O₃ increased with increase in roasting time. Roasting time beyond 120min did not improve extraction.

Figure 3. The flowsheet of preparation of ultrafine α-Al₂O₃ powder from fly ash.
rate to any great extent. This shows that the extraction rate of Al₂O₃ remained almost constant without much increment above 82% after 120min of roasting.

![Figure 5. Effect of temperature on extraction rate of Al₂O₃](image1)
![Figure 6. Effect of mole ratio on extraction ratio of Al₂O₃](image2)
![Figure 7. Effect of time on extraction ratio of Al₂O₃](image3)

**Characterization of AACH and Ultrafine α-Al₂O₃**

Figure 10 shows the XRD pattern of synthetic product from aqueous solution of an ammonium aluminum sulphate (NH₄Al(SO₄)₂). The synthetic powder formed under the experimental conditions was AACH. The Figure 11 shows that, the α-Al₂O₃ product was obtained by calcination of the AACH (ammonium aluminum carbonate hydroxide). Microscopic morphology of the α-Al₂O₃ powder shown in Figure 12, it has a spherical morphology with uniform diameter, and particle size of the powder belongs to the range of ultrafine powder.

![Figure 11. XRD pattern of calcination product.](image4)
![Figure 10. XRD pattern of precipitation product.](image5)
![Figure 12. SEM image of calcination product.](image6)

**Summary**

1) A novel technology for preparation of ultrafine α-Al₂O₃ powder from fly ash by ammonium sulfate roasting technology was proposed. The technology mainly involves four procedures: the extraction of Al₂O₃ by roasted with (NH₄)₂SO₄, Fe removal of solution, the synthesis of AACH and the preparation of α-Al₂O₃.

2) For roasting procedure, the factors influencing the extraction rate of Al₂O₃ from fly ash were investigated detailed. The optimal conditions of coasting procedure were identified as: temperature 380°C, the mole ratio (Al₂O₃:(NH₄)₂SO₄) of 1:6, roasting time 120min. Under these conditions, the extraction rate of Al₂O₃ can reach 82%.

3) The AACH was synthesized and ultrafine α-Al₂O₃ powder was prepared by calcination of AACH at 1200 °C for 120min.

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