Journal of Science and Technology
ISSN: 2456-5660 Volume 5, Issue 5, Sep-October 2020

www.jst.org.in *DOI: https://doi.org/10.46243/jst.2020.v5.i5.pp110-118*

Synthesis and Characterization of Faujasite Type Zeolite From Fly Ash by Hydrothermal Treatment

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To Cite this Article
R. Rama Nachiar, Anitha.V,K.Kavitha and S.Sasi kala, "Synthesis and Characterization of Faujasite Type Zeolite From Fly Ash by Hydrothermal Treatment", Journal of Science and Technology, Vol. 05, Issue 05,Sep-October 2020, pp110-118

Article Info
Received: 17-05-2020 Revised: 12-08-2020 Accepted: 15-08-2020 Published: 18-08-2020

Abstract: *In many countries, thermal power stations are releasing huge quantities of Fly ash leads more environmental issues, while disposing. Various efforts have been conducted by researchers to arrive at some alternatives, that are able to significantly reduce high energy consumed and environmental impacts. The cleaner technologies in concrete production, such as substituting relatively high percentage of cement by fly ash, the use of other natural pozzolans, development of concrete with recycling or waste materials, This paper deals with the extraction of useful Faujasite type Zeolite, from fly ash, collected at Tuticorin Thermal Power Station, by hydrothermal treatment and also discussed the applications of Zeolite. The product formed is insoluble in water and Mineral acids. This is characterized by XRD, FT-IR, and Solid state ^{27}Al NMR.*

***Keywords**: Fly ash, Zeolite, Faujasite, Hydrothermal treatment*

I. Introduction

The greatest environmental impacts, on air, water and soil arise due to the huge quantity of fly ash produced at thermal power station. Fly ash is finely divided inorganic residue, resulting from the combustion of pulverized Bituminous Coal or Lignite in Thermal power stations. Coal is one of the common energy sources for the generation of electricity. The process of generating power from coal, large quantity of fly ash produced. Ash is the solid residue that remains after the combustion of coal within the furnace.

Physical Nature

Fly ash is a grey colored material, abrasive acidic, refractory in nature and having fineness of 4000cm^2/g to 8000 cm^2/g. it posses pozzolanic nature and its particle range between silty and silt clay(i.e.) 150 to less than 1 micron in equivalent diameter.

Chemical Nature

Fly ash is an amorphous Ferro alumino silicate material[1]. Fly ash mainly consists of oxides of silicon, aluminum, iron, calcium, magnesium and sulphur with smaller amount of the alkali and the oxides of titanium, manganese, phosphorus and arsenic[2]. Some of the oxides are present in Free State and others are combined to form silicates, sulphates, phosphates and arsenates.

It is collected from the combustion of coal fired power plants with electrostatic precipitators and bag houses. Fly ash particles are mostly spherical and vary in diameter. Under a microscope, Fly ash looks like tiny solidified bubbles of various sizes. The properties of Fly ash vary with the coal used, grinding equipment, the furnace used and the combustion process.

Fly Ash-TTPS

Fly ash consists of many small (0.01-100µm diameter) glass-like particles of generally a spherical character. During the combustion process many different metal oxides becomes concentrated on the ash spheres, forming a surface coating[2]. It is a highly siliceous material (SiO_2-65.55%) and being extremely fine and such as it is injurious to health and causes silicosis[1]. Apart from this, it also contains traces of several heavy and toxic metals and little organic matter, associated with the oxides. Toxic metals, which are present in fly ash cause severe diseases to human beings Tuticorin Thermal Power Station cosists of five generators of 210 MW capacities. It meets 20% of Tamil Nadu Grid demand at presnt. The average consumption of coal for this thermal power station is about 5 million tonnes per annum. Tuticorin Thermal Power Station produces about 2 million tones of fly ash per year (ie) at the rate of about 5800 tonnes per day. The daily collection of dry fly ash is about 2000 tonnes and wet fly ash is about 3800 tonnes including 20% bottom ash as total generated ash.

Table-1 TTPS- Tuticorin Thermal Power Station

Compounds	TTPS (%)
Silicon as SiO_2	68.67
Aluminum as Al_2O_3	21.35
Iron as Fe_2O_3	4.25
Calcium as CaO	3.24
Magnesium as MgO	2.43
TiO_2	2.33
Na_2O	0.79
K_2O	1.44
MnO	0.30
SO_3	0.42

Utilization Of Fly Ash

Fly ash can be used in various ways, as a raw material for concrete, land reclamation, brick production soil medication and recovery of minerals and elements.Fly ash can be utilized in road construction, cement manufacturing, soil stabilization, floor tiles, wall tiles and distemper and also used in refractory bricks, ceramics manufacturing.

Problems In Disposal Of Fly Ash

Disposal of coal ash requires vast area of land, large amount of energy and water. This creates enormous environmental issues.

Synthesis of Zeolites

The chemical characteristics of the fly ash is indicative parameter for its use as a raw material for the production of Zeolites[3] by hydrothermal treatment[4] which is basically consists of aluminum silicate tetrahedral units. Zeolites are micro porous crystalline solid with well defined structures[5].The Zeolites of general formula $M_{x/n}{}^{n+}[Al_x Si_y O_{2x+2y}]^{x-} zH_2O$[6]. In Zeolites, the ratio of Si +Al/O must equal to 1:2 ratio[7]having three dimensional structure, consist of interlocking tetrahedrons of SiO_4 and AlO_4. These polyhedra are linked by the comers, to produce an open structural form, with internal cavities, in which the molecules (or) cations of various sizes can be trapped.

In Zeolites, the spaces or cavities are interconnected and form long wide channels of varying sizes depending on the mineral. These channels allow the easy movement of the resident ions, and molecules, into and out of the structure. Zeolites are characterized by their ability to lose and absorb water without damage to their crystal structures. In the synthetic Zeolites, the channel sizes may be controlled by the synthesis[6]. The synthesis of Zeolites also involves several other factors such as the Al/Si ratio, the pH, the temperature and pressure, and the presence or absence of seed crystals[6].

Zeolite performs ion exchange filtering, chemical sieves and gas adsorption tasks. The applications of natural Zeolites, similar to those synthesized Zeolite from Fly ash, used as Sorbents for removal of ions and molecules from solutions such as waste water radioactive waste, gases and as replacement for phosphates in detergents.

Zeolites generally act as adsorbents for pollutant molecules due to its excellent ion exchange capacity. They are highly selective scavengers of variety of metal cation's that can be removed from liquid effluents through the process of ion exchange[8]. Zeolite acts as molecular sieves, and they are used to purify natural gases through the removal of impurities such as carbon dioxide, sulphurdioxide ,and water. It is used as catalyst to reduce air pollution, in the industrial production of nitrogen from mixed nitrogen oxides NO_x.

II. Material And Methods

Synthesis Of Zeolite From Fly Ash

Collection Of Fly Ash Sample

Fly ash sample was collected from Tuticorin Thermal Power Station and was air dried at room temperature. A representative sample is separated by using corning and quartering method[20]. Further experiments were carried with this representative sample.

Treatment With Sodium Hydroxide

Fly ash is heated with sodium hydroxide solutions of different concentrations for different time duration.

1. Variations of the concentration of NaOH

Accurately weighed 25g of fly ash is heated with 50 ml of sodium hydroxide (different concentration) at 70^0C for half an hour. Then it is filtered through Buckner funnel using vacuum. The insoluble solid was removed and weighed after drying at 105^0C for an hour. The filtrate is collected and acidified with concentrated hydrochloric acid. A white precipitate is separated out, which was dried at 105^0C for an hour and weighed. The results are summarized below in the table.

Table 2: Variation of concentration with one hour heating

[NaOH], M	White precipitate (g)	Unreacted fly ash (g)
0.5	-	23.558
1.0	-	23.330
3.0	1.522	22.802
5.0	2.583*	22.891
8.0	1.501	21.240

The above experiment was also carried out for two hours. The results are given in the table below.

Table 3

[NaOH], M	White precipitate (g)	Unreacted fly ash (g)
1	-	23.872
2	3.920	22.08
3	7.501	22.65
5	4.07	23.331
7	3.13	23.969

From the above results, it is obvious that the maximum yield was obtained for 3M concentration of NaOH.

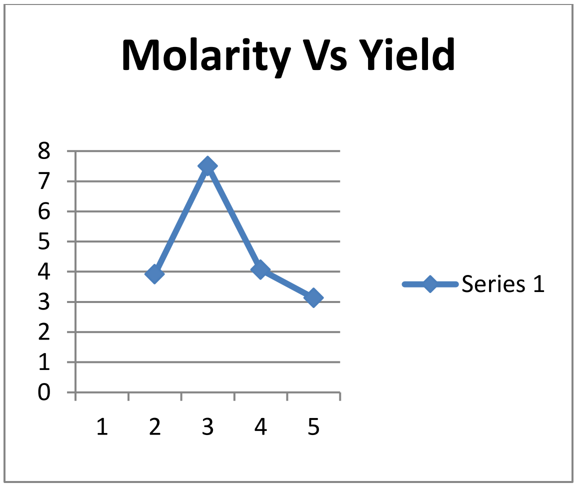


Figure 1: Morality Vs Yield

2. Variation of Time

25g of fly ash was heated with 50mL of 3 M sodium hydroxide at 70^{0}C for different time periods. Then it is filtered through Buckner funnel using vacuum. The insoluble solid was removed which was weighed after drying at 105^{0}C for an hour. The filtrate is acidified with concentrated hydrochloric acid a white precipitate is separated out which is dried at 105^{0}C for an hour and weighed. The results are summarized below in the table.

Table 4: Yield change for variation of time

Time- Hours	Weight of the precipitate (g)	Weight of the unreacted fly ash (g)
2	8.701	22.148
3	4.500	23.160
4	4.378	23.840
5	4.228	23.890
6	4.169	24.044

From the above data, it is clear that the maximum yield is obtained in two hours heating. Hence all the experiments are carried out in 3M NaOH solution for 2 hours time duration.

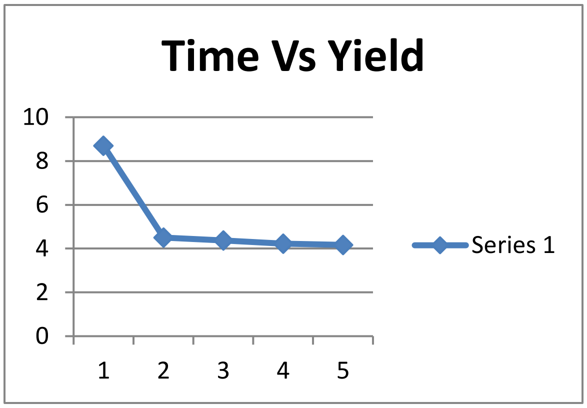


Figure 2: Time Vs Yield

Bulk Preparation Of Zeolite

Bulk preparation of zeolite was carried out by using One kg of fly ash sample with 2 liters of 3M NaOH solution at 70^0C for two hours. Then the reaction mixture was filtered using muslin cloth and the insoluble part of the fly ash was removed and dried at 105^0C in an air oven. The filtrate was neutralized with 225 mL of 10M HCl acid, a white precipitate was separated out, which was filtrated using muslin cloth and dried at 105^0C for two hours. The weight of the precipitate was 314.0g.This compound is partially soluble in water and mineral acids. A 2g of the precipitate is dissolved in 100 mL of solvent and the solubility was determined.

Hence it is presumed that it must be a mixture of two or more compounds to get the pure compound, the precipitate is suspended in 2L of hot water, stirred well and filtered. The precipitate is washed several times with hot distilled water, until chloride impurity is removed. The pure compound so obtained is dried at 105^0C for two hours and weighed. The weight of the pure compound was 142.0g. This compound is insoluble in water (cold and hot) and all mineral acids including aqua regia.

It was characterized by various analytical methods like FTIR, XRD solid state ^{27}Al NMR methods.

III. Spectral Characterization

1. Infra-red spectra

The infra-red spectra of samples were recorded by using BRUKER/IFS-66 V FT-IR instrument using KBr medium at IIT, Chennai.

2. X-Ray Diffraction Analysis

Crystalline constituents of a sample was identified by XRD powder technique using a multipurpose diffractometer of model PAN analytical instrument with copper radiation of wave length 1.54 A^0, at Central Electrochemical Research Institute, Karaikudi. The operating target voltage is 40Kv and current was 300 mA.

3. ^{27}Al NMR Spectra

Solid state ^{27}Al NMR is recorded at Chemistry Department, IIT, Chennai at 104 MHz

4. For pH measurements, ELICO pH meter model L1120 was used.

5. For conductivity measurements, Equiptronics Conductometer setting at 20 micro ohms was used.

IV. Results and Discussion

X-Ray Diffraction pattern, FTIR, ^{27}Al NMR, Spectrum were recorded and interpreted for the Zeolite samples.

FTIR Spectra

The FTIR of fly ash and Zeolite samples are recorded in KBr pellets. The FTIR of fly ash is given in the Fig.1.

Fly ash contains Silicon, Aluminum and Iron as major components, and many others as impurities. FTIR of fly ash shows major peaks at 471,562, 795, 911, 1094, 1633, 1711, 3076and 3436 $cm^{-1.}$The spectrum shows a strong broad band at 1099 $cm^{-1.}$

With a shoulder at still higher frequency corresponding the one at 1094 $cm^{-1.}$ in fly ash, may be due to Si-O asymmetric stretching. Oxides generally exhibit fairly broad bands due to high degeneracy of the vibration state, thermal broadening of lattice dispersion band and mechanical scattering from the powdered samples. Silicates show characteristic absorption band in the region 1111- 1000 $cm^{-1.}$ due to Si-O-Si asymmetric stretching mode of vibration.

The FTIR of zeolite samples shows major peaks at 478, 567, 799, 955, 1099, 1635 and 3434 $cm^{-1.}$ The spectrum is given in the Fig.2

Figure :3-FLY ASH

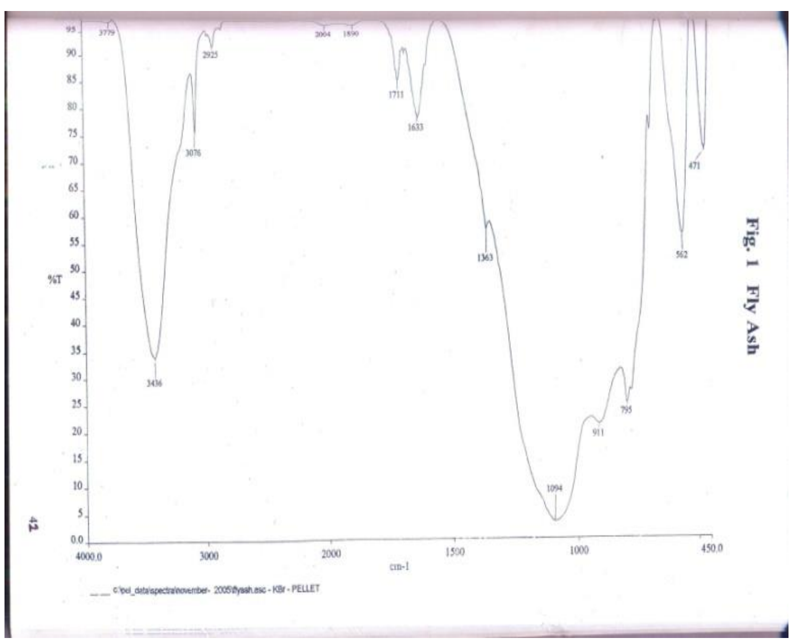
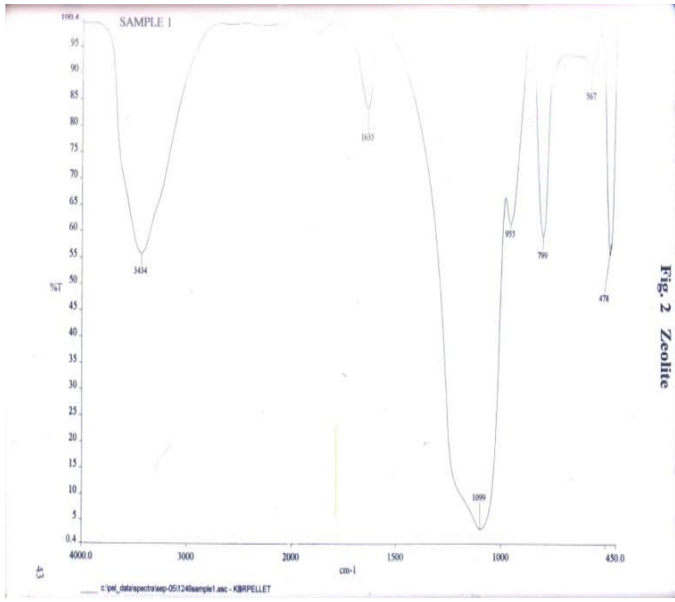
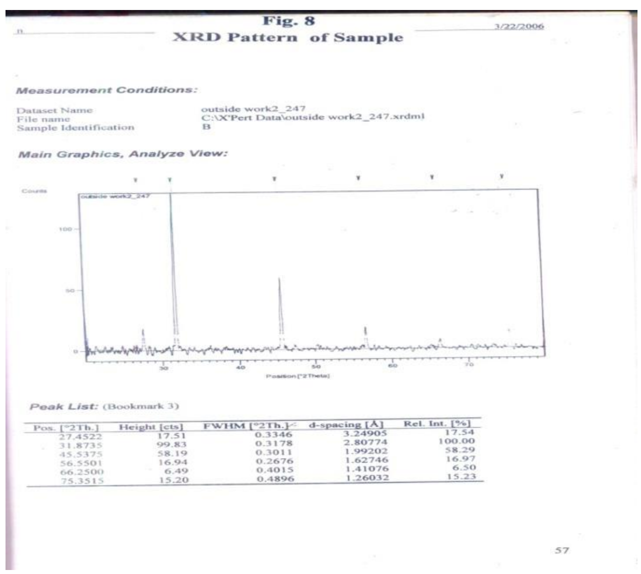


Figure :4- ZEOLITE



XRD of sample



Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
27.4522	17.51	0.3346	3.24905	17.54
31.8735	99.83	0.3178	2.80774	100.00
45.5375	58.19	0.3011	1.99202	58.29
56.5501	16.94	0.2676	1.62746	16.97
66.2500	6.49	0.4015	1.41076	6.50
75.3515	15.20	0.4896	1.26032	15.23

Figure 5: XRD pattern of ZeoliteX-ray diffraction pattern was done using a multipurpose diffractometer at Central Electrochemical Research Institute (CECRI), Karaikudi. It shows main peaks at 27.45^0, 31.87^0, 45.540, 56.550, 66.25^0, &75.35^0. The XRD pattern for zeolite synthesized using fusion followed hydrothermal treatment was given in figureThe compound synthesized using hydrothermal process does not give any XRD pattern. THE values of interplanar distance spacing corresponding to Bragg's reflections (2Θ) for zeolite (3.25, 2.81, 1.99, 1.63, 1.41, and 1.26) were used as a basis for identification of zeolite. This X-ray pattern is very similar to the one, reported by Fanor Mondragon et .al. for the Faujasite type zeolite [9].

Structure of zeolites

Zeolite is an alumino silicate frame work, composed of (Si, Al) O4tetrahedra, each oxygen of which is shared between two tetrahedral. The net negative charge on the frame work is balanced by the presence of cations, like Ca, Na (or) K which situated in cavities within it. Zeolites having open structures, containing larger cavities and larger channels, exhibit the property of molecular absorption (Specific gravity 2-2.3).

An additional feature is the presence of water molecules within the structural channels, are loosely bound to the frame work and cations, can be removed and replaced without disrupting framework bonds. In zeolites water molecules are distributed among a number of possible sites and can jump from to another.

Zeolite framework is structurally independent of the cations. The channel system in the zeolites are formed by different combinations of linked rings of tetrahedral. The wider the channel size, larger the cation (or) molecule, that can be introduced into the structure. Ionic(or) molecular diffusion is affected by water content. Cation exchange capacity diminishes with loss of water.

On the basis of the structure, zeolites can be divided into number of subgroups 31.

i) Natrolite group
ii) Harmotome group
iii) Chabazite group
iv) Faujasite group
v) Mordenite group
vi) Heulandite group

Faujasite type zeolite having 4,6 and12 no. of tetrahedral in rings and minimum diameter of widest channel is 9A'. In the faujasite group zeolites tetrahedral are linked to form cubo octahedral cage-like units which themselves are so joined as to give the structure cubic or pseudo cubic symmetry.

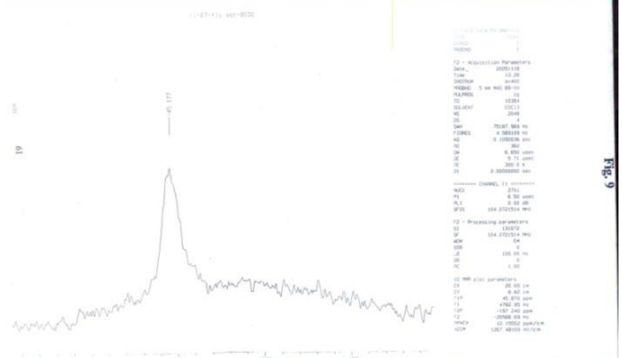
The zeolites form a well defined group of hydrated silicates of aluminum and the alkalies and alkaline earths and are characterized chemically also by having the molecular ratio Al2O3;(Ca,Sr,Ba,Na2,K2)O equal to unity and the ratio;(Al+ Si)=2. When zeolites are heated, water is given off continuously rather than in separate stages at definite temperatures, and the dehydrated or partially dehydrated mineral can reabsorb water usually toits original amount when again exposed to water vapour.

This character is evident from the FTIR of the samples at different temperatures. The peaks intensities at 3434cm-1 and 1635cm-1 which are attributed to entrained water molecules23, decreases gradually, indicating the release of water molecules by zeolite. The same is also proved by LOI experiment which shows 5.5, 7.5, 9.7 and 11.3% sorption capacity at $200^{o}C$, $400\,^{o}C$, $600\,^{o}C$ and $800\,^{o}C$ respectively.

^{27}Al-NMR Spectra

Solid state ^{27}Al-NMR Spectrum of the zeolite is recorded using av 400 model at IIT, Madras. The spectrum shows a single peak at 45.177 ppm when 104.2 MHz frequency is used, indicating the presence of AlO4 tetrahedral in the silicate structure.

Hence from the FTIR analysis, Solid state ^{27}Al-NMR analysis **a**nd XRD pattern, it is concluded that the white compound which is synthesized from fly ash is Faujasite type zeolite, which has the formula (Na_2, Ca) [$Al_2Si_4O_{12}$].$8H_2O$.



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