

## High Alumina Mullite Concentrate Obtained from Reftinskaya TTP Coal Fly Ash by Alkaline Desilication

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### Abstract



One of the potential sources of alumina and mesoporous silica is the coal-fired thermal plants waste known as the coal fly ash (CFA). The studies of the alumina extraction from CFA are often focused on the preliminary desilication, but the efficiency of the alkali desilication is low due to formation of the desilication product –  $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot \text{Na}_2\text{X}$  (DSP). This research is focused on the possibility of CFA desilication without formation of DSP using a leaching process with higher liquid to solid ratios (L/S) and alkali concentrations.

According to the response surfaces, at the  $T = 110\text{ }^\circ\text{C}$ ;  $C(\text{Na}_2\text{O}) = 400\text{ g/L}$ ;  $L/S\text{ ratio} = 20$  and  $75\text{ min}$  leaching duration, the Si and Al extraction degrees were 88 % and 45 %. A very low  $\text{Na}_2\text{O}$  content (0.65 %) is observed in the solid residue at these conditions. It indicates the absence of the DSP formation.

Due to the NaOH leaching of CFA at conditions that prevent the formation of a DSP, mullite particles with an acicular structure are exposed. This leads to a significant increase of the porosity and specific surface area of the solid residue, and, consequently, to an increase in its reactivity. The content of alumina and silica in the solid residue is 41 % and 23 % respectively.

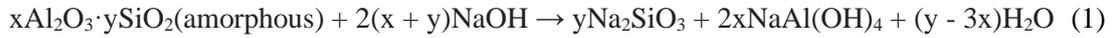
**Keywords:** Coal fly ash, Alumina, Mullite concentrate, Leaching, Desilication.

### 1. Introduction

Coal is one of the main sources of energy worldwide. The ever-increasing energy demand means that coal will remain a key component in energy generation for nearest future [1], with proven reserves of over 1,000 billion tonnes [2]. As a result of coal combustion on thermal power plants (TTP), the solid residue is formed, which is usually referred to as the coal fly ash (CFA). The CFA content of most coals is around 10-20 %, while it reaches ~40 % in the brown coal from the Ekibastuz basin of Kazakhstan Republic [3]. The volume of generated CFA will be increasing for forthcoming years due to the increasing need for energy from coal plants. The degree of CFA utilization is also increasing, but it still does not exceed 70 % in China, USA and India. Moreover, the average utilization rate in the world, according to various estimates, is not more than 25 % [4,5], and there is a large difference between developed and developing countries.

The CFA contains many valuable components, and its recycling can be economically and environmentally beneficial. The alumina content in Russian CFA is not more than 25-30 wt. % and it contains more than 60% of silica ( $\text{SiO}_2$ ). This fact reduces the economic attractiveness of the Russian CFA for sandy grade alumina production [6], since a preliminary removal of silica from the CFA is necessary. The choice of a method depends on the minerals where alumina and silica are concentrated.

The main method for desilication of CFA is leaching by caustic alkaline solution (NaOH). Silica can easily be leached at atmospheric pressure from an amorphous glassy mass. This type of leaching produces a silicate solution that can be used to precipitate mesoporous silica [7]. The desilication degree by this method does not exceed 60 % [8], because of the simultaneous process of Al leaching and the precipitation of an insoluble compound - desilication product (DSP). This process can be described by the following Equation (1) and Equation (2):



where:

$x$  represents various inorganic anions, most often sulfate, carbonate, chloride, aluminate, etc.

The formation of a desilication product in the course of alkaline leaching of fly ash has been used in many studies to produce zeolites [9]. However, large amounts of  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  are lost with the solid residue, if the main goal is to further extract alumina from the residue. The  $\text{Na}_2\text{O}$  content in the solid residue after conventional leaching reaches 12 wt. %. To reduce alkali losses, it was proposed to use preliminary extraction of soluble alumina by acid leaching [10]. Ma et. al. [11] showed that, using dual treatment of CFA by acid and alkali, the silica extraction reaches only 70 %. Leaching of silica from the surface of the CFA particles allows to destruct the Si-O-Al bonds. The alumina extraction degree significantly increases from 40 to 85 % during subsequent acid leaching. This fact is related to formation of DSP readily leached in HCl by Equation (3).



In the previous research devoted to bauxite, it was found that under certain conditions it is possible to keep alumina and silica in liquor for a long time without the formation of the DSP. It made it possible to obtain red mud with high iron content. This opportunity appears mainly by the leaching of sodium aluminate containing sintering products under atmospheric pressure with highly concentrated NaOH solutions. At these conditions, the limited solubility of silica is observed. After reaching supersaturation, regardless of liquor temperature, the DSP formation is beginning.

The main purpose of this study is to show the possibility of increasing the  $\text{SiO}_2$  extraction degree from CFA by NaOH leaching while reducing the loss of NaOH with solid residue by keeping  $\text{Al}_2\text{O}_3$  in the liquor. In addition, to analyze the influence of technological parameters on the CFA desilication degree and creation a process model in this research was used neural networks. For determination the interaction mechanism of CFA with NaOH, the kinetics of leaching process using shrinking core model was studied.

## 2. Materials and Methods

### 2.1 Experiments

CFA leaching by NaOH were carried out in an apparatus consisting of a 0.5 L stainless steel reactor, with openings for injecting chemical reagents, as well as for temperature control and the recycling of evaporated water through a water-cooled reflux condenser. The reactor was temperature controlled. The materials were stirred using an overhead mixer at 700 rpm (if not stated otherwise), which ensured uniform density of the pulp. A predetermined portion of the CFA was added to a prepared alkali solution with the concentration of 400 g/L  $\text{Na}_2\text{O}$ . At the end of the experiment, the leaching pulp was filtered in a Buchner funnel; the leaching cake was washed with distilled water, dried at 100 °C for 240 min, weighed and analyzed by ICP-OES. All

#### 4. Conclusions

1. The raw CFA contains a large amount of amorphous aluminosilicate with high content of easily soluble alumina. The extraction of this alumina by the NaOH simultaneously with silica at low L/S ratio (<15) lead to the formation of DSP.
2. According to the response surfaces, at the T = 110 °C; C(Na<sub>2</sub>O) = 400 g/L; L/S ratio = 20 and 75 min leaching duration, the Si and Al extraction degree were 88% and 45%. A very low Na<sub>2</sub>O content (0.65 mas. %) is observed in the solid residue at these conditions. It indicates the absence of the DSP formation.
3. The results of the kinetic analysis shows that the leaching process limited by the surface chemical reaction at low T <100 °C; at high T >100 °C - limited by the diffusion through the product layer. The apparent E<sub>a</sub> was 73.8 kJ/mol.
4. Due to the NaOH leaching of CFA at conditions that prevent the formation of a DSP, mullite particles with a needle-like structure are exposed. It leads to a significant increasing in the porosity and of the specific surface area of the solid residue, and, consequently, to an increase in its reactivity.

#### 5. Acknowledgments

This work was funded by State Assignment, grant number 075-03-2021-051/5.

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