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## FTIR spectroscopic investigation of alkali-activated fly ash: A test study

### ABSTRACT

*Fly ash is byproduct of thermal power plants. Millions tons of fly ash is produced globally. Fly ash is disposed partly in landfills but it could also be released into the atmosphere in the past. Fly ash is composed of silica, alumina, iron oxide, magnesia and activated carbon. Due to large surface area, fly ash is very suitable for catalysis application. It is well known and well reported that fly ash can be converted into efficient adsorptive material such as zeolites. In the present work, the transformation of fly ash into zeolite was carried out by alkali activation process of aluminosilicates material. The alkali solution releases silicon and aluminum ion into solution, which form afterwards Si-OH and Al-OH groups. FTIR spectroscopy was applied to characterize fly ash chemical activation, in order to conduct a study making intensive use of infrared spectroscopy and further to provide information on chemical bond vibrations in the molecular units of fly ash. The FTIR spectrum of solid base fly ash (SBFA) after chemical activation shows a significant increase in peak intensity of the band for -OH group.*

**Keywords:** fly ash, chemical activation, catalyst, FTIR spectroscopy.

### 1. INTRODUCTION

Fly ash is also known as pulverized fuel ash, is a coal combustion product that is composed of fine particles [1,2]. Treatment of fly ash with alkali solution produces a "zeolite precursor" and it is characterized by a three-dimensional structure and long- and mid-range disorder [1-7]. The product obtained after alkali activation is a material that possesses high surface area and can be used in catalysis, especially in fine chemical, petrochemical and pharmaceutical industries [1,2]. Fly ash consists of silica, alumina, iron oxide, magnesia and in minor amount comprises activated carbon as well [1,5]. Additionally, it is well reported that fly ash has been used as a catalyst, for H<sub>2</sub> production, deSO<sub>x</sub>, deNO<sub>x</sub>, hydrocarbon oxidation etc. [1,6]. Furthermore, it is well reported [1,2,6], that fly ash can be chemically activated by NaOH solution giving though the surface basicity and making it

catalytically active. In the current work fly ash was also chemically activated by an alkali activation process of aluminosilicates material in close resemblance to the studies reported in the literature [1-7]. The aim is to successfully activate fly ash and to acquire a deeper understanding by means of FTIR spectroscopy regarding information on chemical bond vibrations in the molecular units of activated fly ash. FTIR spectroscopy was applied to characterize fly ash before and after chemical activation. IR spectra clearly indicated an augment in the peak intensity of the band for -OH group after chemical activation for the fly ash. Fourier transform infrared (FTIR) spectroscopy technique is rapid and requires minimal or no sample preparation [2,5, 8-12]. FTIR provides a global fingerprint of samples [2,5,8-12].

### 2. EXPERIMENTAL

**Sample preparation:** The solid fly ash used was F-type, rich in silica and alumina content [13]. The activation process was carried out, by rigorously following the procedure reported by Jain et al. [1]. The solid base fly ash (SBFA) was synthesized by chemical activation of fly ash with NaOH (98%, Merck) at different concentrations of

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alkali solutions incrementally increasing up to 50 wt.% [1,2,5]. The chemical activation was carried out in a round flask (equipped with a stirring bar and a condenser) by taking the mixtures of fly ash and NaOH solution, followed by subsequent heating at 110°C under stirring and aging for 2 days preserving the temperature. After ageing, in order to remove leached compounds and excess of NaOH the obtained pulp was washed with distilled water [1,2,5]. The chemically activated fly ash was dried at 110°C for 24 h and thermally stabilized by calcination at 450°C for 4 h in static conditions [1,2,5].

#### Vibrational spectroscopic measurements:

FTIR spectra were collected by Nicolet 6700 spectrometer, manufactured by Thermo Electron, which allows spectral measurements in NIR (12000 - 4000  $\text{cm}^{-1}$ ) and MIR (4000 - 400  $\text{cm}^{-1}$ ) region. This system works in two geometries, the geometry of the transmission and reflectance (Attenuated Total Reflection-ATR). In this study, the transmission geometry is used in the range mid Infra-Red (4000 - 400  $\text{cm}^{-1}$ ) with a resolution of 4

$\text{cm}^{-1}$ . The spectra were analyzed using OMNIC program. Samples were analyzed prior to drying at 120°C for 3 hours.

### 3. RESULTS AND DISCUSSION

The FTIR spectrum of fly ash (FA), before and after chemical activation is shown in Figure 1 (inserted spectra). Fly ash was chemically activated with the highest concentration of alkali solution (50 wt.%) [1,2,5]. The FTIR spectra of solid base fly ash (SBFA) shows a broad band in the region between 3400-3000  $\text{cm}^{-1}$ , which is attributed to surface -OH groups of -Si-OH in excellent agreement with reported IR spectra in the literature [1,2,5]. The broadness of the band is due to the strong hydrogen bonding as well reported in the literature [1,2,5,12]. Jain et al. [1] reported that the hydroxyl groups are not isolated and hence a high degree of association is experienced as a result of extensive hydrogen bonding with other hydroxyl groups.

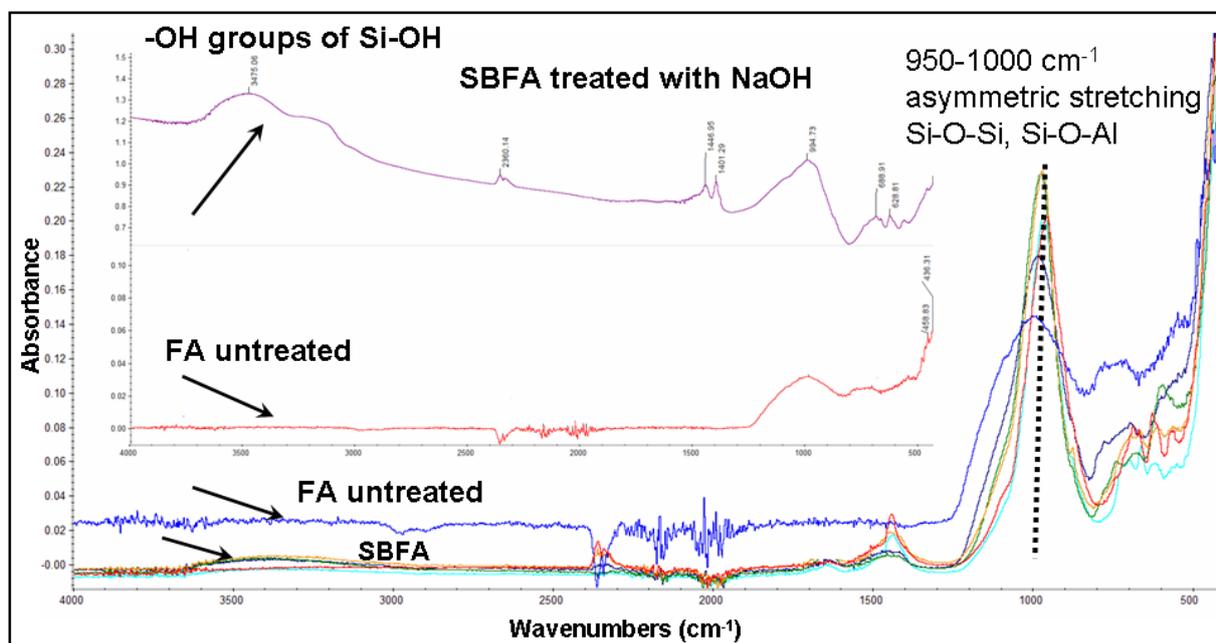


Figure 1. Wide scan FTIR spectrum fly ash (FA, untreated) and a series of wide scans FTIR spectra of solid base fly ash (SBFA, treated) treated with different concentration of alkali solution. The highest concentration was 50 wt.%, of NaOH. The inserted spectra indicate FA before and after treatment with NaOH (with the highest concentration of NaOH, 50 wt.%).

Slika 1. Širok FTIR spekter serije pepela (FA, neobrađen) i serija FTIR spektara pepela od čvrstog baznog pepela (SBFA, tretiranog) tretiranog različitim koncentracijom alkalnog rastvora. Najviša koncentracija je bila 50 tež.% NaOH. Umetnuti spektri pokazuju FA pre i posle tretmana sa NaOH (sa najvećom koncentracijom NaOH, 50 tež.%).

It is relevant to mention that water which absorbs on the surface gives also a broad band in the region between 3400-3000  $\text{cm}^{-1}$ , however, FTIR spectrum of untreated FA displays a flat line

in the region 3400-3000  $\text{cm}^{-1}$ . The latter suggests that the broad band in the FTIR spectrum of SBFA (after chemical activation) in the region 3400-3000  $\text{cm}^{-1}$  belongs to the -OH groups of -Si-OH and not

to the  $-OH$  of water molecules. Furthermore, water gives a characteristic peak at  $1650-1630\text{ cm}^{-1}$  in the IR spectrum, which is attributed to bending mode ( $\delta_{O-H}$ ) of water molecule [1,2,5,12]. In this respect, both FTIR spectra before after chemical activation of fly ash (Figure 1) show no peaks at  $1650-1630\text{ cm}^{-1}$  region. Nevertheless, minor amount of water absorbed on the surface of FA or SBFA cannot be excluded.

Figure 1 gives also a series of wide scans of FTIR spectra activated with NaOH at different concentrations. There is an increase in the peak intensity of the band for the  $-OH$  groups upon increasing the concentration of NaOH incrementally. This is, however, more evident in the peaks intensities appearing in the range  $1000-950\text{ cm}^{-1}$ , which are attributed to the Si-O-Si and Si-O-Al asymmetric stretching [1,2,5,12]. The most intensive peak for the Si-O-Si and Si-O-Al asymmetric stretching belongs to the sample

treated with highest concentration of NaOH, i.e. 50 wt.% [1,2,5,12]. It is also reported that that internal vibrations in silicates appear as wide bands at  $1062, 1064$  and  $1092\text{ cm}^{-1}$  [7]. The latter is in good agreement with the current work.

Figure 2, displays yet again a series of FTIR spectra for SBFA samples with incrementally increased NaOH concentrations in a narrow range  $1400-400\text{ cm}^{-1}$ , including the FTIR spectrum of the untreated FA as well. It is evident from Figure 2 that upon increasing the concentration of alkali solution, the peak position for the Si-O-Si and Si-O-Al asymmetric stretching has moved slightly to lower wavenumbers. The latter may be explained due to the increased population of  $-OH$  groups on the surface. This shift in the range of  $1100-950\text{ cm}^{-1}$  was also reported by Fernandez-Jimenez and Palomo [7]. Additionally, the Si-O-Si bending vibrations appear in the range  $\sim 450-430\text{ cm}^{-1}$ , [1,2,5,12].

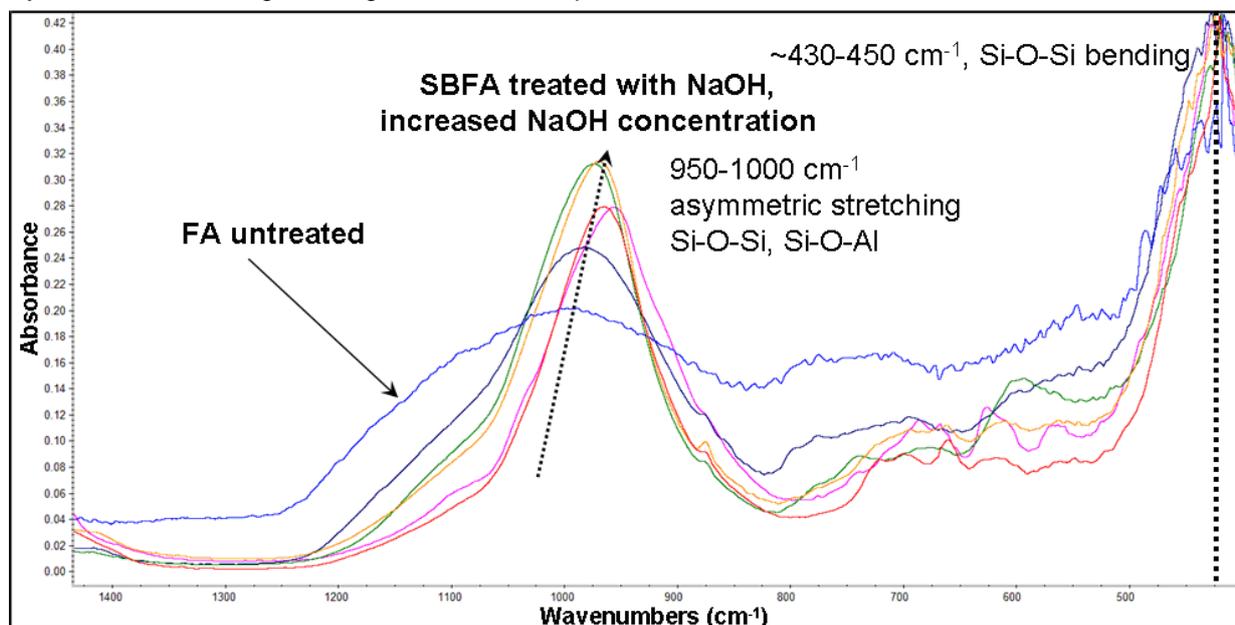


Figure 2. FTIR spectrum of fly ash (FA, untreated) and a series of FTIR spectra of solid base fly ash (SBFA, treated) treated with different concentration of alkali solution in the region  $1400-400\text{ cm}^{-1}$ .

Slika 2. FTIR spektar elektrofilterskog pepela (FA, neobrađen) i serija FTIR spektara pepela od pune baze (SBFA, tretirana) tretirana sa različitim koncentracijama alkalnog rastvora u rasponu  $1400-400\text{ cm}^{-1}$ .

To this end, the spectra of Figure 1 shows signals of SBFA at  $1440-1400\text{ cm}^{-1}$  which are also observed in the IR spectra of SBFA reported in the literature [1,2,5,12].

#### 4. CONCLUSION

In the present work fly ash was activated by alkali solution and further characterized by FTIR spectroscopy. FTIR spectra featured similarities to a large extend with those reported in the literature.

Additionally, FTIR spectroscopy technique proved to be very effective for interpreting and understanding information on chemical bond vibrations in the molecular units of activated fly ash.

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## IZVOD

### FTIR SPEKTROSKOPSKO ISTRAŽIVANJE ALKALNO AKTIVIRANOG PEPELA

*Leteći pepeo je nusproizvod termoelektrana. Milioni tona letećeg pepela se proizvodi širom sveta. Leteći pepeo se delimično uklanja u deponije, ali bi se mogao puštati u atmosferu. Leteći pepeo čine silicijum, glinice, gvožđe oksid, magnezijum i aktivni ugalj. Zahvaljujući velikoj površini, leteći pepeo je veoma pogodan za primenu kao katalizator. Poznato je i prijavljeno je da se leteći pepeo može pretvoriti u efikasan adsorpcioni materijal, kao što su zeoliti. U sadašnjem radu, transformacija letećeg pepela u zeolit izvršena je procesom alkalne aktivacije materijala aluminijum-silikata. Alkalni rastvor daje silicijum i aluminijum jon u rastvoru, koji formiraju posle Si-OH i Al-OH grupe. FTIR spektroskopija primenjena je za karakterizaciju hemijske aktivacije letećeg pepela, kako bi se sproveda studija koja intenzivno koristi infracrvenu spektroskopiju i dalje pruža informacije o vibracijama hemijskih veza u molekularnim jedinicama pepela. FTIR spektar elektrofilterskog pepela (SBFA) nakon hemijske aktivacije pokazuje značajno povećanje intenziteta vršnog opsega za -OH grupu.*

**Ključne reči:** leteći pepeo, hemijska aktivacija, katalizator, FTIR spektroskopija.

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