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Extraction of Alumina from Coal Fly Ash Generated from Inner-Mongolia Chinese Coal

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Abstract

Generated during the combustion of coal for energy production, coal ash is an industrial by-product and an environmental pollutant recognized by all. Continuous research is conducted to identify opportunities for the ultilization of fly ash. However, it hasn't been well and fully utilized throughout the world for quite some time. Coal fly ash from Inner-Mongolia Guohua Junggar Power Plant typically contains 50% alumina, 40% silica, 3% lime, 1.5% titania, and 1.5% hematite. Due to the availability of high quantity of alumina in fly ash and large quantities of alumina imported by China, an alumina extraction from fly ash project, funded by Chinese Ministry of Science and Technology (MOST) and Shenhua Group, was initiated by NICE. An improved alkali lime sintering method has been developed for alumina extraction. Alumina product suitable for alumina electrolysis, with a valuable by-product white carbon black, can be produced from high alumina fly ash of Junggar by this novel process.

Keywords: high alumina fly ash, alumina extraction, sinter.

1 Introduction

The generation of combustion waste is a global problem with severe implications for human health, environment and industry. On the one hand, high storage, transport and disposal costs must be faced by plant operators and waste management companies and, on the other hand, leaching of elements that are of environmental concern through the soil to the groundwater may impact negatively the terrestrial and aquatic ecosytems [1]. Coal consumption for power generation accounts for 70% of total coal production in China with 350 million tons of fly ash produced in 2010. The accumulation of large amount of fly ash has caused great pressure on economic construction and ecological environment. Coal fly ash, consisting of fine inorganic particles having Al_2O_3 and SiO_2 as the main components, could represent a very important source of pre-mined minerals particularly alumina, which is presently extracted from bauxite resources. Several studies have shown the feasibility of recovering alumina from fly ash [2,3].

In China, high alumina fly ash, with as high as 50% of Al_2O_3, are being produced in the Junggar Power Plant of Inner-Mongolia [4] and it is believed as a potential source of valuable alumina. In order to understand and utilize this high alumina fly ash, petrology and mineralogy of the feed coal as well as the chemistry of the fly ash were studied using optical microscopy, inductively coupled plasma atom emission spectrometry (ICP—AES), X—ray diffraction(XRD) and field emission scanning electron microscopy linked with energy—dispersive X—ray spectrometry (FESEM—EDX). The results show that the predominant minerals in the feed coals are kaolinite and boehmite, averaged 71.1％ and 21.1％ among the total crystal minerals, respectively. The high level of Al_2O_3 in the fly ash is yielded during the transformation and de—composition of kaolinite and boehmite in the feed coal at a high temperature, commonly between 950～1200℃. Very low level (1.9％) of quartz in all minerals of the coal has correspondingly elevated the $A1_2O_3$ to SiO_2 ratio of the fly ash up to 1.50, which is three times of common fly ash in China. Other minerals have a very low level in the feed coal, leading to very low levels of other oxides (impurity) in the fly ash. These results lay a foundation for value-added utilization of the high alumina fly ash.

The recovery of alumina from fly ash is based on the application of hydrometallurgical processes such as acid or base leaching, precipitation, solvent extraction and re-crystalization [5-8]. Nitric acid and hydrochloric acid leaching processes for the recovery of alumina and other minerals have been developed a long time ago, however these processes found little practival application due to the highly corrosive nature of concentrated chloride or nitrate solutions [9]. In addition, hydrochloric acid and nitric acid are expensive lixiviants in terms of acid cost and large evaporative losses make these processes largely uneconomic. Lastly these processes also constitute an environmental hazard. The traditional Bayer process for the recovery of alumina from Bauxite (low in silica) involves the dissolution of alumina and trace amounts of silica in sodium hydroxide. According to Burnet et al. [10] and Jackson [11], pressure leaching of fly ash with alkaline solution prior to the precipitation of $Al(OH)_3$ is a major concern of the Bayer process.

This paper will present recent research results of alumina extraction from high alumina fly ash in NICE. A novel method, pre-desilication improved alkali lime sintering, has been developed by NICE. An alumina extraction efficiency of 85% was achieved by this proposed process. The leached residue, could be considered as by-products as white carbon black, wollastonite, silica gel and lightweight aggregate. A 10,000 tonne/year alumina extraction from fly ash demonstration plant is under design and will be constructed at Inner-Mongolia Guohua Junggar Power Plant.

2 Experimental

A flow diagram for the proposed process is shown schematically in Fig. 1.

The detailed experimental procedures followed during the leaching of fly ash with sodium hydroxide, sodium carbonate and calcium carbonate are described below.

2.1. Characteristics of fly ash

Representative sample of fly ash from Inner-Mongolia Guohua Junggar Power Plant was chosen as our research object, whose characteristics are described as below. This fly ash contains 50.71% Al_2O_3 wt.% and 40.01 wt.% SiO_2 (Table 2); it consists of mainly silicate minerals, being a mixture of flake like and nearly spherically-shaped particles (Fig. 3), with a specific surface area of 4.99/ m^2/g and an agglomerate size of 5～20 μm. The XRD analysis (Fig. 2) shows that predominate minerals such as corundum, mullite, quartz and calcium oxide are present in the coal fly ash.

2.2. Pre-desilication

A 100g representative sample of fly ash was added into a 1000 mL mechanically stirred reactor. A 300 mL of 3.75 mol/L NaOH solution was transferred to the reactor containing ash. A pre-desilication experiment was carried out at 95℃ for 3 h in order to dissolve the amorphous silica species present in the coal fly ash [12]. The leached residual ash was separated from the solution by filtration. 100 mL hot water (about 95℃) was used to remove all the residual leach liquor that was absorbed by the leached ash. After that, drying the washed leached residual ash at 105℃ for 3 h. Finally, the dried leached ash and the leach liquor were submitted for XRD and XRF analysis.

The main chemical reaction for pre-desilication described above is as follows:

$$2NaOH\ (aq) + SiO_2\ (gls) \rightarrow Na_2SiO_3(aq) + H_2O \quad (1)$$

The main component contained in the leach liquor is Na_2SiO_3.

2.3. White carbon black preparation

Approximately 100 mL leach liquor was added into a 1000 mL mechanically stirred reactor, then CO_2 was slowly put into the reactor containing leach liquor, a carbonation experiment was carried out under 100 r/min at 85℃ for 0.5 h, CO_2 flow rate was 500 mL/min. When the carbonation reaction finished, a silicic acid colloidal precipitation was obtained by filtration. 30 mL hot water (about 85℃) was used to wash the silicic acid colloidal precipitation, then drying the washed precipitation at 120℃ for 4 h, eventually, white carbon black was obtained and submitted for XRD and SEM analysis.

The following reactions occurred during the preparation of white carbon black, including carbonation step and particle formation step [13].

$$Na_2O\cdot SiO_2(l)+CO_2(g)+nH_2O(l) \rightarrow Na_2CO_3(l)+SiO_2\cdot nH_2O(s) \quad (2)$$

$$SiO_2\cdot nH_2O \rightarrow SiO_2\cdot kH_2O +(n-k)H_2O \quad (3)$$

$$Na_2CO_3+CO_2+H_2O=2NaHCO_3 \quad (4)$$

2.4. Sintering of leached fly ash

About 50 g dried leached ash mixed with 30 g lime stone and 60 g soda ash were placed into a muffle furnace and sintered at 1000-1050℃ for 3 h to produce clinker for the next leaching step.

2.5. Leaching of sintered clinker

A 100g clinker was leached with NaOH solution (5%) at 90 ℃ for 15 min in a 3:1 liquid to solid ratio. The leached residues were separated from the leach liquor by filtration. The water-washing step was taken to remove the residual leach liquor absorbed by residues. Via XRF analyses, Al extraction efficiency of 91% was achieved. According to Shuangchen Ma [14], the leach liquor was sodium aluminate solution.

2.6. Desilication of sodium aluminate solution

The sodium alumina solution containing SiO_2 of 3% need to be desilicated in order to produce high purity Al_2O_3. The sodium aluminate was firstly desilicated by adding crystal seeds, then deeply desilicated by adding saturated lime milk at 100℃ for 1 h in a 30:1 CaO to SiO_2 mole ratio in order to improve the silicon index [15]. Finally, the silicon index of fine sodium aluminate reached more than 1100.

2.7. Precipitation of $Al(OH)_3$ from sodium aluminate solution

Aluminum hydroxide was prepared by putting CO_2 into the refined sodium alumina solution for carbonation decomposition [16]. The optimized condition are: the concentration of Al_2O_3 in the sodium aluminate solution is 60g/L, reaction temperature is 40℃, flow rate of CO_2 is 500 mL/min, the percentage of dispersant is 3%, pH value of the end point is 11.

2.8. Al_2O_3 preparation

Alumina products were obtained by calcining alumina hydroxide at 1050 ℃for 40min. This product contains 98.9 wt.% Al_2O_3 and impurities such as 0.05 wt.%Na_2O and 0.02 wt.% SiO_2. As shown in Table 4, Al_2O_3 product satisfied NO.1 degree has been obtained.

3 Conclusion

In conclusions, an improved alkali lime sintering method has been developed for alumina extraction. Alumina product suitable for alumina electrolysis, with a valuable by-product white carbon black, can be produced from high alumina fly ash of Junggar by this novel process. Above all, the beneficial utilization of fly ash for Al_2O_3 extraction can not only reduce environmental pressure but also bring extra profit.

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Table 1 Phase semidefinite quantity analysis results

Sample	Corundum	Mullite	Calcium Oxide	Quartz	Glass phase
FA001	9.4550%	16.4700%	1.2200%	3.3550%	69.50%

Table 2 Chemical composition of fly ash from Inner-Mongolia Guohua Junggar Power Plant (wt.%)

Component	FA001
SiO_2	40.01
Al_2O_3	50.71
Fe_2O_3	1.41
FeO	0.35
MgO	0.47
CaO	2.85
Na_2O	0.12
K_2O	0.50
H_2O^-	0.024
TiO_2	1.57
P_2O_5	0.17
MnO	0.021
LOI	1.41
S	0.22
Total	99.81

Table 3 Comparison of properties and composition between white carbon black (WCB-01) product and Chinese Standard

Items	WCB-01	GB10517-89
SiO_2 /wt %	90.85	≥90
Weight Loss / wt%（105℃ 2h）	5.23	4.0~8.0
Ignition Loss / %（900℃2h）	4.88	≤7.0
DBP /cm^3/g	3.05	3.00-3.50 (Rubber filling)
pH value	8	5.0~8.0
Cu / mg·kg^{-1}	19.5	≤30
Mn / mg·kg^{-1}	2.53	≤50
Fe / mg·kg^{-1}	312	≤1000

Table 4 Properties comparison between Al_2O_3 product and Chinese standards

Degree	Grade	Al_2O_3 wt%⩾	SiO_2 wt%⩽	Fe_2O_3 wt%⩽	Na_2O wt%⩽	LOI wt%⩽
NO.1	Al_2O_3-1	98.6	0.02	0.03	0.55	0.8
NO.2	Al_2O_3-2	98.5	0.04	0.04	0.60	0.8
NO.3	Al_2O_3-3	98.4	0.06	0.04	0.65	0.8
NO.4	Al_2O_3-4	98.3	0.08	0.05	0.70	0.8
Al_2O_3 product		98.96	0.02	0.00	0.05	0.92

Fig. 1 A flow diagram of the proposed process of extracting alumina from fly ash

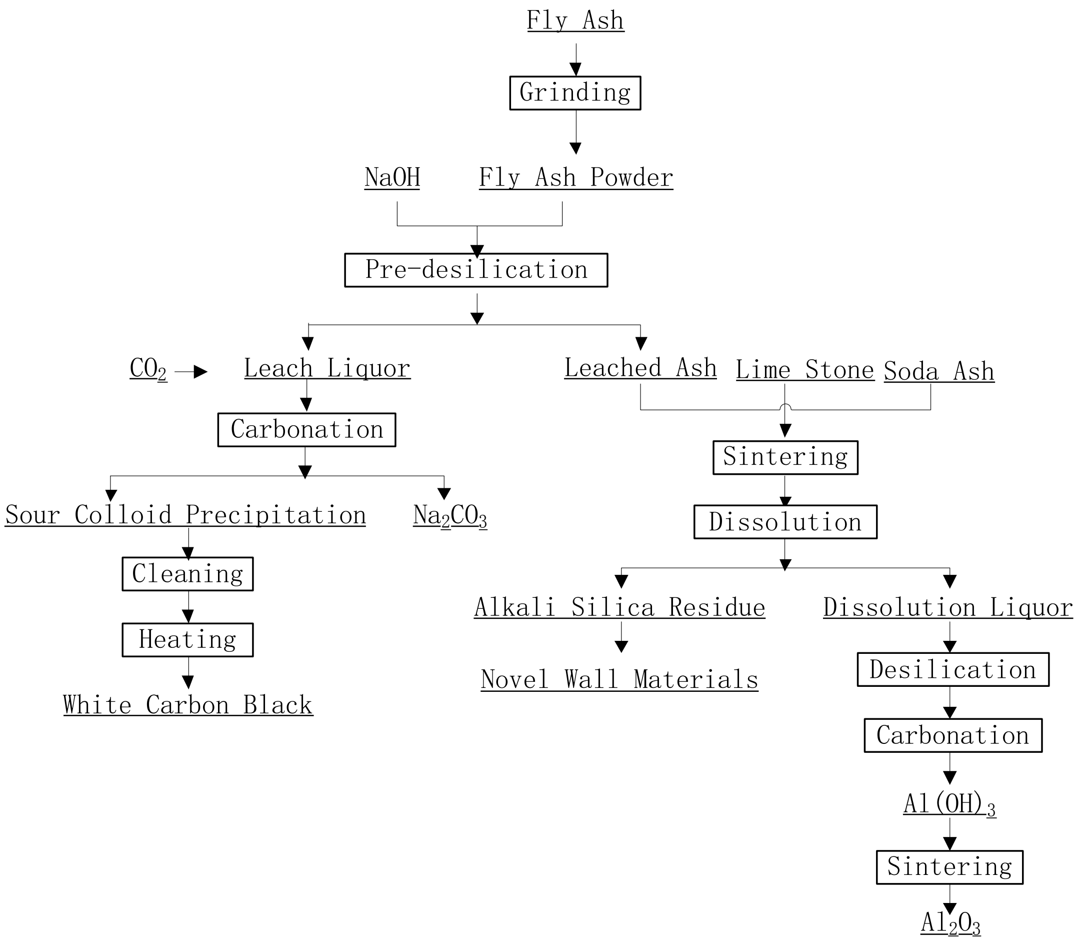

Fig.2 XRD analysis result for the sample of fly ash (FA001)

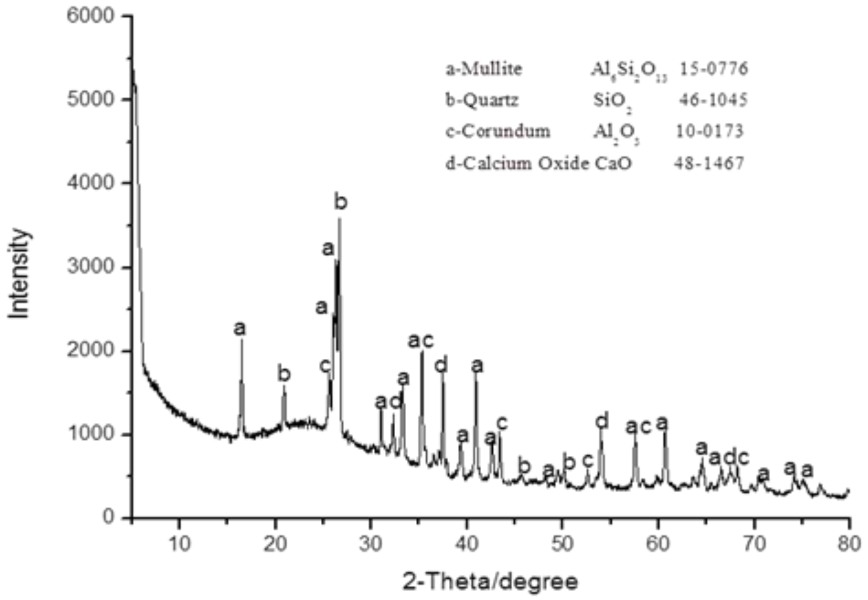

Fig. 3 SEM diagram of fly ash (FA001)

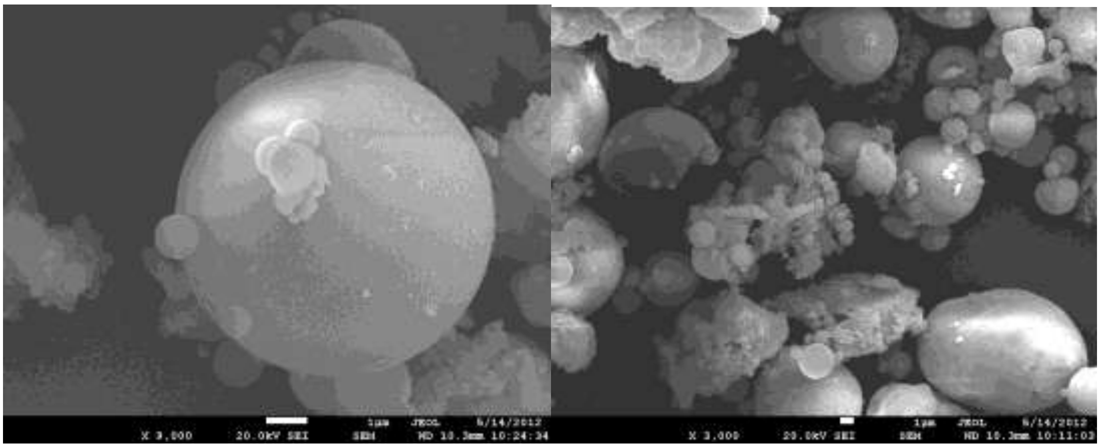

Fig.4 SEM diagram of white carbon black product