Extracting Alumina From Coal Fly Ash With Ammonium Bisulfate Leaching

Laishi Li[1], Yusheng Wu[2]
1. Professor
2. Professor
Shenyang University of Technology, Shenyang, P.R China
Corresponding author: lilaishi@sut.edu.cn

Abstract

Coal fly ash (CFA) is the solid waste produced by power plants. The main chemical components of fly ash are alumina and silica. Alumina content in some coal fly ash is more than 35 %, even 50 %, which is called high alumina fly ash. A process was developed using ammonium bisulfate solution to extract alumina from fly ash. Most alumina and ferric oxide of the CFA was leached into the solution. All of silica was retained in solid phase. The separation of aluminum and silicon was realized by this method. The conditions were studied in the lab, which are leaching temperature, leaching time, concentration of the ammonium bisulfate solution and mass ratio of ammonium bisulfate and the CFA. Metallurgical grade sandy alumina, ferric hydroxide and residue with high silica were obtained. The alumina extraction rate can be approximately 90 % with high alumina fly ash from Inner Mongolia of China.

Keywords: alumina, coal fly ash, ammonium sulfate, ammonium bisulfate.

1. Introduction

Coal-burning power plants consume pulverized solid fuels and produce large amount of coal fly ash (CFA) as a residue [1]. Through chemical analysis, the main compositions of CFA are alumina and silica. At present, about 800 million tons of CFA has been generated every year all around the world. In 2015, about 620 million tons of CFA has been generated in China [2-4]. Metallurgical alumina is the raw material of aluminum; its value is much higher than concrete. The use of CFA as a feedstock to make alumina is one potential application. Alumina has been produced using the limestone sintering process [5–8], soda-lime sintering process [9,10], leaching by acid with ammonium fluoride process [11,12]. A number of problems in these processes existed, such as the volume of residue caused from the sintering processes is very large—normally 8 to 10 times to initial CFA, it would cause the secondary pollution; HF caused from adding ammonium fluoride process is harmful to workers and local resident, etc.

CFA sourced from Inner Mongolia and processed using ammonium bisulfate in this paper. The advantages of this process is that it generates less residue and provides greater use of the residue compared with the limestone sintering process and soda-lime sintering process. The advantages compared with the acid leaching process, ammonium bisulfate and ammonium aluminum sulfate are much less corrosive than acid. The residue of limestone or soda-lime sintering processes is calcium hydrate garnet, which can only be used in cement industry. The main composition of the residue of the process of this paper is silica, which can be used to make white carbon black and other chemical products. The output of metallurgical alumina was 72.53 Mt in 2018 in China, it was 62 % of the global alumina output. The experiments of fly ash using ammonium bisulfate solution leaching unit of the process were finished and the optimum conditions were carried out in this paper.

2. Experimental

2.1. Materials and Reagents

The fly ash in the experiments was from Inner Mongolia. The main composition of the CFA is listed in Table 1.

Table 1. Composition of the fly ash (mass fraction, %).

Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	TiO_2	Others
45.05	40.21	4.36	4.4	0.35	1.43	4.2

The water in the experiments is redistilled water.
The reagents are analytical.

2.2. Experimental and Analytical Instruments

The sealed muffle furnace (KFB11Q, China) is used in heating and sintering experiments. The different concentration ammonium bisulfate solution was gotten on the magnetic stirrer (RCT S25, IKA, Germany). Steel bombs (6 × 150 ml), which were heated by hot oil, were used in leaching experiments. The temperature can reach 200 °C mostly. Buchner funnel and vacuum pump were used to separate liquid and solid after leaching and washing. The phase composition and microstructure were observed by XRD (Shimadzu XRD-7000, Japan). The XRF (ARL Perform'X 4200, USA) is used to analyze chemical content in the solid samples.

2.3. Methodology

The ammonium bisulfate, which would be used to leaching the CFA, was gotten by sintering ammonium sulfate at 300 °C in the sealed muffle furnace. The CFA was crushed and grinded below 200 mesh and mixed with different concentration ammonium bisulfate solution. The CFA slurry was put into the steel bombs, and put the bombs into oil bath to heat to the temperature required. The slurry was separated between the solid and the liquid. The residue, the solid part, was washed by hot water. Then, the residue samples were analyzed chemical content. The formula used for calculating the extraction rates of alumina and ferric oxide is expressed as the formula (1).

$$\eta = \frac{(A/S)_{CFA} - (A/S)_{residue}}{(A/S)_{CFA}} \times 100\% \qquad (1)$$

where:
η the alumina extraction efficiency, %
$(A/S)_{CFA}$ the mass ratio of alumina to silicon dioxide of CFA
$(A/S)_{residue}$ the mass ratio of alumina to silicon dioxide of the residue.

3. Results and Discussion

The alumina extraction rate can be stabilized about 90 % under the optimum conditions. Figure 1 is the XRD spectra of the CFA and the residue after leached. It shows that the main crystalline phase of CFA and the residue is anhydrite ($CaSO_4$), the halo peak between 20° to 25° is for amorphous phase of SiO_2, and the halo peaks between 45° to 48° and 65° to 68° are amorphous phase of metakaolin which disappeared in the spectra of the residue.

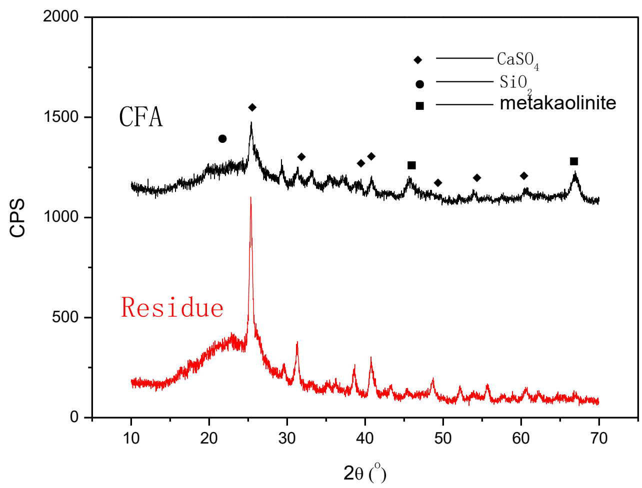

Figure 1. XRD spectrum of the CFA and the residue.

3.1. Influence of Ammonium Bisulfate Concentration on Alumina Extraction

The relation between the concentration of ammonium bisulfate solution and the alumina extraction rate is shown in Figure 2.

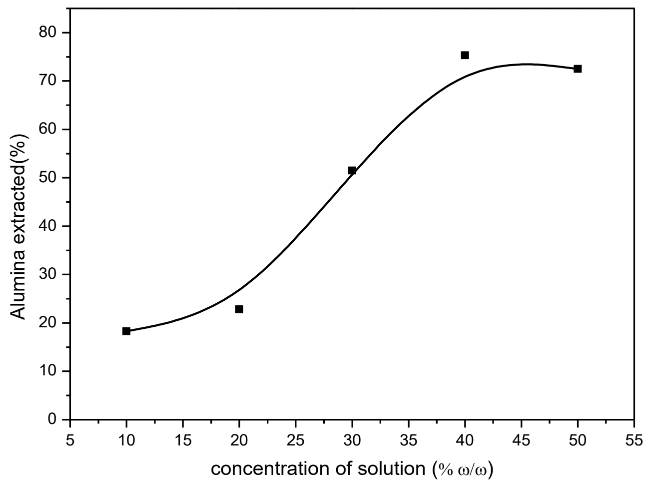

Figure 2. Influence of ammonium bisulfate concentration and the alumina extraction.

The extraction rate increases with the concentration of the solution increasing firstly, then it decreases with the concentration increasing. The concentration of the solution lower the concentration of H^+ is lower, so the extraction rate is small with low concentration solution. On the other hand, if the concentration of the solution is too high, H^+ is not ionized completely, so the extraction rate is also low with high concentration. The best concentration is 40 % as shown in the figure 2.

3.2. Influence of the Leaching Temperature on Alumina Extractin

The experiments were carried out with concentration of the solution of 40 %, leaching time 60 min, the mass ratio of ammonium bisulfate and the CFA 5.0. The results are shown in figure 3.

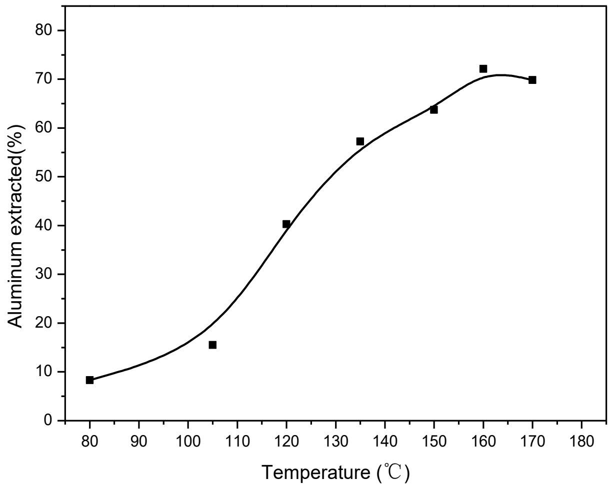

Figure 3. Influence of the leaching temperature on alumina extraction.

The extraction rate increases with the leaching temperature increasing. The leaching capacity of H^+ is improved by high temperature. At 160 °C, the extraction rate can reach 72.1 %.

3.3. Influence of the Leaching Time on Alumina Extraction

The experiments were carried out with concentration of the solution at 40 %, leaching temperature of 160 °C, the mass ratio of ammonium bisulfate and the CFA 5.0. The results are shown in Figure 4.

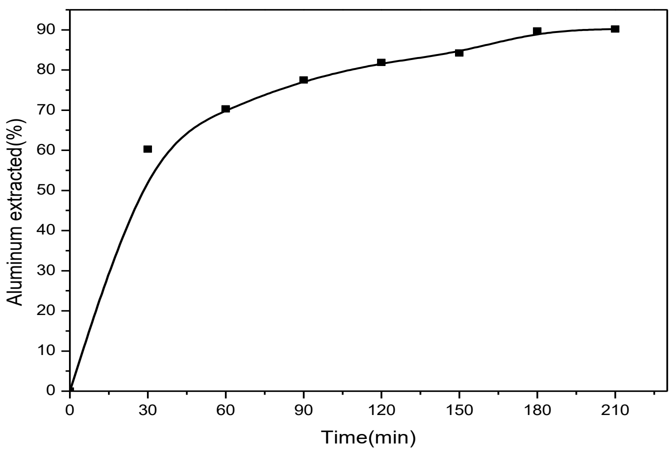

Figure 4. Influence of the leaching time on alumina extraction.

The extraction rate increases with the leaching time longer and the curve is flatting after 180min. The extraction rate can reach 89.7%

3.4. Influence of the Mass Ratio of Ammonium Bisulfate and CFA on Alumina Extraction

The main reactions of ammonium bisulfate solution leaching the CFA are as formulas (2) and (3):

$$6NH_4HSO_4(aq)+Al_2O_3(s)=2NH_4Al(SO_4)_2(aq)+2(NH_4)_2SO_4(aq)+6H_2O(aq) \quad (2)$$

$$6NH_4HSO_4(aq)+Fe_2O_3(s)=2NH_4Fe(SO_4)_2(aq)+2(NH_4)_2SO_4(aq)+ 6H_2O(aq) \quad (3)$$

As per the composition of the CFA, the mass ratio of ammonium bisulfate and the CFA is 3.23 in theory. The experiments were carried out with concentration of the solution at 40%, leaching temperature 160 °C, leaching time 180 min. The results are shown in figure 5.

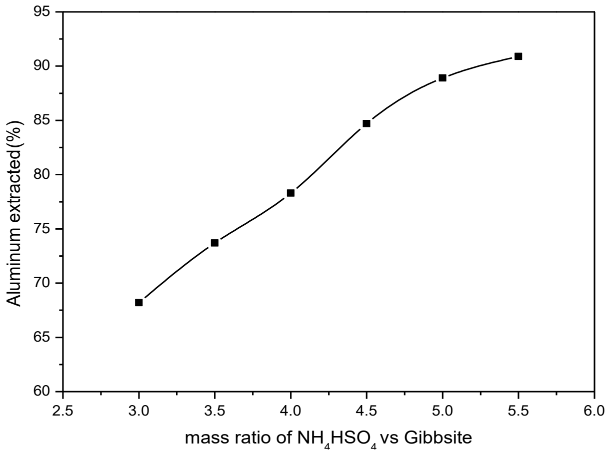

Figure 5. Influence of mass ratio of ammonium bisulfate and CFA on alumina extraction

It showed that the molar ratio higher the extraction rate higher and the curve is starting to level after the ratio is 5.0.

3.5. Confirmatory Experiments

The confirmatory experiments were carried out with mass ratio of 5.0, the leaching temperature was 160 ℃, the leaching time 180 min and the concentration of the solution 40 %. The alumina extraction rate was about 90 %. Ammonia water was added into the solution that was separated from the slurry after leaching and adjusted the pH to 5 - 5.5 to precipitate aluminum hydroxide. The ammonium sulfate solution was recycled after evaporation.

4. Conclusions

A new process is presented to extract alumina from CFA. Metallurgical grade sandy alumina and residue with high silica were obtained.

Alumina had been extracted from with the CFA leached by ammonium bisulfate solution. Ammonium sulfate can be recycled.

The alumina extraction rate can be stabilized about 90 % with mass ratio of 5.0, a leaching temperature of 160 °C, a leaching time 180 min and concentration of the solution 40 %.

5. Acknowledgements

This project is sponsored by "Liaoning BaiQianWan Talents Program".

6. References

1. Wang F Y, Wu Z Y. Fly Ash Utilization Handbook, 2nd Ed. [M]. Beijing: China Electric Power Press, 2004. 3–6(in Chinese).
2. Ding J, Ma SH, Shen S, Xie ZL, Zheng SL, Zhang Y. Research and industrialization

progress of recovering alumina from fly ash: A concise review.[J] *Waste Management*, 2017, 60: 375-387.
3. Izquierdo M, Querol X. Leaching behaviour of elements from coal combustion fly ash: an overview.[J] *Int J Coal Geol*, 2012, 94: 54–66.
4. Wu Y S, Yang X, Li L S, et al. Kinetics of extracting alumina by leaching coal fly ash with ammonium hydrogen sulfate solution.[J] *Chemical Papers,* 2019,73: 2289-2295.
5. Matjie R H, Bunt J R, Van H. Extraction of Alumina from Coal Fly Ash Generated from a Selected Low Rank Bituminous South African Coal [J]. *Miner. Eng*., 2005, 18(3): 299–310.
6. Gui Q, Fang L R, Yang Y F. Preparation of Nanometer Aluminum Hydroxide by Using Fly Ash Ecologically [J]. *Journal of Fly Ash*, 2004, (2): 20−22(in Chinese).
7. Zhou H L, Jiang T, Liu K, et al. Extraction Alumina from Fly Ash [J]. *Light Metals*, 1994, (8): 19–20(in Chinese).
8. Zhang B Y, Zhou F L. The Limestone Sintering Process to Produce Alumina with Fly Ash [J]. *Light Metals*, 2007, (6): 17−18, 27(in Chinese).
9. Tang Y, Chen F L. Extracting Alumina from Fly Ash by Soda Lime Sintering Method [J]. *Mining and Metallurgical Engineering*, 2008, 28(6): 73−75(in Chinese).
10. Liu Y Y, Li L S, Wu Y, et al. Further Utilization of Fly Ash—Extracting Alumina [J]. *Light Metals*, 2006, (5): 20–23(in Chinese).
11. Femandez A M, Ibanez L, Llavona M A, et al. Leaching of Aluminum in Spanish Clays, Coal Mining Wastes and Coal Fly Ashes by Sulphuric Acid [A]. Welch B J. *Light Metals 1998* [C]. San Autonio: The TMS Aluminum Committee, 1998. 121−130.
12. Cheng J L, Tao Z N. Extraction Aluminium from Fly Ash [J]. *Environment Review*, 1994, (4): 14–15(in Chinese).