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A Case Study for Synthesis of Zeolite-A from Indian Flyashes of Bituminous Origin

S.S. RAYALU*, J.S. SAPRE†, S.U. MESHRAM‡, K.N. MUNSHI**
and R.N. SINGH††
Environmental Materials Unit, National Environmental Engineering Research Institute,
Nehru Marg, Nagpur-440 020, India
Tel: (0712)-2226071, Ext. 414; E-Mail: ssrayalu@yahoo.com

Attempts were made to synthesise zeolites from flyash of different origins and elemental characteristics. Influence of elemental content especially SiO_2, Al_2O_3, Fe_2O_3 and CaO has been studied in detail. The flyash investigated herein are both from bituminous coal but with different LOI content which seems to be detrimental for synthesis of zeolite-A from flyash. The physico-chemical characteristics of zeolites synthesised from flyash from Shriram Fertiliser Company Limited (FASBC) and flyash from Tamil Nadu Electricity Board (FATBC) are comparable with commercial zeolite-A.

Key Words: Flyash, Zeolite-A, Highly crystalline, Synthesis, Optimisation, Characterisation.

INTRODUCTION

India with its dependence on coal for total power generation is expected to have adverse effect on the environment due to concomittant simultaneous flyash generation. With 200 billion tonnes of coal reserves, the country is bound to depend on coal as one of the formidable energy sources; which, in turn, continues to generate flyash. Also, with the power generation projects in pipeline, it is expected that the country would generate 110 million tonnes per annum of flyash by 2001–02. Flyash is generated during combustion of coal and contains a number of metallic and non-metallic oxides like SiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, Mn_2O_3, and TiO_2 and/or their complexes such as quartz, aluminosilicates, ferrite, mullite, haematite, etc., in varying amounts. It is collected through ash collection systems such as electrostatic precipitators (ESP) and is disposed of in the form of slurry to ash ponds[1]. ASTM (D 5239-92) has classified fly ash in two categories, *viz.*, (a) Class F fly ash; (b) Class C fly ash.

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†Nagpur University, Nagpur-440 020, India.

‡Senior Research Fellow, Environmental Materials Unit, National Environmental Engineering Research Institute, Nagpur-440 020, India.

**Emeritus Professor, Department of Chemistry, Nagpur University, Nagpur-440 020, India.

††Director, National Environmental Engineering Research Institute, Nagpur-440 020, India.

In class F fly ash, the sum of silica + alumina + iron oxide corresponds to a minimum of 70%. The maximum loss on ignition for class F fly ash corresponds to 6%. In class C fly ash, the sum of silica + alumina + iron oxide corresponds to a minimum of 50%. The maximum loss on ignition for class C fly ash also corresponds to 6%. In the light of the ASTM classification, Indian fly ash and bottom ash specimens may the classified as ASTM class C or ASTM class F fly ash depending on the parent coal composition.

Nearly 80% of the existing Thermal Power Plants in India use the wet ash disposal system. This mode of disposal has however resulted in the growth of a number of ash ponds in the vicinity of thermal power plants and in some cases close to the urban centres. Presently, a number of ash ponds are lying abandoned in the country after exhausting their storage capacity[2].

The impact of ash ponds near thermal plants on the local environment can be categorized as: effect on local air quality; leaching of trace elements into surface and ground water resources; accumulation of heavy metals in soils and vegetation near ash ponds. To avoid these environmental hazards it is realized that utilization of fly ash is imperative. However, the ash utilization scenario in India is not very encouraging. It is being used in very low percentage in the manufacture of concrete and cement; in landfills and embankments; in filling of mines, quarries and pits; in road construction; in building materials and in agriculture[2]. The usage of flyash for zeolite production is an innovative application and has emphasis on resource recovery. However, the quantity of flyash expected to be consumed is not substantial. A major voluminous application of zeolite-A is its use as a phosphate substitute for conventional builders, *viz.*, zeolites. Problems are anticipated in substitution of conventional builders with zeolite-A because of the procurement problem and prohibitive costs associated with commercial zeolites. This necessitates the need to explore the possibility of utilizing flyash as a raw material for production of value-added products, *viz.*, zeolites; wherein National Environmental Engineering Research Institute has successfully developed zeolite-A for its proposed application as detergent builder. This process has been patented and reported elsewhere[3]. The synthesis of zeolite-A from lignite and sub-bituminous coal based flyash has been discussed elsewhere[4]. Synthesis of zeolites from flyash has been reported by several workers[5–8] using different flyashes and reaction conditions. This paper addresses to synthesis of zeolite-A from two different sources of bituminous coal based flyash which is of class F type and comparison of the physico-chemical characteristics of the as synthesized samples[9].

EXPERIMENTAL

Bituminous coal based flyash sample were collected from Tamil Nadu Electricity Board (TNEB) and Shriram Fertilizers & Co. SFC) Pvt. Ltd., Kota, Rajasthan. All flyash samples were collected from the hopper of electrostatic precipitator. The flyash samples collected from TNEB and SFC Ltd. are designated as FATBC and FASBC respectively.

All chemicals were purchased from E. Merck and of analytical grade. The indigenous commercial Zeolite-A was procured from Zinco Lab Pvt. Ltd., Mumbai and the international grade Zeolite-A was procured from Wako, Japan and Degussa, Germany.

Characterization of flyash: The flyash samples were characterized with respect to SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MnO, CaO, MgO, Na_2O and K_2O.

The flyash based Zeolite-A (FAZ-A) samples were synthesized[3] by fusing flyash and sodium hydroxide in certain proportion. A homogeneous fusion mixture was obtained by grinding flyash and sodium hydroxide in a definite ratio. The mixture was heated at a temperature ranging between 550–650°C for a certain period of time. The resultant fused mass was cooled, milled and mixed thoroughly in distilled water with simultaneous addition of sodium aluminate. Commercial zeolite-A was added as seeding to the mixture, prior to crystallization. The slurry so obtained was subjected to aging for a certain period of time. The amorphous aluminosilicate gel was then subjected to crystallization at a temperature ranging between 90–105°C for certain time. The solid crystalline product was separated by filtration and washed thoroughly till the filtrate pH was 10–11 and dried at a temperature of 50–60°C.

Depending upon the chemical composition of flyash samples some additional pre-treatment steps were included to improve the quality of FAZ-A. FASBC contains unburnt carbon and hence it was subjected to ashing. FATBC were subjected to sieving and acid treatment so as to remove impurities, *viz.*, Fe_2O_3, which decreases calcium binding capacity (CBC) of FAZ-A and imparts colour to it.

In the FAZ-A synthesis, the reactant system was enriched with sodium aluminate to maintain the SiO_2/Al_2O_3 ratio as 1.0 : 1.1. The composition of sodium aluminate employed is Na_2O : 50.3%, Al_2O_3 : 29.4%.

Characterization of FAZ-A: The CBC of FAZ-A samples was determined preparing 0.05% $CaCl_2$ stock solution and adjusting its pH to 10–11. Preweighed (0.5 g) FAZ-A sample and zeolite-A standard were added to 500 mL of stock solution and stirred for 15 min. The solutions were then filtered. These Ca^{2+} solutions along with the stock solution were titrated complexometrically using standardized 0.01M EDTA solution. The amount of Ca^{2+} ions exchanged by zeolite was expressed in terms of meq of Ca^{2+}/100 g of zeolite on anhydrous basis. The sorption capacity of FAZ-A was determined by heating it at 800°C for 1 h. Powder X-ray diffraction (XRD) analysis was performed using CuK_α as a source of X-rays in the range of 5–60° using X-ray diffractometer, Model Philips PN-1830. d-Spacing values reported in literature for zeolite-A (12.2 ± 0.2, 8.60 ± 0.20, 7.05 ± 0.15, 4.07 ± 0.08, 3.68 ± 0.07, 3.26 ± 0.05, 2.96 ± 0.05, 2.73 ± 0.05, 2.60 ± 0.05) have been used as a basis for identification and quantification of crystalline phase. For the elemental analysis, FAZ-A samples were dissolved in a mixture of acetic and nitric acid and analyzed by ICP-AES (Model YJ24) for Al_2O_3 while SiO_3 was estimated using instrumental/conventional methods. Na_2O was estimated by using flame photometer (Modiflame 127 FPM compressor unit 122). The particle size analyses were conducted using Fritch particle size analysette 22. The colour of the samples was examined by measuring brightness with a Carlzeiss photoelectric reflection photometer (ELREPHO) with $BaSO_4$ as standard.

RESULTS AND DISCUSSION

The chemical analysis of flyash from different sources is presented in Table-1. Amongst the two flyash samples the FATBC have higher alumina content as compared to FASBC. The FATBC with higher Al_2O_3/SiO_2 ratio are more favourable for their use as raw material for zeolite-A synthesis as they require less sodium aluminate addition, thereby reducing the cost of production of zeolite-A synthesis.

The CaO content in FATBC and FASBC is negligible. The flyash also contains large amount of unburnt carbon which may interfere in the fusion step thereby affecting the quality of fused product. This unburnt carbon is estimated on the basis of loss on ignition (LOI) content and found to be higher in FASBC as compared to FATBC.

The iron oxide content in flyash gets decomposed during fusion process and has probability of being incorporated into the zeolite matrix. This renders a brownish tinge to the Zeolite-A product. Thus, lower percentage of iron oxide content in flyash is favourable for synthesis of zeolite with better optical brightness. The percentage of iron oxide content in FATBC is more as compared to FASBC. The iron oxide is present mostly as magnetite and hence is being resolved by its magnetic separation.

The other elements present in trace amount include TiO_2, MnO, MgO, Na_2O and K_2O. These elements along with other anions like carbonate, sulphate, etc. appear to promote nucleation and crystallization of FAZ-A which is observed to be less for this system in comparison with conventional zeolite synthesis. On the basis of characteristics of flyash it may be inferred that FATBC is a more amenable material for synthesis of FAZ-A in comparison with FASBC. Process optimization has been studied using bituminous and lignite based flyash from Koradi thermal power station, Nagpur and Neyveli Lignite Corporation Limited, Neyveli and has been discussed elsewhere. Optimal process parameter for synthesis of zeolite - A from flyashes have been used as a basis for synthesis of zeolite-A from FASBC and FATBC.

Zeolite-A from FASBC: The samples synthesized using FASBC are designated as ZA-1–ZA-4 and the details of experimental conditions are presented in Table-2. The FAZ-A (ZA-1) synthesized from FASBC without ashing, and using 20 mL of sodium aluminate of composition (Na_2O 50.3%, Al_2O_3 39%) shows 56.8% crystallinity and CBC of 370 meq/100 g. It was observed that the flyash contains large amount of unburnt carbon and may be the reason for low CBC and crystallinity in ZA-1. The flyash sample was then subjected to pretreatment sieving for particle size < 170 μ showing improved crystallinity (77%) and CBC (460 meq/100 g). Further improvement in CBC and crystallinity was achieved by subjecting the sample to sieving and ashing for reducing LOI content with addition of 15 mL of sodium aluminate of same composition. This shows an increase in crystallinity (59%) and CBC (405meq/100g). FAZ-A (ZA-4) synthesized by using flyash subjected to sieving and ashing and addition of 20 mL of sodium aluminate with similar composition shows substantial improvement in crystallinity (100%) and CBC (515 meq/100 g).

TABLE 1
COMPARATIVE CHEMICAL COMPOSITION OF DIFFERENT FLYASH SAMPLES

Type of Flyash	FASBC (%)	FATBC (%)
SiO_2	64.65	60.52
Al_2O_3	25.11	30.70
Fe_2O_3	1.91	2.72
TiO_2	1.55	1.76
MnO	0.04	Nil
CaO	Nil	Nil
MgO	Nil	1.05
Na_2O	0.18	0.12
K_2O	0.11	1.00
LOI	6.45	2.12

Zeolite-A from FATBC

The sample synthesized from FATBC is designated as ZA-5 to ZA-8 and the details are presented in Table-2. FAZ-A synthesized (ZA-5) from FATBC without sieving and under conditions delineated in Table-2 shows 60% crystallinity with low CBC of 430 meq/100 g. The usage of FATBC with particle size of 170 μm under conditions delineated for ZA-6 resulted in FAZ-A with crystallinity of 70% and CBC of 450 meq/100 g, whereas FAZ-A (ZA-7) synthesized using FATBC of particle size 53 micron shows increased crystallinity to 100% and CBC of 490 meq/100g. This may be due to enrichment of SiO_2 and Al_2O_3 in smaller particle size of flyash and removal of extraneous material.

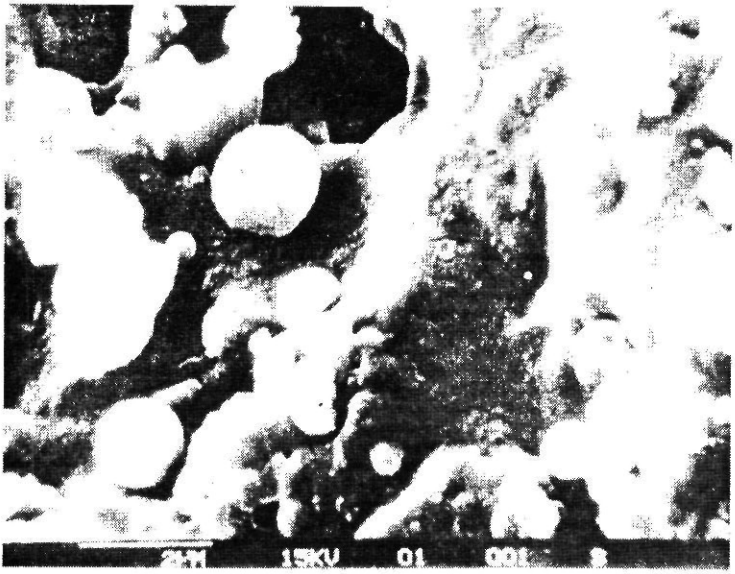
FATBC has lower SiO_2 content as compared to FASBC. This has implications on the synthesis of FAZ-A, wherein addition of 15 mL of sodium aluminate of composition Na_2O 50.3 and Al_2O_3 39.0 (Table-3) is sufficient for FAZ-A (ZA-8) synthesis with 100% crystallinity and CBC of 530 meq/100 g sample. However, further increase in sodium aluminate, *i.e.*, 20 mL of same composition resulted in lowering of CBC (ZA) (490 meq/100 g) with almost similar crystallinity. This may be explained on the basis that excess of soda associated with sodium aluminate may result in the formation of sodalite with a consequent decrease in CBC and crystallinity. Table-3 is showing the comparative characteristics of flyash based on commercial zeolite-A.

P.1 shows that morphologically flyash is amorphous with some cenospheres and pleurospheres. The morphological characteristics of FAZ-A indicate its highly

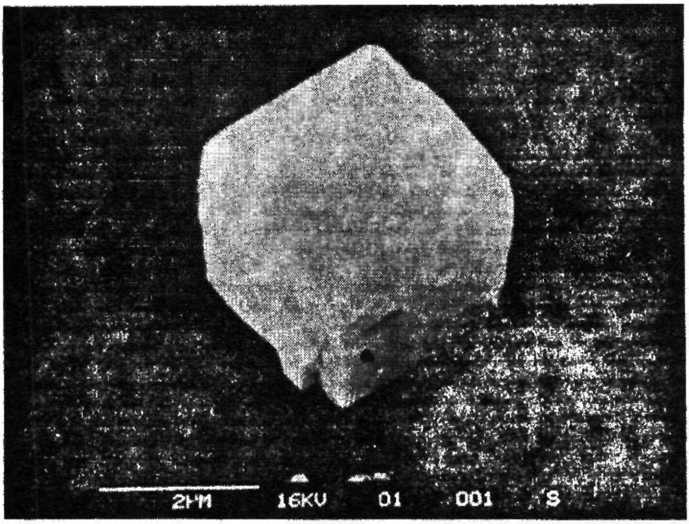
TABLE-2
PHYSIO-CHEMICAL CHARACTERSTICS OF FASBC AND FATBC SAMPLES WITH RESPECT TO VARIATION IN EXPERIMENTAL CONDITIONS

Flyash and Caustic Soda Ratio = 1 : 1.2, Fusion temperature = 600°C, Fusion time = 1.5 h, Mixing and aging time = 8 h

Sample	Pre-treatment step	Sodium aluminate composition	Sodium aluminate ($NaAlO_2$) (mL)	Seeding (g)	Cryatallization time (h)	Sorption capacity (%)	Calcium binding capacity (meq/100 g)	Crystallinity (%)	Degree of crystali-zation (%)
ZA-1	–	SA-II (Na_2O 50.3%, Al_2O_3 39%)	20	+ve	3	18.2	370	56.8	–
ZA-2	Sieving by 170 micron	SA-II (Na_2O 50.3%, Al_2O_3 39%)	20	+ve	3	20.0	460	77	84.43
ZA-3	Re-ashing at 600°C for 2 h and sieving by 53 micron	SA-II (Na_2O 50.3%, Al_2O_3 39%)	15	+ve	3	20.5	405	59	83.80
ZA-4	Re-ashing at 600°C for 2 h and sieving by 53 micron	SA-II (Na_2O 50.3%, Al_2O_3 39%)	20	+ve	3	21.5	515	100	88.00
ZA-5	–	SA-II (Na_2O 50.3%, Al_2O_3 39%)	20	+ve	3	19.8	430	60	83.42
ZA-6	Sieving by 170 micron	SA-II (Na_2O 50.3%, Al_2O_3 39%)	20	+ve	3	20.2	450	70	85.90
ZA-7	Sieving by 53 micron	SA-II (Na_2O 50.3%, Al_2O_3 39%)	20	+ve	3	21.0	490	100	86.45
ZA-8	Sieving by 53 micron	SA-II (Na_2O 50.3%, Al_2O_3 39%)	15	+ve	3	21.7	560	100	88.10



P. 1. SEM photograph of flyash



P. 2. SEM photograph of flyash based Zeolite-A crystalline nature. It was observed that amorphous microparticles of aluminosilicate transform into agglomerate, which then transforms into crystals of FAZ-A (**P.2**) without appreciable change in size.

The XRD pattern of Zeolite-A synthesized from FATBC, FASBC and commercial zeolite-A are presented in Figs. 1, 2 and 3. The similarity in the XRD

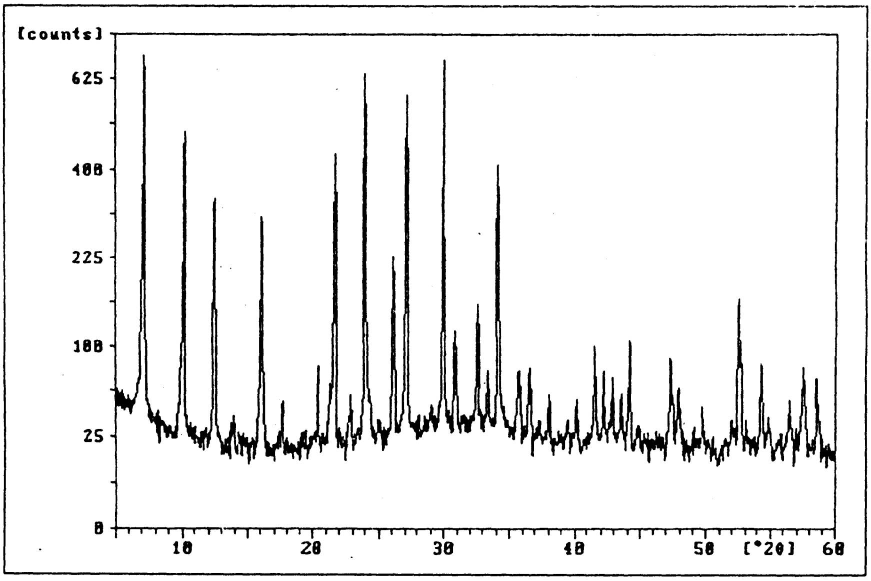


Fig. 1. XRD pattern of FAZ-A (FATBC)

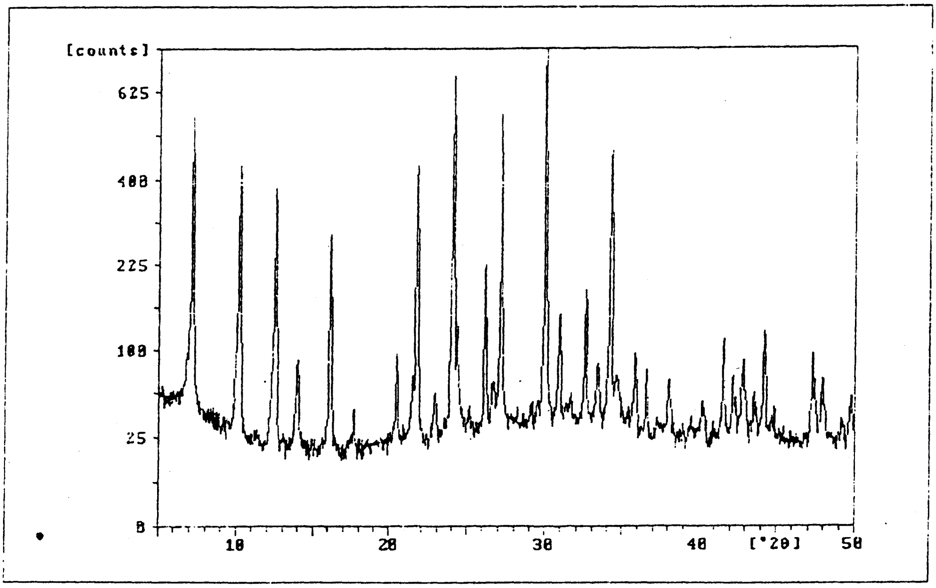


Fig. 2. X-ray diffractogram of FASBC

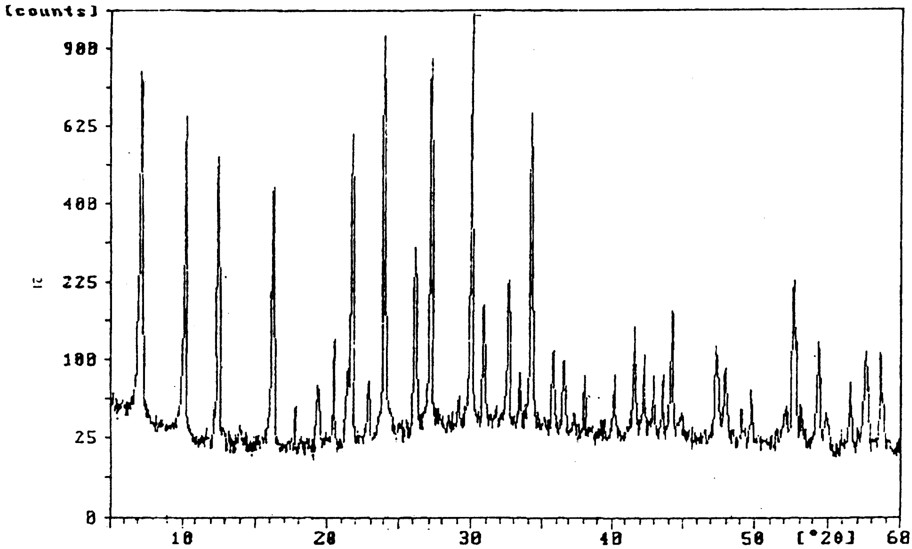


Fig. 3. X-ray diffraction pattern of Degussa (Zeolite-A)

reflections of these samples and the commercial zeolite-A (Fig. 3) shows a similarity in the product and formation of highly crystalline structure.

TABLE-3
COMPARATIVE CHARACTERISTICS OF FLYASH BASED AND COMMERCIAL ZEOLITES

Sr. No.	Typical specifications	FAZ-A from FASBC	FAZ-A from FATBC	Commercial zeolite-A*
1.	Appearance	Creamish	Creamish	White
2.	Average partcle size (μ)	2–3	1.5–2	2–3
3.	Calcium-binding capacity (meq/100 g)	370–45	490–560	540–560
4.	Density (g/cm^3)	2.1	2.11	2
5.	Tapped density	0.5	0.54	0.5
6.	Moisture content (5) (ignition loss at 800°C)	18–20	205–21	19–20
7.	pH of 1% slurry	9–10	9–10	10–11
8.	Crystalline form	A type zeolite	A type zeolite	A type zeolite
9.	Crystallinity (%)	100%	100%	100%
10.	Silica content (%)	–	31 ± 0.5	33 ± 0.5
11.	Alumina content (%)	–	27.5 ± 0.5	27.5 ± 0.5
12.	Na_2O content (%)	–	15.5 ± 0.5	16.5 ± 0.5
13.	Si/Al molarratio	–	–	0.9–1
14.	TCLP test	–ve	–ve	–ve

**Source*: Zinco Lab. Pvt. Ltd.

It can be inferred from above that the results of characteristics of FAZ-A from FATBC are more amenable for zeolite-A production than FASBC with and without pretreatment. Hence, a comparison of FAZ-A synthesized from different flyashes under exactly identical conditions (without any pretreatment) gives an insight into the most flyash suitable substrates for FAZ-A synthesis.

Conclusion

The processes being formulated for synthesis of zeolite-A from different flyashes will provide a good database for the synthesis of highly pure, crystalline, small and uniform cubic crystals. The characteristics like calcium binding capacity, crystallinity, elemental analysis, particle size, and sorption capacity of FAZ-A are comparable to those of commercial Zeolite-A. These characteristics suggest the possibility of its usage as a substitute for detergent builders.

The use of flyash of similar coal type (bituminous) but from different sources and charging condition under exactly identical optimal conditions of synthesis do not produce the zeolites of same quality. However, the same can be achieved through slight modification in the process; in specific, by addition of appropriate quantity of sodium aluminate and by incorporation of some pretreatment steps *viz.* sieving, ashing etc.

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