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Research paper

A three step process for purification of fly ash zeolites by hydrothermal treatment

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ABSTRACT

Over the decades, synthetic zeolites have been synthesized from the fly ash by resorting to its hydrothermal activation with NaOH, in one step. However, the activated ash (the residues) has been found to exhibit lower cation exchange capacity. Based on X-ray diffraction spectrometry, main culprits have been identified as Quartz and Mullite (i.e., the inactivated or residual fly ash), which are in the form of impurities in the zeolites (i.e., Na-P1, in majority). Also, such impurities have been verified from the field emission gun-scanning electron microscopy of the residues. The purification of these zeolites still remains a big challenge and requires a special attention. In such a situation, this manuscript demonstrates a "*three-step hydrothermal process*"; the residues obtained after Step-2 and Step-3 of this process significantly gain in their characteristics viz. cation exchange capacity by 185 and 14% and specific surface area by 478 and 33.42%, respectively. In addition, lowering of the specific gravity and improvement in the SiO_2/Al_2O_3 ratio of the residues are indicative of the formation of more porous and silica rich zeolites, in a purified form. Accordingly, an attempt has been made to assimilate the outcome of the adopted process and develop a conceptual model to exhibit various complexities involved in overall conversion of the fly ash to pure zeolites.

1. Introduction

Several researchers have employed conventional hydrothermal treatment of fly ash (HTF) and its conversion to fly ash zeolites (FAZ), which can be an alternative to some natural as well as man-made commercial zeolites, synthesized by using costlier chemicals (Adamczyk and Bialecka, 2005; Inada et al., 2005; Kolay and Singh, 2001a,b,c, 2002; Kolay et al., 2001; Murayama et al., 2002; Nugteren et al., 2001; Singh and Kolay, 2002). In addition, they have demonstrated the presence of impurities (IMP), in the FAZ. The IMP mainly consist of traces of partially activated glass and majority of inactivated Quartz and Mullite crystals, in the alkali activated fly ash (AFA), the residue. These impurities are responsible for lowering the cation exchange capacity (CEC) of the FAZ and hence their purity, which in turn affects their suitability for industrial applications (viz., as an adsorbent which uptakes heavy metal from contaminated soil and water). In these circumstances researchers' focus has been to develop methodologies, which would facilitate removal of the IMP from the FAZ. However, such studies have been limited to the usage of higher molar solutions of NaOH (Rayalu et al., 2000), high temperature of the treatment (Adamczyk and Bialecka, 2005; Kim et al., 1997) and/or prolonged periods of hydrothermal activation of a fly ash (Scott et al., 2001). However, metastable FAZs have been reported to dissolve in high alkaline environment during prolonged activation, and hence, these efforts did not significantly improve the purity of the FAZ (Fansuri et al., 2008; Mortier, 1978; Nugteren et al., 2001). Thus, efforts are necessary to optimize the molarity of the NaOH solution and duration of activation. In this context, the hydrothermal treatment of the fly ash was conducted by employing different molarities (M = 0.5 and 1.5) of NaOH solutions, and a duration of 12 h in one step activation, as established by Singh and Kolay (2002). However, the CEC of the end products (i.e., residues) has been reported to be less than 150 meq/100 g, which hints at impurities of up to 70% in the AFA, as compared to the CEC value of 500 meq/100 g, which is exhibited by the pure zeolites (e.g. Na-P1) (Mortier, 1978; Scott et al., 2001).

In such circumstances, the main challenges are to investigate the zeolitization potential of the residues, and to establish a suitable process for the treatment of their impurity content, resulting in pure form of polycrystalline zeolites (Fansuri et al., 2008; Hollman et al., 1999; Querol et al., 2002, 2007). In this context, a process of recycling the residues, up to three steps, by employing a hydrothermal system at 100 °C, is being proposed in this manuscript. In short, this process aims at using the supernatant (i.e., spent NaOH solution as a by-product) for further activation of the residues and improving their characteristics (viz., physico-chemical, mineralogical and morphological), conforming to increased yield of zeolites. Also, this study is focused to ascertain a suitable step of the treatment, which yields better zeolites. Apart from these efforts, this manuscript finally

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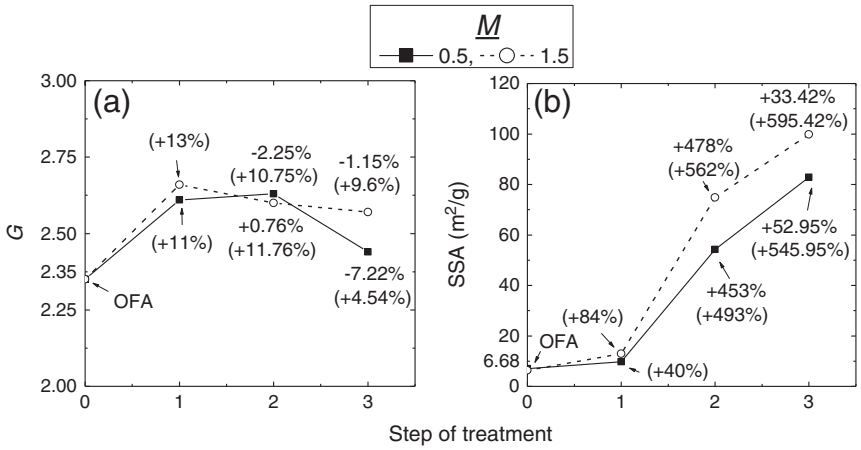

Fig. 1. Effects of recycling and step of the treatment on (a) G and (b) SSA of the fly ash and residues, where percentage increase (plus sign) and decrease (minus sign) in the parameter after, Steps-2 and 3, are marked. The data shown within parenthesis represent variations w.r.t. virgin fly ash, OFA.

attempts to clarify some complexities in the treatment-cum-purification process, as a conceptual model.

2. Experimental investigation

2.1. Materials and process

The virgin or original fly ash (OFA) was procured from a hopper of electrostatic precipitator of a thermal power plant in Maharashtra, India. The NaOH used for preparing its stock solution (i.e., 0.5 M to 1.5 M) in deionized water, was supplied by Thomas Baker, Mumbai, India. In order to activate most of the constituents of the ash and synthesize pure fly ash zeolites, a solution to the fly ash ratio (L/S = 10) (Watek et al., 2008) was maintained for preparing a fly ash–NaOH slurry (Jha and Singh, 2012). The hydrothermal treatment of this slurry was carried out in three successive steps, each for 12 h. Step-1 of the treatment was followed by a Step-2, as recycling of the residue and the supernatant, obtained from Step-1. Similarly, the Step-3 was also a recycling of the residue and the supernatant, obtained from Step-2 (Jha and Singh, 2011). The many intermediate processes involved in each step of the treatment are: (i) separation of the residues from the solution (by a centrifuge working at 1000 rpm for 30 min), (ii) double washing (up to pH = 10) of the residues with distilled water, (iii) drying (by setting oven temperature at 100 °C for 12 h) of the residues and finally, (iv) a grinding (by hand, using a mortar and pastel). Especially, the grinding of the residues was intentionally done to peel off all fly ash zeolites, deposited as thin film on the surface of the impurities. In this way, the inactivated underlying portion of the ash was brought in contact with the reagent solution, the supernatant. To examine the effect of recycling and molarity, residues were characterized for their physico–chemico–mineralogical, morphological characteristics and FTIR analysis was conducted to identify the functional groups present in them. For the sake of brevity, the residues have been designated by combining two parameters; (i) the molarity (M) of the NaOH used in Step-1 and (ii) a designation for the step of treatment. For example, the designations such as 0.5-S1, 0.5-S2 and 0.5-S3 correspond to the residues obtained after the treatments by using 0.5 M NaOH in Step-1, Step-2 and Step-3, respectively.

2.2. Physical characterization

Specific gravity (G) and specific surface area (SSA) of the residues were determined by employing a Helium gas Ultra Pycnometer (Quantachrome, USA; ASTM D 5550-06) and following the standard ethylene glycol monoethyl ether (EGME) method (Arnepalli et al., 2010; Cerato and Lutenegger, 2002; Jha and Singh, 2011), respectively. The results (i.e., average of the three trials) obtained from these investigations are depicted in Fig. 1(a, b).

2.3. Chemical characterization

2.3.1. X-ray fluorescence (XRF) studies

An XRF set up (Phillips 1410, Holland) was used for determination of the chemical composition (in term of major oxides) of the residues, by following the procedure available in the literature (Jha and Singh, 2011, 2012; Singh and Kolay, 2002) and the results are presented in Tables 1 and 2.

2.3.2. Determination of the CEC

The cation exchange capacity (CEC) of the residues was determined by following the ammonium acetate method (Adamczyk and Bialecka, 2005; ISIRC, 1992; Querol et al., 2007). Accordingly, the sample was initially saturated with Na^+ and freed from organic impurities after being washed thrice with sodium acetate solution and subsequently with 99% isopropyl alcohol, respectively. Finally, the Na^+ was exchanged with NH_4^+ after washing the sample thrice by ammonium acetate solution. The results, average of three tests, are presented in Fig. 2.

Table 1
Chemical composition (% by weight) of the OFA and AFA samples.

Sample	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	K_2O	BaO	CaO	MgO	MnO_2	P_2O_5	SrO	TiO_2
OFA	26.0	63.8	5.1	0.05	0.66	0.14	1.88	0.39	0.16	0.16	0.25	1.52
0.5-S1	27.9	57.7	5.4	4.67	0.55	0.12	1.62	0.38	0.05	0.05	0.04	1.48
0.5-S2	25.5	58.3	5.0	5.53	0.63	0.09	1.63	0.32	0.04	0.06	0.04	1.51
0.5-S3	33.8	52.5	3.7	5.79	0.61	0.08	1.64	0.36	0.04	0.05	0.04	1.28
1.5-S1	39.8	41.2	4.63	9.29	0.33	0.09	1.88	0.36	0.05	0.06	0.04	1.58
1.5-S2	26.4	53.1	5.89	10.2	0.29	0.09	1.84	0.41	0.05	0.05	0.04	1.56
1.5-S3	25.1	55.4	5.78	9.42	0.30	0.10	1.80	0.41	0.05	0.04	0.04	1.49