

The Preparation of Silicon and Aluminum Extracts from Tuncbilek and Orhaneli Fly Ashes by Alkali Fusion

M. Sari Yilmaz, N. Karamahmut Mermer

Abstract—Coal fly ash is formed as a solid waste product from the combustion of coal in coal fired power stations. Huge amounts of fly ash are produced globally every year and are predicted to increase. Nowadays, less than half of the fly ash is used as a raw material for cement manufacturing, construction and the rest of it is disposed as a waste causing yet another environmental concern. For this reason, the recycling of this kind of slurries into useful materials is quite important in terms of economical and environmental aspects.

The purpose of this study is to evaluate the Orhaneli and Tuncbilek coal fly ashes for utilization in some industrial applications. Therefore the mineralogical and chemical compositions of these fly ashes were analyzed by X-ray fluorescence spectroscopy, Fourier-transform infrared spectrometer, and X-ray diffraction. The silicon (Si) and aluminum (Al) in the fly ashes were activated by alkali fusion technique with sodium hydroxide. The obtained extracts were analyzed for Si and Al content by inductively coupled plasma optical emission spectrometry.

Keywords—Extraction, Fly ash, Fusion, XRD.

I. INTRODUCTION

COAL fly ash, an industrial by-product, is derived from combustion of pulverized coal and air in thermal power plants. Coal-based electricity generation contributes approximately 40.5% of the total electricity production in the world [1]. By the year 2010, the amount of fly ash produced worldwide is estimated to be about 780 million tons annually [2]. The recycling rate of the fly ash is 10% of the generated amount in Turkey [3]. It has been widely used in various areas such as the manufacture of bricks, cellular concrete blocks, road construction, landfill application, ceramics, agriculture, insulating bricks, recovery of metals, and dam constructions.

Recently, numerous studies in the literature shows that utilize fly ashes have been used in the synthesis of zeolites, zeolite-carbon composites, geopolymers, ceramic materials, aerogels and mesoporous silica materials [4]-[11]. Although it has been used in a wide range of industries, there is still a proportion which is disposed of in ponds or landfill [12]. The fly ash is generated in large quantities and its improper disposal has cause water and soil pollution, disrupt ecological cycles and pose environmental hazards.

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The development of new recycling methods for coal fly ash is pressing and ongoing need for economic and environmental implications. Therefore the mineralogical and chemical composition of fly ashes must be known.

In the present study, chemical composition and crystallographic structure of two different Turkish fly ashes (Orhaneli and Tuncbilek) were investigated X-ray fluorescence (XRF), Fourier-transform infrared (FTIR) spectrometer, and X-ray diffraction (XRD) analyses. The Si and Al in fly ashes were activated by fusion with sodium hydroxide. The concentrations of Si and Al were determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

II. EXPERIMENTAL

A. Materials and Characterization

The Orhaneli and Tuncbilek fly ashes were supplied from Bursa Orhaneli and Kutahya Tuncbilek Thermal Power Plants Turkey, respectively. The fly ashes were ground to pass through a $-0.841+0.250$ mm sieve and stored before analysis. Orhaneli and Tuncbilek fly ashes denoted as F_O and F_T , respectively.

XRD patterns of F_O and F_T were recorded using a Philips PANalytical X'Pert-Pro diffractometer using $CuK\alpha$ radiation ($\gamma=1.540$ Å) at operating parameters of 40 mA and 45 kV with step size 0.02° (Fig. 1).



Fig. 1 XRD equipment

The chemical compositions of samples were determined by

PANalytical MiniPal4 XRF spectrometry equipped with an array of 12 analyzing crystals and fitted with a Rh X-ray tube target was used.

Infrared spectra of the fly ash samples were obtained using a Perkin Elmer Spectrum One FTIR spectrometer with Attenuated Total Reflectance (ATR) accessories in the spectral range of 4000 and 650 cm^{-1} with a spectral resolution of 4 cm^{-1} in the transmittance mode (Fig. 2).



Fig. 2 FTIR equipment

The Si and Al content of obtained extracts were determined by Perkin Elmer Optima 2100 DV ICP-OES equipped with a cross flow nebulizer, a spray chamber and a quartz torch with a quartz injector tube, was used for Si, Al and Na determination (Fig. 3). High purity Argon was used for plasma generation, nebulization and as auxiliary gas.



Fig. 3 ICP-OES equipment

B. Fusion Method

Alkali fusion was based on [13]. According to this method, the fly ash sample was mixed with sodium hydroxide in the weight ratio of 1:1.2 at 550°C for 1 h to obtain fused product which was cooled to room temperature. The resultant fused mixture was milled again and then stirred in shaking incubator with appropriate amount of distilled water at room temperature for 24 h. After stirring, the solution was separated from the mixture by a filtration process. Concentrations of Si and Al in the filtrates were determined by ICP-OES. A schematic flow diagram of the fusion process was presented in Fig. 4.

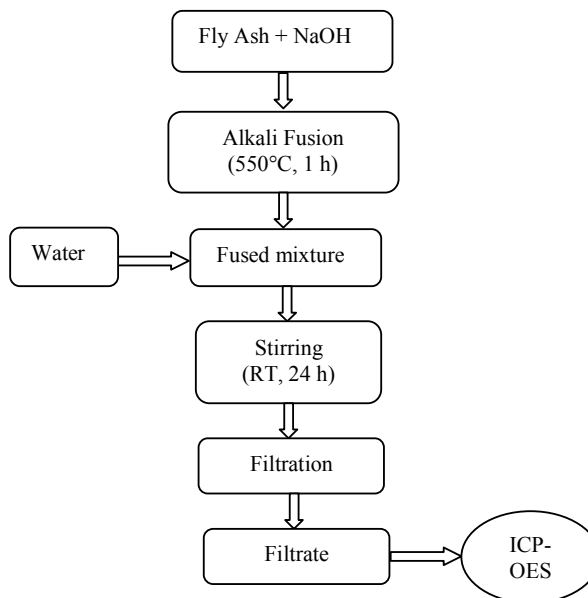


Fig. 4 Flow chart of fusion process

III. RESULT AND DISCUSSION

A. Characterization of F_o and F_T

The chemical compositions of fly ash samples were listed in Table I. It was seen that Si content of F_o was lower than F_T . However, Al content of F_o was higher than F_T .

TABLE I
CHEMICAL COMPOSITION OF FLY ASHES

wt. %	F_o	F_T
SiO_2	52,5	61,2
Al_2O_3	26,5	21,9
Fe_2O_3	8,51	8,23
K_2O	1,99	1,40
MgO	3,20	3,50
TiO_2	0,60	0,74
CaO	4,22	1,82
Na_2O	0,40	0,30
SO_3	2,10	0,88
Si/Al	1,75	2,46

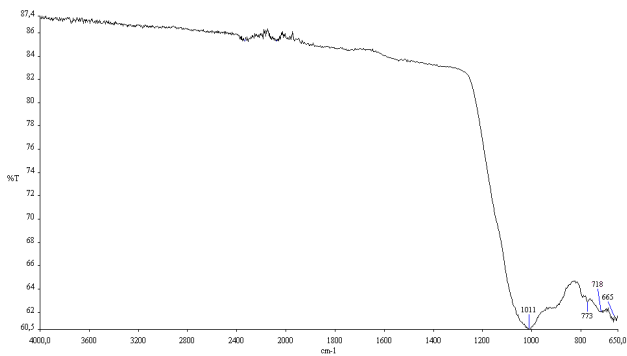
FTIR spectra of fly ash samples were demonstrated in Fig. 5. The spectrum of F_o exhibited bands at 1011 and 773 cm^{-1} corresponding to asymmetrical and symmetric Si-O-Si vibrations. The absorption peak at 665 cm^{-1} was attributed to Al-O vibration (Fig. 5 (a)) [14].

The spectrum of F_T exhibited bands at 1071 and 796 cm^{-1} corresponding to asymmetrical and symmetric Si-O-Si vibrations. The absorption peak at 659 cm^{-1} was attributed to Al-O vibration (Fig. 5 (b)) [14].

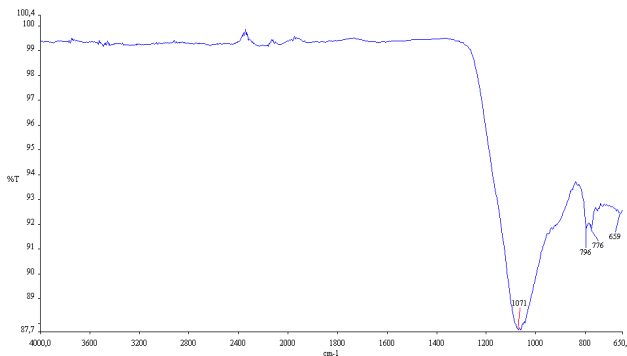
XRD patterns of fly ash samples were given in Fig. 6. It was seen that F_o mainly consists of quartz (SiO_2 , PDF no: 03-065-0466), mullite (Al_3SiO_9 , PDF no: 01-088-2049), and ferrosilite (FeSiO_3 , PDF no: 01-076-0888).

F_T mainly consists of quartz (SiO_2 , PDF no: 03-065-0466), mullite ($\text{Al}_{4,52}\text{Si}_{1,48}\text{O}_{9,74}$, PDF no: 01-079-1457), and hematite

(Fe₂O₃, PDF no: 01-073-0603).



(a)



(b)

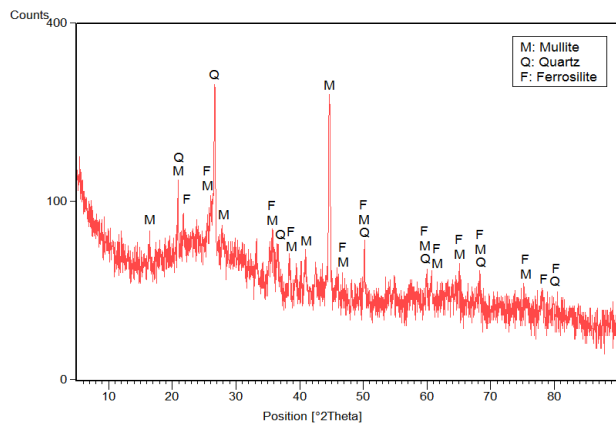
Fig. 5 FTIR spectrum of (a) F₀ and (b) F_T

B. Characterization of F₀ and F_T

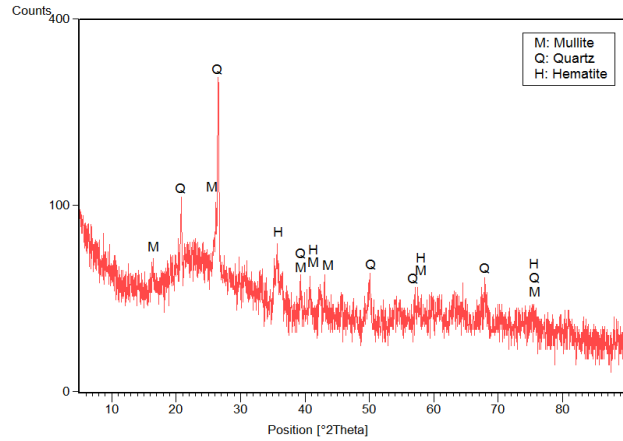
Concentrations of Si and Al in the alkali extracts of F₀ and F_T were listed in Table II. It was seen that the contents of Si and Al in the extract of F_T were higher than in the F₀.

TABLE II
CONCENTRATIONS OF SI AND AL IN THE EXTRACTS OF F₀ AND F_T

Alkali Extracts	Si, ppm	Al, ppm	Si/Al
F ₀	4745	269,40	17,61
F _T	10710	390,10	27,46



(a)



(b)

Fig. 6 XRD pattern of (a) F₀ and (b) F_T

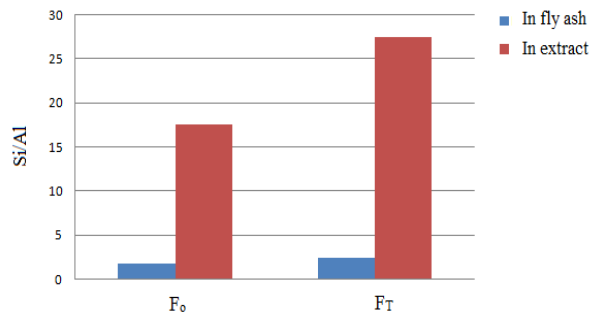


Fig. 7 Comparison of the Si/Al ratio in the obtained extracts and initial fly ashes

Comparison of the Si/Al ratio in the obtained extracts and initial fly ashes were demonstrated in Fig. 7. It was seen that the Si/Al ratios in the obtained extracts of F₀ and F_T were higher than in the initial fly ashes. The difference in Si/Al extracted amounts and ratio was due to the different mineralogical and chemical composition of fly ashes and in addition the different solubility degree of Si and Al.

IV. CONCLUSIONS

In this study the mineralogical and chemical compositions of two different type fly ashes were investigated by XRD and XRF analyses. From the XRD results, F₀ mainly composed of quartz, mullite, and ferrosilite. F_T mainly consists of quartz, mullite, and hematite. In addition, Si and Al in F₀ and F_T were activated by fusion with sodium hydroxide. According to ICP-OES analysis, concentrations of Si and Al in the extracts of F₀ were lower than in the F_T. The results will be helpful for the potential application of coal fly ash and on the environmental impact of its subsequent use.

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