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Investigation of Various Parameters for Synthetic Zeolite Production From Turkish Fly Ashes

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Burning of coal in coal-fired electrical power generation plants produces solid waste in the form of boiler slag and fly ash. A large portion of this production is accounted for the coal fly ash. Coal combustion by-products in Turkey are about 45 million tons per year. This study focuses on the synthesis of zeolites from Soma and Yatagan power plant ashes in laboratory scale and on determining the conditions, which govern the related processes. In an alkaline ambient, fusion and hydrothermal treatment were applied as the test methods. The samples obtained from the experiments were investigated by electron microscope SEM and XRD. The final product was observed and determined to be sodalite, which has very similar crystal structure and properties as zeolite.

Key Words: Coal combustion, Fly ash, Synthetic zeolite,

INTRODUCTION

Huge quantities of coal are used in electric power plants thoughtout the World. The disposal of the ash generated from the combustion of coal causes a serious environmental problem[1]. Coal fly ash discharged from the coal electric a power plant occupies a great part of the total amount of coal ash. In recent years there has been a great deal of research conducted to reduce the cost of disposal of this waste and to minimize the environmental impacts. About half of discharged coal fly ash is used as the raw material of cement, but the rest of coal fly ash is disposed in the land fill[2]. Zeolite synthesis from coal fly ash is a minor but interesting product, with high environmental applications. The conversion of coal fly ash to zeolite[2] has been investigated about 20 years. Zeolites may be easily obtained from coal fly ash by relatively cheap and fast conversion processes. Zeolites have been obtained by hydrotermal reaction of fly ash in previous studies[3]. Synthetic zeolites, which can be produced in many different ways, have favourable advantages compared to natural zeolites. Owing to the high content of reactive phases such as aluminosilicate glass and the high specific surface area of fly ash, these combustion wastes are suitable starting materials for the synthesis of zeolites. The most prominent of these advantages are high ion exchange capacity, wide surface area and high adsorption capacity.

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The zeolite synthesized from coal fly ash is mixed with various agricultural materials, which are consumed in large quantities for the purpose of water purification and soil improvement, *etc*. Many researchers report that the zeolite crystal production from coal fly ash by hydrothermal reaction is possible, but the detailed reaction mechanism of hydrothermal synthesis has not yet been adequately clarified.

EXPERIMENTAL

Coal fly ash samples were collected from electrostatic precipitators of Soma and Yatagan thermal power plants for zeolite synthesis. Samples were used directly in the experiments without any preparation. After homogenization, samples were prepared for analysis and experimental work. Physical and chemical properties of the coal ash were measured. Diffraction and fluorescence (XRD-XRF) analyses have been made to determine qualitatively the mineralogical characterization and elementary content of the samples and SEM analyses have been carried out morphological investigation. The elementary composition of the material has been determined by the chemical analysis method and these analyses have been read on the atomic absorption spectrometer.

Zeolite synthesis from fly ash: In experimental work, fly ashes were used in original size. Experimental procedure is given Fig. 1.

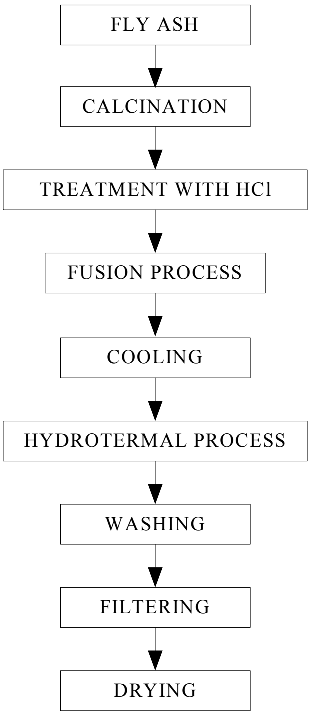


Fig. 1. Process flow diagram for synthesis of zeolite from fly ash

Calcination of fly ash: The unburnt carbons along with other volatile materials present in fly ash were removed by calcination at 800 °C for 2 h.

Treatment with HCl: The fly ash samples were treated with HCl for enhancing activation in zeolite formation. The acid treatment helped to eliminate the fly ash and removed iron to a certain extent, thereby increasing the activity, thermal stability and acidity of the zeolite. Along with SiO_2 and Al_2O_3, fly ash contains several other components that are undesirable in zeolite synthesis. Some of these components are detrimental during catalytic applications of zeolites and can be removed by acid treatment. HCl was used to reduce the concentration of iron, which were located mainly in the outer part of the ash particles and also to leach some amount of Al_2O_3. It helped in increasing the SiO_2 content of the reaction mixture.

Further process: The sodium hydroxide present in the reaction mixture acts as an activator during fusion to form soluble silicate and aluminates salts, which further take part in zeolite formation during hydrothermal process. Na^+ cation also plays an important role in zeolite formation. Sodium ions are known to stabilize the sub-building units of zeolite frameworks and usually are required for zeolite synthesis under hydrothermal conditions. The effects of NaOH to fly ash ratio on SiO_2/Al_2O_3 as well as on Na/Al ratio of the prepared zeolite were studied by varying the ratio from 1/1-1/5.

Higher the sodium contents in the reactant mixture during fusion, the higher is the production of water-soluble sodium silicates. Increased formation of sodium silicates again, enhances the yield of zeolitic materials produced in subsequent stages. Crystallization of the zeolitic materials occurs through nucleation reaction and crystal growth. Nucleation depends upon the alkalinity. Crystallinity of synthesized zeolite increases with increase in NaOH/fly ash. The mineralogical study indicated the presence of mullite and quartz as major reactive phases during zeolite synthesis from fly ash, after alkali activation. Silicate anions react readily with Al(III) precursors to form alumina silicate compounds. In alkaline solutions, aluminum gives negatively charged tetrahedral $[Al(OH)_4^-]$ species, a structure consistent with its incorporation into zeolite framework during hydrothermal treatment. The general reaction scheme describing the zeolite synthesis process is as follows[4]:

$$\begin{aligned}
&NaOH + Al_2O_3{\cdot}SiO_2 \longrightarrow Na_2SiO_3 + Na_2AlO_2\\
&NaOH_{(aq)} + Na_2Al(OH)_{4(aq)} + Na_2SiO_{3(aq)} \longrightarrow\\
&\big(Na_x(AlO_2)_y(SiO_2)_y{\cdot}NaOH{\cdot}H_2O\big)(jel) \longrightarrow\\
&Na_p\big(AlO_2)_p(SiO_2)_q\big){\cdot}nH_2O
\end{aligned}$$

The properties of synthesized zeolitic materials are also affected by fusion temperature change either affirmative or negative. SiO_2/Al_2O_3 ratio increases with fusion temperature, attains the maximum at around 600 °C and then decreases. During fusion, the silica and alumina present in the fly ash react with the alkali and form

Na-salts soluble in water. The crystallinity was also found to change with fusion temperature and the maximum value was obtained at 600 °C.

Hydrothermal treatment: During hydrothermal treatment, the alumina silicate salts crystallize as various zeolitic materials. The faujasite, like zeolites, nucleates and crystallizes more readily at lower temperature. The recommended crystallization temperature[4], which gives a reasonable rate and well developed crystals, is about 100 °C. In this study, the hydrothermal treatment temperature was kept at 90 °C. Hydrothermal treatment time was found to influence the surface area. It is clear that the surface area of the prepared zeolite increases gradually with increasing treatment time up to 6 h. A decrease in surface area is observed in present studies.

RESULTS AND DISCUSSION

The results of chemical analysis of the samples is given in Table-1. It is seen that ashes from different power plants have different compositions and different particle size.

TABLE-1
CHEMICAL COMPOSITION AND NOMINAL UNDER SIZE (AS TO SCUHMANN PLOT) OF FLY ASH

	Soma	Yatagan
CaO (%)	21.59	15.98
SiO_2 (%)	44.19	46.75
Al_2O_3 (%)	18.45	19.14
Fe_2O_3 (%)	5.71	5.07
MgO (%)	0.66	0.76
SO_3 (%)	3.97	6.63
Na_2O (%)	0.99	0.19
K_2O (%)	1.93	1.63
BaO (%)	0.15	0.13
KK	0.71	2.56
SiO_2/Al_2O_3	2.39	2.44
Nominal undersize (k μm)	300	145

Representative X-ray diffraction (XRD) pattern of Soma and Yatagan fly ashes are shown in Figs. 2 and 3. The crystalline phase of both ashes consists of quartz and orthoclase and the amorphous glass phases are detectable.

The composition of fly ash depends on the type of burning process. Dry incineration, for instance, operating at a temperature range between 1000 and 1200 °C, produces predominantly glass spheres and quartz and orthoclase. Orthoclase is a potassium aluminosilicate with a chemical composition of $KAlSi_3O_8$.

Yatagan fly ash does not have a homogeneous size distribution as shown in Fig. 4. Quartz, orthoclase and illite were determined as massive materials and these minerals kept their original crystalline lattice after burning.. Microcrystalline structure similar to Fe_2O_3 was observed on the surface of coarse fly ashes. Fine fly ash is seen as bigger particles due to agglomeration.

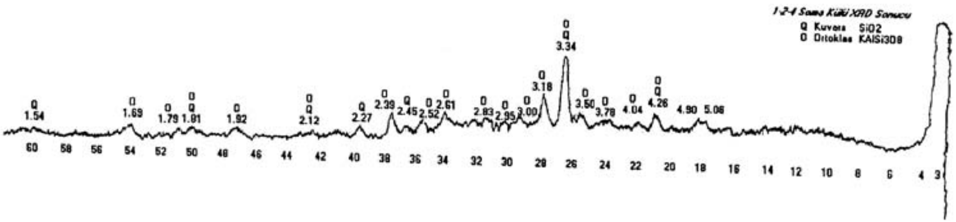


Fig. 2. X-Ray diffraction patterns of soma fly ash sample

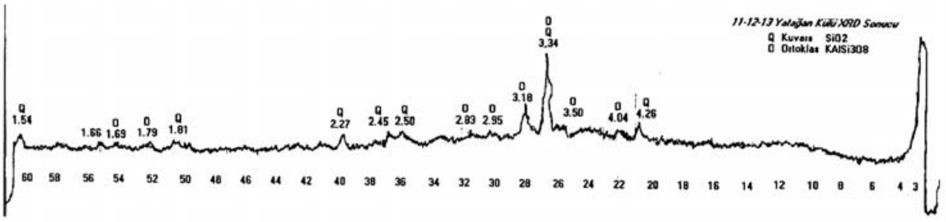
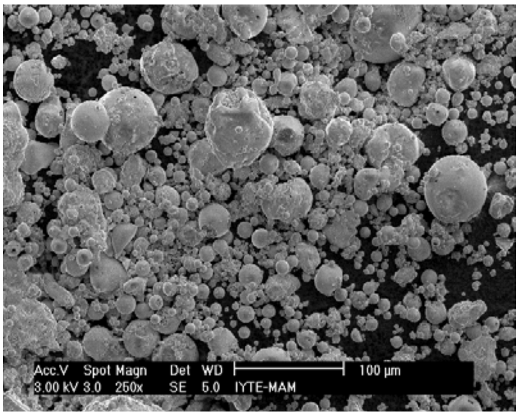


Fig. 3. X-Ray diffraction patterns of yatagan fly ash sample



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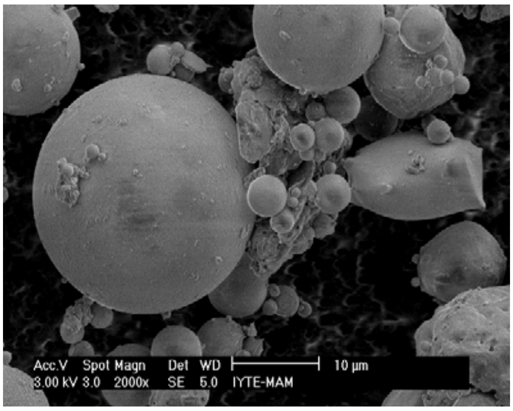

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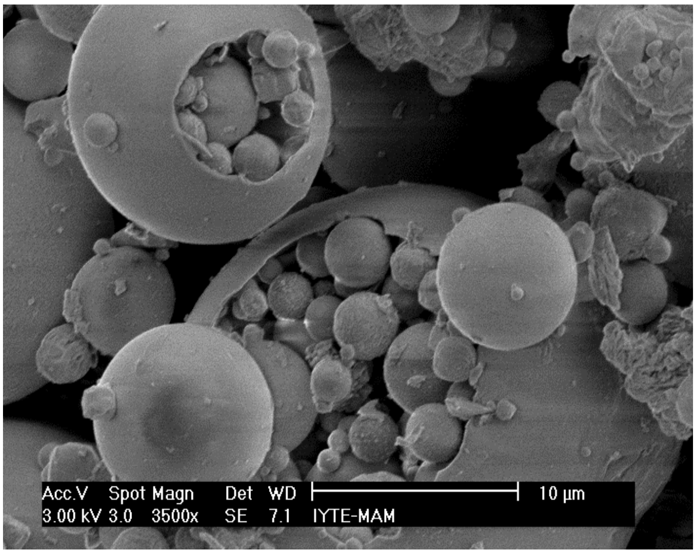

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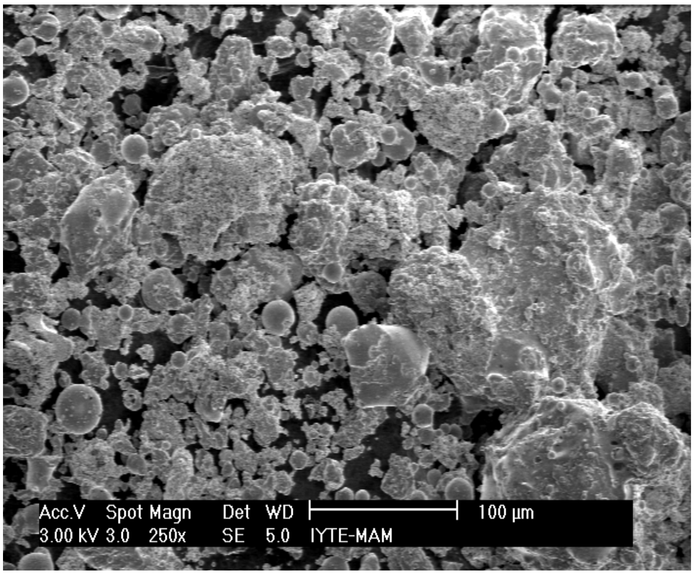
Fig. 4. Scanning EM of Yatagan coal fly ash

Soma fly ashes have different size spheres and hemisphere amorphous particles (Fig. 5). As a result of microanalysis interpretation, it is believed that angular particles are mainly clays and porous structure is unburnt carbon. Deformed half spherical particles are due to cooling of clays within coal structure after burning process.



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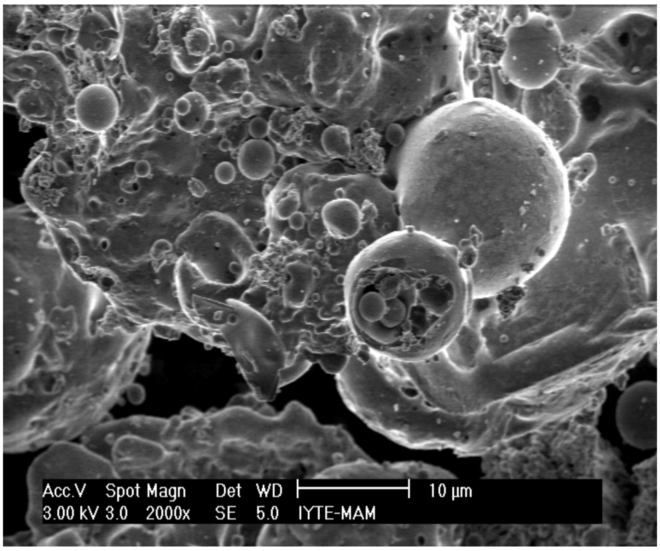

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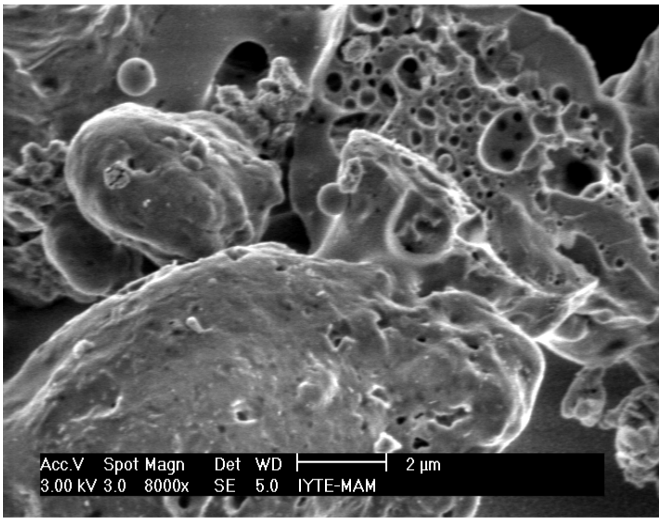

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Fig. 5. Scanning EM of Soma coal fly ash

Effect of NaOH on fusion process: In this study, NaOH was used as an alkaline source for zeolite synthesis. Fly ash/NaOH ratio was altered from 1/1, 1/2, 1/3, 1/4, 1/5.

In many activation processes, alkaline reaction is controlled by the molarity of sodium hydroxide solutions, SiO_2/Al_2O_3 proportions, reaction time and temperature. Increasing pH values (pH > 10), the solubility of the amorphous silica also increases.

Monomeric silica and aluminum complexes are formed and the reaction proceeds towards negatively charged ion complexes[5]:

$$Si(OH)_4 + H_2O + OH^- \rightleftharpoons (H_2O)Si(OH)_5^-$$

The $Al(OH)_4^-$ complexes are subjected to further dehydration steps[5]:

$$2Al(OH)_4^- \rightleftharpoons [(OH)_3\,Al\text{-}O\text{-}Al(OH)_3]^{2-} + H_2O$$

The following zeolitization from fly ash represents an equilibrium reaction between the solution and the solid phase. By temperature elevation, the solubility of the silica and aluminium ions increases and condensation reactions by neoformations of crystals lead towards a complete solution of the amorphous original material by forming more and different zeolite phases:

$$[Na_a(AlO_2)_b(SiO_2)_e \cdot NaOH \cdot H_2O \rightleftharpoons Na_x[(AlO_2)_x(SiO_2)_y \cdot zH_2O + \text{solution}]$$

The X-Ray diffraction patterns of the products obtained in various NaOH concentrations of Soma and Yatagan fly ashes are shown in Figs 6 and 7. The XRD pattern of the products mainly represent the presence of crystalline sodalite $[(Na_8)(Al_6Si_6O_4)Cl_2]$ but not zeolite. Zeolite minerals and sodalite are members of silica groups minerals. They have similar framework and are alike crystal structures.

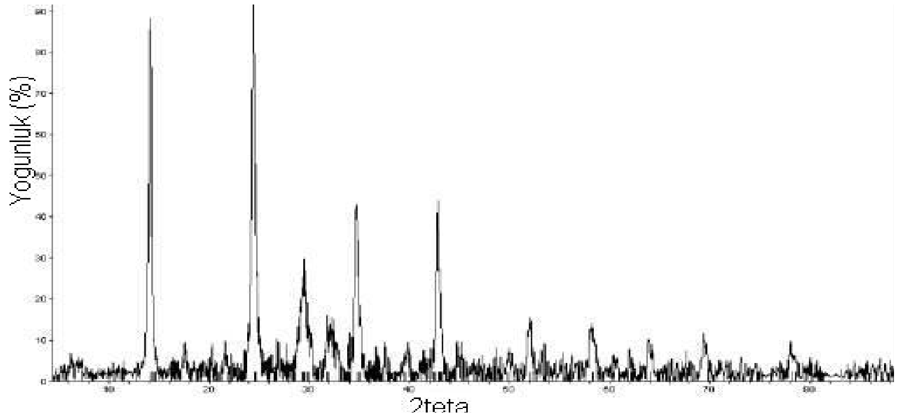

Fig. 6. X-Ray diffraction of Soma fly ash (1/3 NaOH-treated)

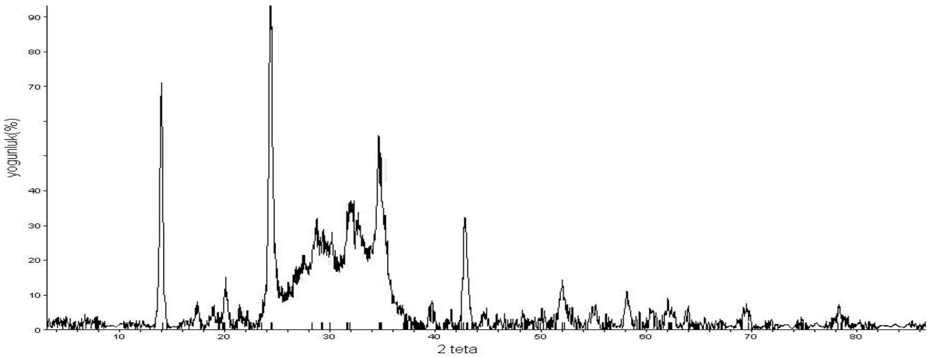

Fig. 7. X-Ray diffraction of Yatagan fly ash (1/3 NaOH-treated)

As a result, Zeolite A is formed by sodalite SiO_4 tetrahedra, the difference between these two structures is the addition of secondary units to the zeolite structure (Fig. 8).

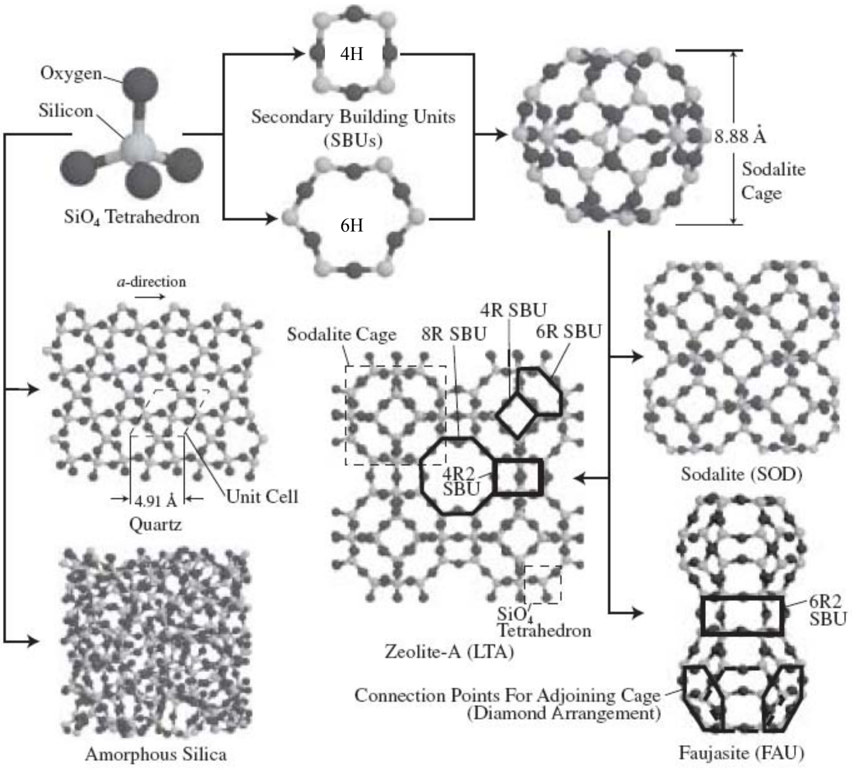

Fig. 8. Sodalite and zeolite-A crystal structure (Ref. 6). The letters of the figure are not clear. Try to use higher analysis

SEM analysis showed that the structures of fly ash samples were changed by sing different amount of NaOH. The variations in the amount of NaOH caused different hydrothermal reactions at the same fusion temperature. The same observations were reported by the earlier studies[7-9]. Products of experiment were not enough to characterized by SEM images (Figs. 9 and 10). X-Ray diffraction data was used for identification of zeolite structure and type.

Conclusion

In this study, artificial zeolite mineral A extraction has been aimed from Soma and Yatagan ashes. However SEM and XRD data and their interpretation indicated that sodalite mineral, which has similar properties to zeolite-A, has been obtained. The reasons for this occurrence are thought to be as follows: (i) It is a well known fact that synthesizing process normally materializes in a 2-12 h period. However,

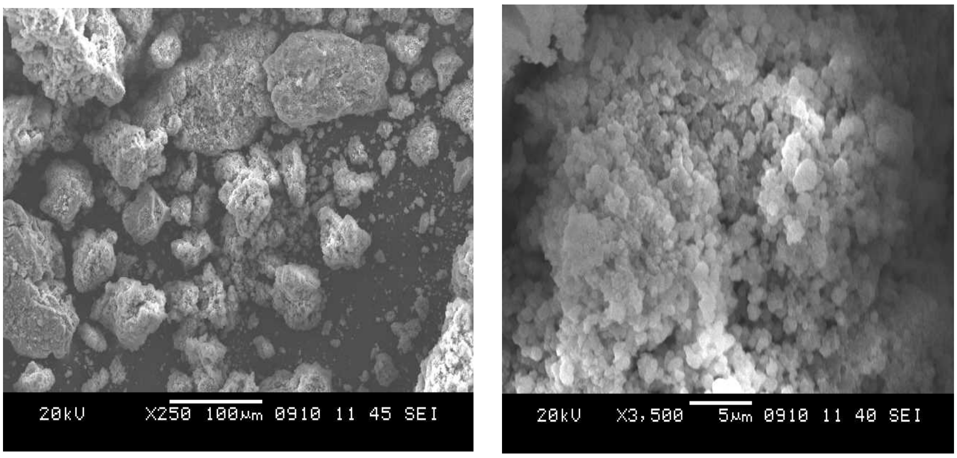

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Fig. 9. SEM of 1/3 NaOH-treated Yatagan coal fly ash

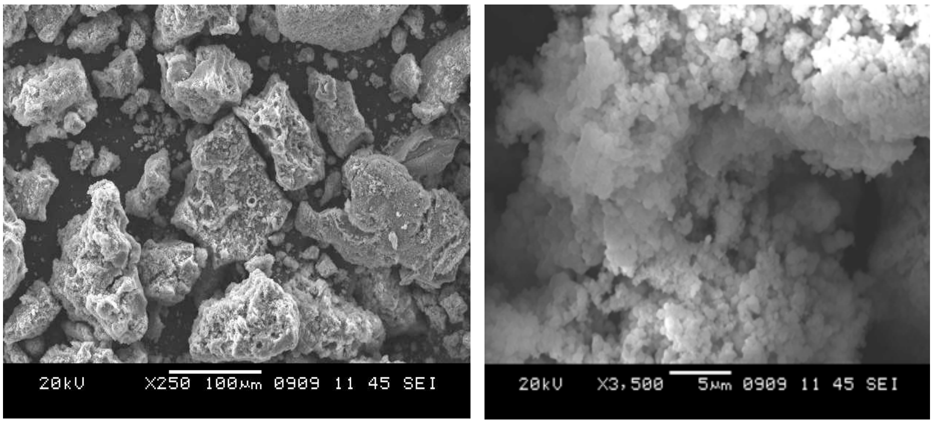

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Fig. 10. SEM of 1/3 NaOH-treated Soma coal fly ash

some zeolite synthesis processes can be completed only in first 2 h. In this case, further synthesizing may cause the structure become tightly wedged and turn into the sodalite[10]. (ii) It can be assumed that if the experimental environment becomes alkaline and NaOH, which is used to obtain sodium source, is used too much, it can lead to sodalite formation, which has more stable structure. This invention overlaps with the results of some other experiments[11]. (iii) HCl was used to remove the impurities from the surfaces of the fly ash particles. Although the samples were washed with pure water and filtered after the HCl treatment. There may remain sum free Cl^- in the samples and it is considered that Cl^- may change place (ion exchange) with H_2O molecules in the structure occurred. This phenomenon can be one of the possible reasons that caused the sodalite formation. Both zeolite and sodalite have similar crystal structure; in the centre there is a Si atom and at the corners Al atoms. If the spaces in crystal structure are filled by other anions that not exist in the crystal structure, different formations could be occurring. (iv) The low amount of silica in the original fly-ash samples may cause the formation of sodalite $[(Na_8)(Al_6Si_6O_4)Cl_2]$ instead synthetic zeolite A $[(Na_{12})(Al_{12}Si_{12}O_{48})_{27}\cdot H_2O]$ formation.

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