

## FLY ASH TREATMENT TECHNIQUES FOR OBTAINING ARTIFICIAL ZEOLITES

**Silvana Gjyli**

Department of Industrial Chemistry, Faculty of Natural Sciences,  
University of Tirana, Albania

**Arjan Korpa**

Department of Chemistry, Faculty of Natural Sciences, University of  
Tirana, Albania

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### ABSTRACT

This paper provides a technical solution to converting industrial waste of coal fly ash found in the area into chief value products such as zeolite. Recycling this solid is of great benefit in terms of quality, cost effectiveness and environment. Applying fusion method subsequently followed by hydrothermal treatment for the synthesis of zeolites is a means to address highly crystalline zeolite with maximum BET surface area. Different experimental conditions were tested such as type of water used (distilled water and seawater), action of acid pre-treatment, alkaline ratio, crystallization time (from 1 to 72 h), and temperature of crystallization (from 40 to 90 °C). One of the optimal synthesis conditions for Zeolite X was the pretreated fly ash, NaOH/FA ratio of 1.25, fused at 550°C for 1 h, crystallization 60 °C for 72 h using distilled water. Meanwhile, the optimal synthesis condition for zeolite A was the pretreated fly ash, NaOH/FA ratio of 1.25, fused at 550 °C for 1 h, NaAlO<sub>2</sub>/FA ratio of 0.5 crystallization 90 °C for 6 h using distilled water. The fly ash and synthesized zeolite samples were analyzed via XRF, XRD, SEM, BET. The results showed that Zeolite type X and A were synthesized with a high crystallinity and high value of surface area up to 412 m<sup>2</sup>/g, suitable for application.

**Keywords:** fly ash; acid pre-treatment; zeolite synthesis

### 1. INTRODUCTION

Industrial waste is defined as waste generated by manufacturing or industrial processes. The major generators of industrial solid wastes are the by-products of combustion power plants producing coal fly ash. Accumulation of massive amounts of such residues causes serious environmental, aesthetic, economic and social problems. The re-evaluation of “wastes” in which significant energy has been invested and lost through

disposal via their conversion into sustainable construction materials and products is probably the best way to recover this energy (Goumans *et al.* 1991). Fly ash produced from thermal power plants is one of the waste by-products with major potential for recycling.

Seung *et al.* (1999), Kula (2002), Wu (2002), Korpa *et al.*, (2013) said that fly ash offers a large spectrum of utilization possibilities that have been recognized so far by reporting its application areas such as building industry, underground mining etc. However, they said that it still leaves room for searching new application methods that would enable its values and particularly its chemical composition to be more fully exploited. The high content of silica and alumina fly ash make it a suitable feedstock in the synthesis of high value zeolitic material and therefore competing with zeolites made from pure industrial chemicals, which is of great importance for the sustainable resource management (Hums 2016; 2017).

Using the zeolites synthesized from fly ash is of particular interest, because it allows undesirable waste to be converted into a high value-added product. Zeolites are crystalline, hydrated aluminosilicate compounds that have three-dimensional structures arising from a framework of tetrahedral units  $\text{SiO}_4$  and  $\text{AlO}_4$ , each tetrahedral unit being linked by an oxygen atom. The three-dimensional structure is constructed from pores of molecular dimension. The framework is generally open and contains channels and cavities in which are located cations, water molecules (Breck 1974) and it is accessible for the adsorption of small molecules.

Zeolites are technologically useful in various sectors because of their high selectivity, stability and exchange, sorption and catalysis capacity. A hydrothermal process is the most common method to convert fly ash into zeolites. However, some studies reported that zeolites produced from fly ash have a low purity and low sorption efficiency (Franus and Franus 2013; Cardoso 2015). Alkali fusion has been a general method for decomposing materials containing Si and Al in chemical analysis (Breck 1974; Chang 1998; Belviso 2018) converted fly ash to zeolite by a significantly improved fusion method in which NaOH was fused with fly ash prior to conventional zeolite synthesis. Thus far, few studies on the synthesis of zeolite using seawater for crystallization have been carried out (Yu *et al.*, 2014). The advantages of using seawater not only include reducing the treatment costs obviously incurred from the use of distilled water, but also the lower cost of heating water to the necessary reaction temperature when using warm seawater from power plants. Ion exchange and catalytic ability of zeolites allows for their usage in industries. Zeolites can be used for base-catalyzed reactions, because of the alkaline and alkaline earth elements they host inside their structural cavities (Corma *et al.* 1990; Ziosi 2014; Gjyli 2019). In this exploratory project, specific innovations pertaining to utilization of this waste that is highlighted

aims to provide an alternative method for recycling CFA using seawater. The synthetic zeolites were characterized in terms of mineralogy and morphology by instrumental analysis and chemical methods. Furthermore, the effects of seawater salinity on the reaction that occurs during the formation of zeolite from CFA were investigated.

## 2. MATERIALS AND METHODS

### *Materials*

The main raw material, coal fly ash (Class F type) sample was supplied from the BauMineral Gmb, a German power plant company. Sodium hydroxide, sodium aluminate and hydrochloric acid were purchased from Sigma Aldrich, respectively  $\geq 97.0\%$  purity, anhydrous pellets, 99.9%  $\text{NaAlO}_2$  powder and ASC, reagent 37% HCl.

### *Zeolite synthesis procedure*

Initially raw fly ash (FA) was added to HCl, with 20% w/w acid concentration under the acid/FA ratios of 15 ml acid/g FA (Panitchakarn *et al.* 2014). The mixture was constantly stirred at the rate of 300 rpm at 80 °C for 2 h. Once stirred, the solid sample was filtered off from the acid solution and repeatedly washed with distilled water until the solution reached the neutral pH and then dried overnight at 90°C in oven.

Whether pre-treated or not, the fly ash was mixed with sodium hydroxide anhydrous pellets, in a weight ratio NaOH/FA of 0.75 and 1.25 by initially grinding the fly ash with sodium hydroxide using a ball mill for 20 min to obtain a fine homogenously ground material. Subsequently, the mixture was fused at 550 °C for 1 h in a muffle furnace to convert insoluble fly ash mineral phases into soluble sodium silicate and sodium aluminate (Querol *et al.* 2002; Belviso *et al.* 2009; Ruengam 2009). Once cooled down, the product was crushed and was added  $\text{NaAlO}_2$  to make the ratio  $\text{NaAlO}_2/\text{FA}$  of 0.5 and 1 to investigate the effect of the ratio of Si/Al (Korpa *et al.*, 2013). The mixture was dispersed in a weight ratio of 1/5 ml of seawater or distilled water. Crystallization was then performed under static condition (40, 60 and 90°C) for 1-72 h. The crystal products were separated and washed several times with distilled water for a pH of around 10–11. The wet solid was finally dried overnight at 105 °C and then calcined at 550 °C for 5 h, and used as previously described.

### *Characterization methods*

The X-ray fluorescence (XRF) (PANalytical AXIOS Spectrometer) was applied for the chemical composition for major chemical constituents and trace elements.

The mineral characterizations of both fly ash and zeolite products were determined via powder X-ray diffraction (XRD) using a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator, using copper radiation Cu-K $\alpha$ . The analysis was carried out within the angle range of 2-70  $2\theta$  and step size 0.02 $^\circ$ .

The morphology and the chemical composition of the main mineral components of the examined materials in the micro area domain were determined using the electron scanning microscope (SEM). The equipment used was a Zeiss Supra 40 scanning microscope, which was additionally equipped with a chemical composition analysis system based on energy dispersion scattering the EDS EDAX. The Alpha Bruker FT-IR spectrometer in the range 400-4000  $\text{cm}^{-1}$  was used for the infrared spectroscopic analysis of the prepared zeolite and fly ash. The specific surface area of the zeolite samples was determined applying the N $_2$  adsorption - desorption technique involving Brunauer-Emmett-Teller (BET), Sorpty 1750 Fison instrument, after a preliminary degassing step under vacuum at 150  $^\circ\text{C}$ .

### 3. RESULTS AND DISCUSSION

In the present paper, zeolite samples were synthesized from fly ash through fusion followed by hydrothermal treatment. The chemical composition of fly ash determined by means of XRF contains mainly 78 % SiO $_2$  + Al $_2$ O $_3$ , whereas the impurities consist of metallic oxides such as Fe $_2$ O $_3$  and CaO. Other elements including K $_2$ O, TiO $_2$ , SO $_3$  and MgO are present on trace (Table 1 (defined as class F coal fly ash corresponding with ASTM C618)). The FA contained a reasonable fraction of Si and Al, which was considered a potential raw material for the synthesis of zeolite.

The X-ray diffraction pattern of fly ash primarily represents the presence of amorphous material (mainly SiO $_2$ , Al $_2$ O $_3$ ) and with the remaining crystalline phase consisting of quartz and mullite.

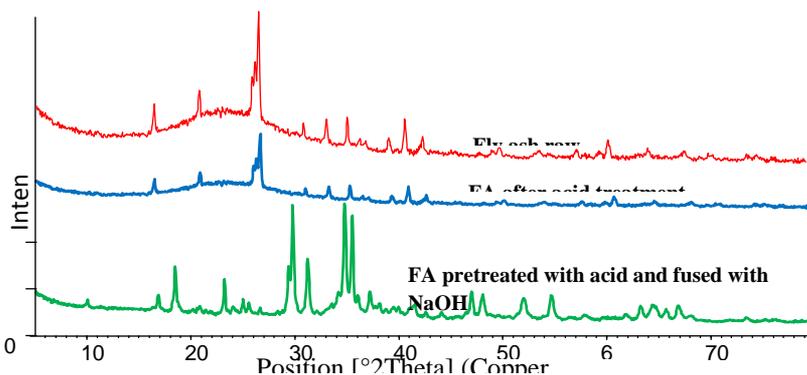
**Table-1.** Chemical composition of raw and acid-treated fly ash and of the zeolites production analyzed by XRF.

Chemical composition (wt. %)	Fly ash raw	After acid treatment	Zeolite X Distilled Water	Zeolite X Sea Water	Zeolite A Distilled Water
SiO $_2$	50.96	61.66	45.76	45.22	39.31
Al $_2$ O $_3$	27.45	24.20	26.99	25.44	34.94
Fe $_2$ O $_3$	7.02	5.47	6.1	5.69	2.96

CaO	4.22	1.07	1.26	2.08	0.67
K <sub>2</sub> O	3.34	3.21	1.43	1.32	0.76
TiO <sub>2</sub>	1.74	1.92	1.9	1.54	0.96
SO <sub>3</sub>	1.52	0.18	0.05	0.07	0.01
MgO	1.28	0.75	0.87	3.51	0.38
Na <sub>2</sub> O	0.92	0.68	15.19	13.87	19.22
P <sub>2</sub> O <sub>5</sub>	0.77	0.23	0.07	0.02	0.04
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1.86	2.55	1.70	1.78	1.12

The results of XRF analyses reported in the Table 1 and the presence of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> show that fly ash contains several other components that are undesirable to synthesized zeolites. Some of these components act as poison during the catalytic applications of zeolites (Ojha *et al.*, 2004). This fly ash used as raw material was treated with acid-washing to dealuminate and reduce the concentration of iron and alkali oxides and to enhance Si and Al compositions. The Table 1 shows that most of the impurities (Fe<sub>2</sub>O<sub>3</sub>, CaO, and other impurities) up to 8 % in fly ash can be removed by treatment with 20% w/w of hydrochloric acid and enhance SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> compositions up to 86 % respectively. These results agree with that of (Shivpuri *et al.*, 2011) and (Panitchakarn *et al.*, 2014) who reported that heavy metals showed a high leachability in acidic conditions.

The prepared zeolites were characterized in order to investigate the dependence on the synthesis conditions.



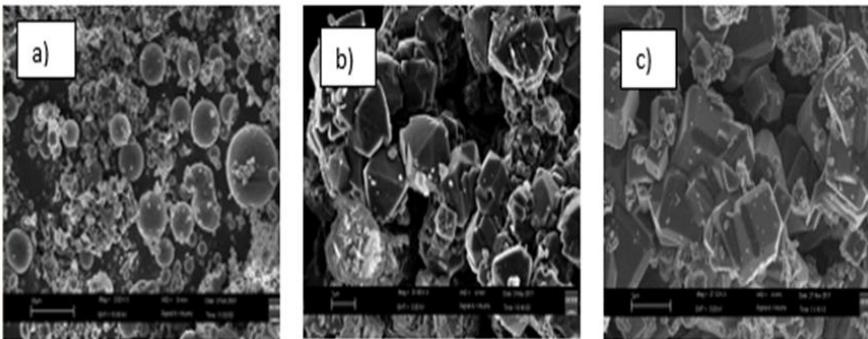
**Fig. 1.** X-ray diffraction patterns of raw fly ash, fly ash pretreated with acid, fly ash pretreated with acid and fused with NaOH/FA 1.25 at 550°C for 1 h.

We have made numerous experiments using different NaOH /fly ash/ ratio, hydrothermal, fusion, crystallization time, distilled or sea water, pretreatment of fly ash with acid, the addition of NaAlO<sub>2</sub> etc. to determine the optimal conditions for the synthesis of pure zeolites based on degree of crystallinity and BET value of the synthesized product.

The figure 1 depicts X-ray diffraction patterns of fly ash before and after pretreated with acid. The results showed that the fly ash mineralogical composition did not change during treatment since it was still characterized by the presence of both mullite and quartz as well as by a large amount of amorphous materials. XRD of the same sample of fly ash after a pretreatment with acid, was fused with NaOH/FA 1.25 at 550 °C for 1 h fig. 1, indicates the formation of sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) and sodium aluminosilicate (NaAlSiO<sub>4</sub>).

The proposed synthesis based on pre-fused treatment and following hydrothermal process, gave different products depending on the reaction conditions and parameters chosen.

The figure 2 (a- c) depicts the scanning electron microscopy (SEM) images of the aforementioned products. The scanning electron micrographs (SEM) of the raw fly ash, is depicted in (fig. 2a). SEM observation shows the typical morphology of fly ash characterized by the majority of spherical particles, related to the cooling effect of flue gas under power plant conditions.

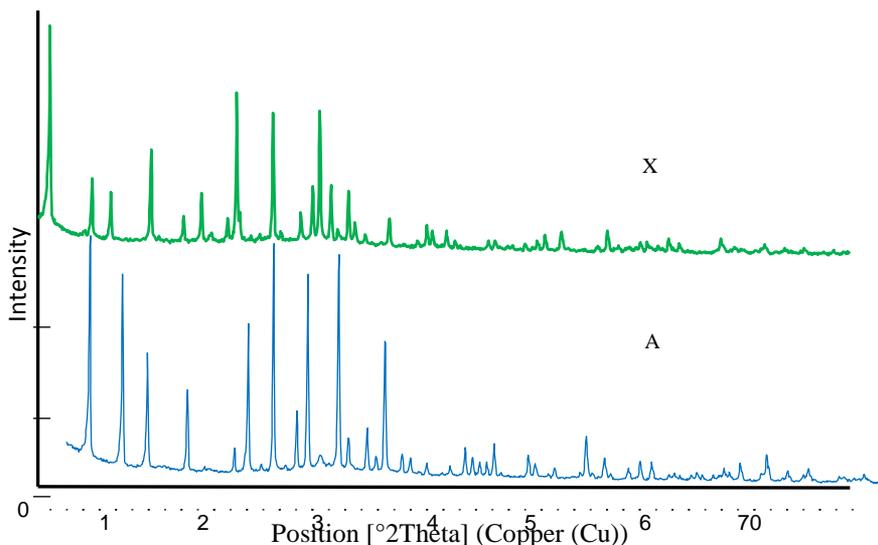


**Fig. 2.** Scanning electron microscopy (SEM) images of raw fly ash (a), zeolite type X (b), zeolite type A (c).

The absence of the fly ash spherical particles (as evident from the SEM images b and c) shows high conversion rate of fly ash to crystalline zeolite under hydrothermal conditions. The zeolite X has octahedral morphology and the zeolite type A contains lumps of cubic shape —both typical shapes of artificial zeolites.

Crystalline phases indicating zeolite peaks of type X and type A synthesized from fly ash appeared through the hydrothermal treatment, as shown in Fig. 3. (top) zeolite X and (bottom) zeolite A. The resulting aluminosilicates were rapidly dissolved in the hydrothermal synthesis, in a weight ratio of 1/5 ml of seawater or distilled water, followed by crystallization under static condition (40, 60 and 90°C) for 1-72 h which finally contributed to the formation of zeolitic crystals type X.

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**Fig. 3.** X-ray diffraction patterns of synthesized zeolite from fly ash type Zeolite X (top) and Zeolite A (bottom).

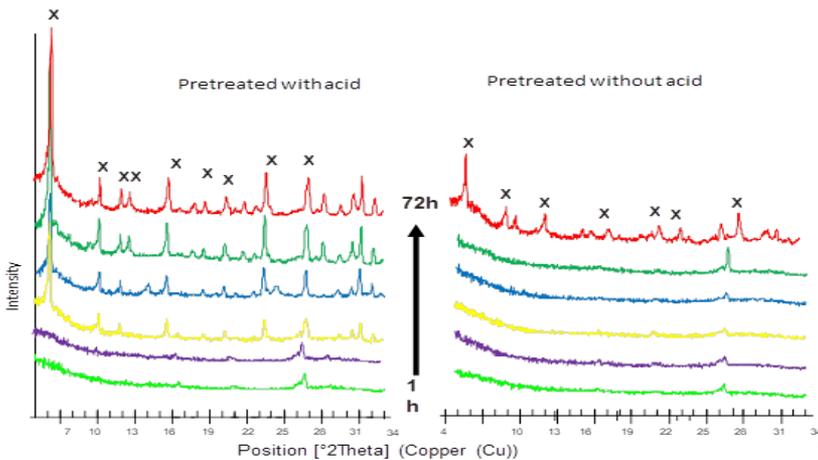
Meanwhile, when the experiment is repeated adding sodium aluminate after the fusion at 550°C for 1 hour, the zeolite type A product with a higher purity (80–97%wt of purity) was achieved (fig. 3). A high degree of crystallization was shown because no considerable amounts of amorphous material were detected.

Since the large pore and high-BET zeolites (X and A-type) are the focus of this experimental work, the impact of the synthesis conditions and reaction parameters on type and structure of the products obtained is discussed and analyzed .

For further confirmation, the IR spectrum of fly ash and zeolite X and A was recorded representative IR spectra formed confirm the presence of zeolite with the two most intense bands at 860–1230  $\text{cm}^{-1}$  and 420–500  $\text{cm}^{-1}$  (Flanigen 1971).

The synthesis of zeolite X was favored by the  $\text{SiO}_2 / \text{Al}_2\text{O}_3$  wt ratio  $> 1.86$  or otherwise expressed in the  $\text{SiO}_2 / \text{Al}_2\text{O}_3$  mole ratio of 3.1 which is suitable for the synthesis of zeolite X. These results agree with those of (Tanaka *et. al.*, 2002 and Izidoro 2013), who reported that zeolites such as (Na-X and Na-Y) formed in the  $\text{SiO}_2 / \text{Al}_2\text{O}_3$  molar ratio of more than 1.

The results reveal that without addition of  $\text{NaAlO}_2$  the zeolite A could not be synthesized, who reported that a single phase zeolite type A was formed at the Si / Al molar ratio of not more than 1.



**Fig. 4.** X ray diffraction (XRD) patterns of zeolite type X synthesized from fly ash pretreated with acid (left) and fly ash pretreated without acid (right).

The figure 4 depicts the (XRD) patterns of zeolite type X synthesized from fly ash pretreated with acid,  $\text{NaOH}/\text{FA}$  1.25, crystallization temperature  $60\text{ }^\circ\text{C}$ ; from 1 to 72 h time of crystallization, using distilled water (left) that result with highest value of surface area  $412\text{ m}^2/\text{g}$ . On the right of the figure it is depicted the zeolite type X synthesized from fly ash pretreated without acid,  $\text{NaOH}/\text{FA}$  1.25, crystallization temperature  $60\text{ }^\circ\text{C}$ ; from 1 to 72 h time of crystallization, using distilled water with a value of surface area up to  $186\text{ m}^2/\text{g}$ . The difference of treatment or not with acid affect in the purity and intensity of the peaks of zeolite. Here, the XRD pattern showed the weak reflections attributable to zeolite X when fly ash was not pretreated.

Among the zeolite synthesized from fly ash treated with  $\text{HCl}$  provided the highest purity material (87% of  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ ), Table 1, the chemical composition of zeolite products synthesized from the nontreated fly ash show a purity of 79% ( $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ ).

The Si/Al molar ratio of the treated fly ash was adjusted, by adding sodium aluminate as a source of aluminum, to investigate the effect of the ratio of Si/Al (Lee 2010).

If the sodium aluminate in 0.5 and 1 ratio  $\text{NaAlO}_2/\text{FA}$  is added, Si/Al ratio changes 1,12 thus defining the synthesis of A-type zeolite after 4 hours. Based on these results, the zeolite synthesized from fly ash with addition of sodium aluminate in a ratio 0.5  $\text{NaAlO}_2/\text{FA}$  had the highest purity and yield, then when was used the ratio 1  $\text{NaAlO}_2/\text{FA}$ .

Zeolite have been successfully synthesized from fused fly ash by using seawater as a crystallization medium. Seawater was evaluated for the synthesis of zeolite instead of distilled water using fly ash as raw material; the zeolites were synthesized by alkali fusion.

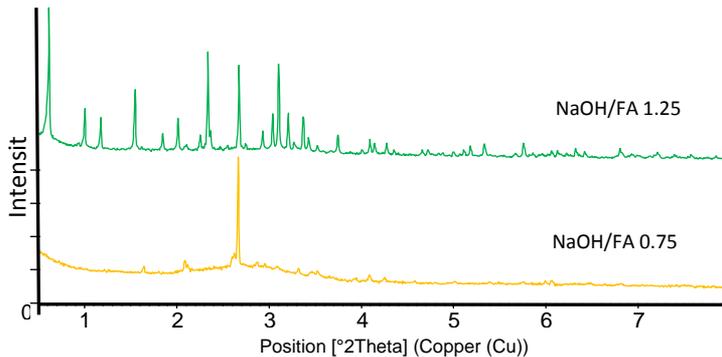
The synthetic product phase detected when distilled water has been used was generates production of zeolite X with a value of specific surface area  $412 \text{ m}^2/\text{g}$ , meanwhile when sea water was used was synthesized zeolites type X with a value of specific surface area  $362 \text{ m}^2/\text{g}$ .

The use of seawater improves the zeolite synthesis and the action is more pronounced at lower incubation temperature. When sea water is used instead of distilled water to produce zeolite X, the zeolite has lower purity and specific surface area but higher catalytic activity than when distilled water was used (Gjyli *et al.*, 2019).

In short time of crystallization 24 h, low temperature  $60 \text{ }^\circ\text{C}$  and low ratio of  $\text{NaOH}/\text{FA}$  0.75, the use of sea water was favorable compared to distilled water in the synthesis of zeolite type X.

However, it was confirmed from XRD profile, when it was used sea water, time of crystallization 72 h, crystallization temperature  $90 \text{ }^\circ\text{C}$  and ratio of  $\text{NaOH}/\text{FA}$  1.25 was generated production of sodalite, an undesired secondary product during zeolite synthesis.

Meanwhile, crystallization is the process that forms the crystal framework of the zeolite, which occurs faster at higher crystallization temperatures. The surface area increased from 44 to  $412 \text{ m}^2/\text{g}$  as the crystallization temperature increased from  $40$  to  $60 \text{ }^\circ\text{C}$ , and then dropped to  $318 \text{ m}^2/\text{g}$  at  $90 \text{ }^\circ\text{C}$ . Experiments confirm the influence of crystallization time on the products' structure. The zeolite A had synthesized within 4 hours. The zeolite X had synthesized for 24 hours.



**Fig. 5:** XRD patterns of Zeolite X and geopolymers formed at NaOH/FA 1.25 (top) and NaOH/FA 0.75 (bottom).

The sodium hydroxide added to fly ash not only works as an activator, but also adjusts the sodium content in the starting material. The NaOH/FA ratio of 1.25 seemed to be optimal for zeolite X and zeolite A, compare with NaOH/FA ratio of 0.75 fig. 5.

Insufficient concentration of alkali might lead to minimal extraction of alumina-silicates from fly ash which adversely affects the crystallization process.

Except NaOH ratio, the other parameters used during the synthesis of samples in the Figure 5 are acid treated and pre-fused FA, crystallization temperature 60 °C, crystallization time 72h and distilled water.

The purity of the zeolite product was enhanced by the increase of alkaline condition (i.e., high NaOH), which enhanced the zeolitization reaction. However, a further increase in the NaOH/FA ratio beyond 1.5 is not recommendable because the alkalinity might activate the decomposition of Si and Al to sodium silicate and aluminate in the framework or could form hydroxysodalite instead of zeolite.

#### 4. CONCLUSIONS

The present paper reveals a new way of zeolites synthesizing from industrial solid wastes such as fly ash. The syntheses of zeolites type X and A from fly ash were completed by alkali fusion followed by hydrothermal treatment. Chemical composition of the obtained material was identified as a single-phase zeolite A when the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  wt. ratio was 1.12. The latter was controlled by adding the  $\text{NaAlO}_2$ , and the zeolite X was slightly produced at  $\text{SiO}_2/\text{Al}_2\text{O}_3$  wt. ratio 1.86. In addition, the results showed that acid-washing conditions and synthesis conditions (i.e., NaOH ratio, time of crystallization,

temperature, type of water used) have a significant impact on the chemical and physical properties of the synthesized zeolite products.

The use of seawater improves the zeolite synthesis and the action becomes noticeable at lower incubation temperature. This was reflected in the results where the % of zeolite X increased linearly when the crystallization temperature increased from 40 to 60 °C. However, when it was used seawater above a certain reaction temperature at 90 °C saw a drastic drop of crystallized zeolitic elements and decompose into other stable structures, such as formation of undesired zeolite products with low water content like sodalite. These synthetic products of Zeolite X and A has a wide range of application as catalysts, absorber etc. for commercial products and environmental problems with very high efficiency.

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