Utilization of Reftinskaya TPP Coal Fly Ash by Ammonium Bisulfate High-Pressure Leaching for Aluminum Extraction

Dmitry Valeev[1] and Andrei Shoppert[2]
1. Senior research fellow
Laboratory of Sorption Methods, Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences, Moscow, Russia
2. Associate professor
Department of Non-Ferrous Metals Metallurgy, Ural Federal University, Yekaterinburg, Russia
Corresponding author: dmvaleev@yandex.ru

Abstract

Reftinskaya TPP is the largest coal-fired power plant in Russia. It annually generates more than 4 million tons of coal fly ash (CFA), while over 180 million tons have been accumulated in the landfill. The alumina (Al_2O_3) content makes up to 27 wt% that allows this type of raw material to be considered for alumina refining. Due to the high silica (SiO_2) content (up to 65 wt%), traditional alkali methods cannot be used. In this research, we studied the acidic method using mixture of ammonium bisulfate (NH_4HSO_4) and sulfuric acid (H_2SO_4) as a leaching agent. A high-pressure reactor was used to intensify the leaching process. The effect of temperature, leaching time, solid to liquid ratio on the Al extraction degree was studied. The behavior of macro and micro impurities has been investigated. The samples of the solid residue after leaching were analyzed by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), and laser diffraction (LD) methods.

Keywords: Coal fly ash, Alumina, High-pressure leaching, Ammonium bisulfate.

1. Introduction

Coal fly ash (CFA) – the main by-product from coal combustion process in Coal-fired Heat and Power Plant (CHP). About 30% of Russian CHP's use coal as a fuel. According to the Energy Strategy of Russia until 2035, this amount of coal is a reserve fuel in the CHPs operations, and its consumption in Russia will not decrease during the next 10 years [1].

Russia's largest power plant, Reftinskaya TPP, located in the Sverdlovsk Region (GPS coordinates: 57.112213, 61.704545). Coal from the Ekibastuz deposit of the Kazakhstan Republic (GPS coordinates: 51.740395, 75.365637) is used at this plant. Annually over 4 Mt of CFA is generated at Reftinskaya TPP, and the total amount in the CFA on landfill exceeds 180 Mt. According to order of the Government of the Russian Federation to increase the amount of the CFA utilization from 8% to 50% by 2030, new methods of CFA utilization are actively developed in Russia [2].

One of the most promising methods is aluminum extraction with further alumina production (Al_2O_3 powder) [3]. In view of the shortage of alumina produced in Russia by alumina refineries [4], the issue of increasing the production and use of alternative sources of alumina is relevant. Reftinskaya TPP is located ~90 km from the Ural Aluminum Smelter and CFA from its landfill could become an alternative to bauxites if a suitable technology will be developed.

Since the silica (SiO_2) content in Russian CFA exceeds its alumina content by over 2 times, the traditional alkaline process cannot be used, due to high reagent consumption of lime sintering process and high alkali losses of high-pressure leaching [5]. Acidic methods are the most promising, as silica does not react with acids. When alumina is obtained from aluminum salts -

sulfate or chloride, alumina has high content of sulfate or chloride ion, and particle morphology represents the shape of the initial salt crystals. Such alumina does not meet the requirements for bulk density and cannot be used in the further electrolysis process without its significant modification. However, the use of mixed acid-alkali method makes it possible to obtain alumina of the required chemical composition and physical properties [6].

The bisulfate method allows to combine acid leaching and alumina calcination from gibbsite, which is obtained by increasing the pH of the ammonium sulfate liquor due to sparging of ammonia gas [7]. Recent studies are based on the preliminary roasting of CFA with ammonium bisulfate. In this work, direct leaching in a high-pressure reactor was studied, which allowed intensifying the leaching process.

2. Materials and Methods

2.1 Materials and reagents

Raw CFA samples were collected from the Reftinskaya TPP (CFA silo storage #1). Ammonium sulfate CAS No. 7783-20-2, sulfuric acid CAS No. 7664-93-9 (both from SigmaTek, Russia) and distilled water were used in the present study.

2.2 Experiments

A roll-type dry PBSts 22/8 magnetic separator (Magnetit LLC, Russia) was used to separate the magnetic and non-magnetic fractions from raw CFA. For separation, 300 g of CFA was used for one test. The applied magnetic intensity was 0.15 T. The recovery level (R) of iron from raw CFA was calculated by following equation:

$$R = [(\gamma \times \beta)/\alpha)] \times 100\% \tag{1}$$

where: γ is the amount of the magnetite concentrate relative to the initial mass of the raw CFA; β is the magnetite grade in concentrate; α is the magnetite content in the raw CFA.

The magnetic separation efficiency index (E) was employed as an efficiency criterion:

$$E = [(R - \gamma)/(100 - \alpha)] \times 100\% \tag{2}$$

After magnetic separation non-magnetic fraction was leached by 40% NH_4HSO_4 + 7.5M H_2SO_4 mixture in a high-pressure reactor (Deschem, China). The duration time at 160-200 ºC was 30-90 min. The solid to liquid ratio (S:L) varied from 1:5 to 1:10. Slurry after leaching was filtered and washed by hot water (90 ºC) to obtain the liquor and solid residue. The solid residue was washed with distilled water, dried at 110 ºC for 2 h and analyzed by physical and chemical methods. The Al extraction degree was analyzed using machine learning with artificial neural networks (ANNs) included in the «Statistica 13» software.

2.3 Analytical methods

Mineralogy of the CFA samples were measured by X-ray diffraction (XRD) using a Difrei-401 X-ray diffractometer (JSC Scientific Instruments, Saint Petersburg, Russia) using a Cr-Ka radiation source and a 2θ range from 5º to 140º with 30 min exposure time. The operating mode of the X-ray source was set to 25 kW/4 mA. The mineral phases were analyzed by Match! 3 software. The average particle size and specific surface area of the CFA samples were determined by laser diffraction method (LD) using a Analysette 22 NanoTec (Fritsch, Germany) and by Brunauer-Emmett-Teller method (BET) using NOVA 1200e (Quantachrome Instruments, UK).

3. Results and discussion

3.1 Dry magnetic separation

Iron in raw CFA is mainly presented in the magnetite (Fe_3O_4) and hematite (Fe_2O_3). Magnetite is concentrated on the surface of aluminosilicate spheres in the crystals with a size of 1-10 µm. It is practically impossible to separate hematite from raw CFA by dry magnetic separation [8]. Figure 1 shows a flowsheet of the magnetic separation of the raw CFA. As can be seen from Figure 1, about 8.5 wt. % of the CFA proceed into the magnetic fraction, while the iron content in it increases four times to 13.87 wt. %. The iron content in the non-magnetic fraction decreases 1.38 times to 2.48 wt. %.

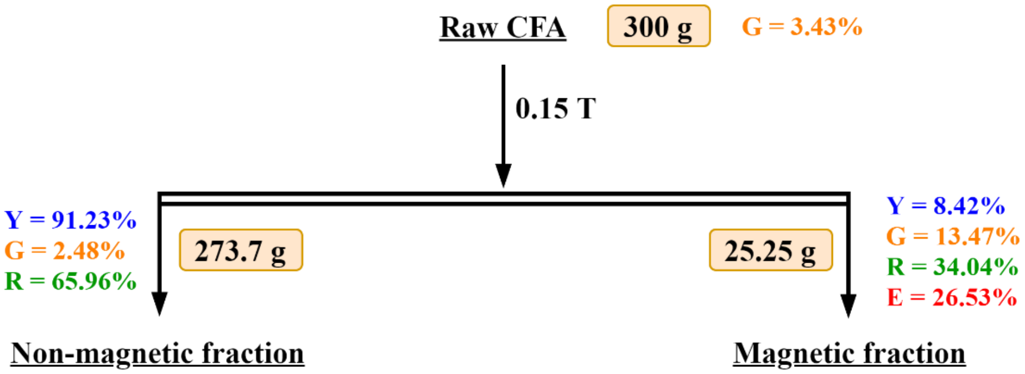


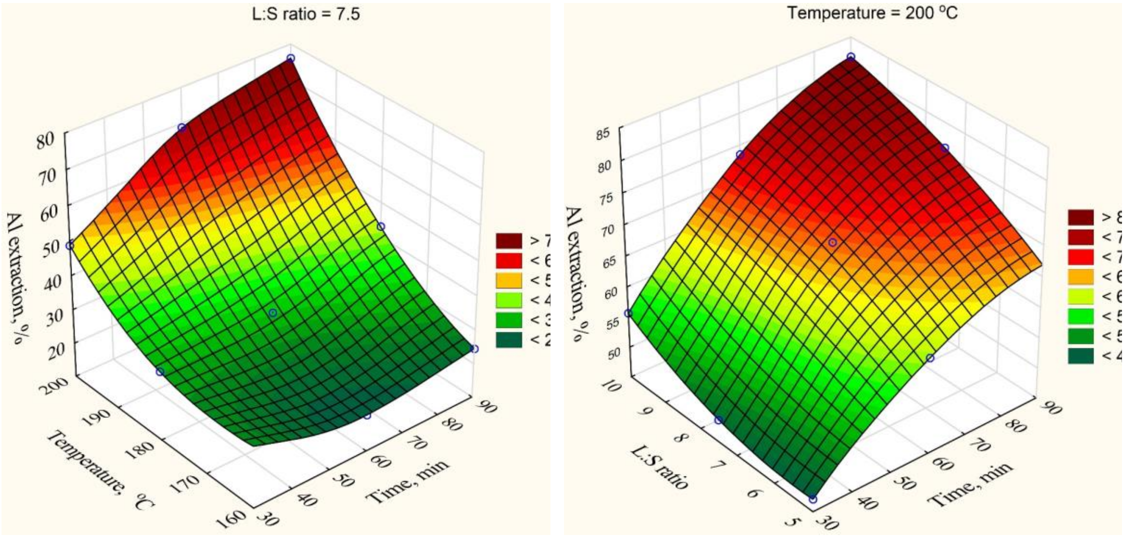
Figure 1. Flowsheet of the Reftinskaya TPP CFA enrichment process using dry magnetic separation: Y – the amount of the fraction relative to the initial mass of the raw CFA, G – iron content, R – recovery level of iron, E – magnetic separation efficiency index.

Table 1. Chemical composition of the CFA samples from Reftinskaya TPP (Asbest, Russia) after magnetic separation.

Sample	Main components, wt. %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	C
Raw CFA	64.10	26.45	3.43	1.49	0.78	1.17	0.52	0.54	1.52
Magnetic fraction	55.93	24.19	13.87	2.53	0.92	0.89	0.22	0.67	0.78
Non-magnetic fraction	65.10	26.76	2.48	1.40	0.77	1.20	0.55	0.53	1.21

3.2 High-pressure leaching of non-magnetic fraction by NH_4HSO_4 + H_2SO_4 mixture

Xu et al. showed that the optimum extraction of Al from CFA was at ammonium bisulfate (AB) to sulfuric acid (SA) ratio 1:1. An increase of AB:SA ratio to 1:2 and 1:3 does not significantly increase Al extraction degree [9]. So, in this research we used AB:SA ratio 1:1. The response surfaces predicted by the ANNs for Al extraction, depending on the leaching duration, the S:L ratio at the T = 160 - 200 °C were shown in Figure 2. Temperature provides the main effect of the increase in the Al extraction degree (Figure 2a). At T = 180 ºC the Al extraction degree is less than 50%. At T = 200 ºC this value is more than 70%. As can be seen on Figure 2b, at the S:L ratio more than 1:7.5 and the leaching duration more than 60 min, the Al extraction degree is higher than 75%.



(a) **(b)**

Figure 2. Neural network response surfaces for Al extraction degree: (a) T = 200 ºC, S:L ratio = 1:5-10, τ = 30-90 min; (b) S:L ratio = 1:7.5, T = 160-200 ºC, τ = 30-90 min. Blue points are the experimental data.

The obtained data correlate with Hu et al. study, however, since most of the aluminum in Reftinskaya CFA is found only in mullite ($3Al_2O_3 \cdot 2SiO_2$), and not in mullite and corundum (α-Al_2O_3) as in CFA from Guohua Zhungeer Power Plant, the leaching duration can be reduced from 300 to 90 min, with a decrease in the maximum leaching temperature from 220 to 200 ºC.

Figure 3 show the XRD patterns of CFA samples after leaching. The raw CFA consists of two mineral phases: mullite and quartz, and a glassy amorphous phase. The amorphous phase, in addition to mullite, also consists of potassium and calcium feldspars, but not seen on XRD pattern due to the small amount and relatively close peaks position with quartz.

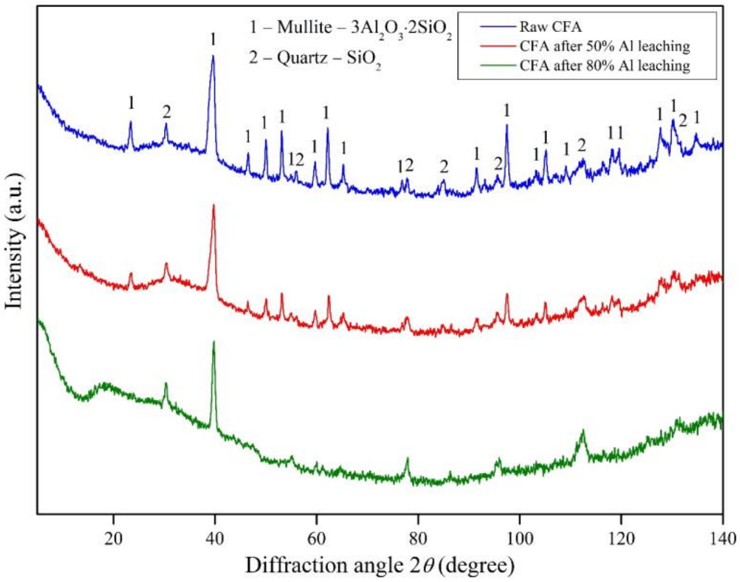


Figure 3. XRD patterns of the CFA samples after high-pressure NH_4HSO_4 + H_2SO_4 leaching.

The peaks corresponding to the mullite are presented at sample after 50% Al leaching are less intensive compared to the raw CFA data. Mullite peaks are not present after 80% Al leaching. A halo that corresponds to an amorphous phase can still be observed at 2θ = 10 - 50º but became more pronounced than in the initial CFA. It can be assumed that most of the mullite phase might have transformed during leaching into an amorphous phase. This amorphous phase apparently represents residual (undissolved) SiO_2.

It can be seen from Table 2 that the particle size distribution of CFA samples decreases after leaching. In the raw CFA average diameter of 108.5 µm, the volume of larger and smaller particles gradually decreased. After leaching, the main fraction represents the particles with a diameter less than 123 µm, with an average diameter of particles of 67.8 µm. A decrease of the average particle size during the leaching process correlates with a simultaneous increase of the BET for CFA particles. At the raw CFA the BET value is 4.65 m^2/g. A significant increase in the specific surface area is observed after acid leaching. The BET of the solid residue increases to 16.93 m^2/g after 90 min leaching by $NH_4HSO_4 + H_2SO_4$ mixture at T = 200 ℃, and S:L ratio = 1:10.

Table 2. The physical properties and particle size distribution of the raw CFA and the solid residue after acid leaching

Samples	Specific surface area (BET) (m^2/g)	Total pore volume (cm^3/g)	Particle size distribution (µm)		
			Dx (10)	Dx (50)	Dx (90)
Raw CFA	4.65	0.80	4.2	34.1	160.3
Solid residue	16.93	9.83	5.1	40.7	123.6

The chemical composition of the solid residue obtained at optimal parameters of CFA acid is presented in Table 3. The yield of solid residue was 74.65% of the raw CFA. The unreacted aluminum mainly remains in the solid residue in the aluminosilicates: mullite and feldspar type particles [10]. This fact correlated with the previous research by Ding et al. [3]. These phases are present either in small amounts or in an amorphous state, and in both cases cannot be detected by XRD. According to the research by Jena et al., feldspars are poorly soluble in acid even after amorphization by the long-time mechanical activation process [11].

Table 3. Chemical composition of the solid residue after CFA leaching by $NH_4HSO_4 + H_2SO_4$ mixture.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	C
83.55	9.19	1.88	0.55	0.37	1.24	0.47	0.10	2.66

4. Conclusions

The data obtained in this study show that the CFA of Reftinskaya TPP can be utilized by high-pressure leaching with a mixture of $NH_4HSO_4 + H_2SO_4$ at T = 200 ℃, τ = 90 min and S:L ratio = 1:10. The Al extraction degree at these parameters exceeds 76%. The acid liquor can be used for the further $Al(OH)_3$ precipitation and for the production of sandy grade alumina.

5. Acknowledgements

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6. References

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