Improvement in optical brightness of fly ash based zeolite-A for use as detergent builder

J S Udhoji, A K Bansiwal, S U Meshram & S S Rayalu*
Environmental Materials Unit, National Environmental Engineering Research Institute, Nagpur 440 020

Received 19 October 2004; accepted 18 March 2005

A process has been formulated for synthesis of fly ash-based Zeolite-A (FAZ-A), whose optical brightness (58.2%) is slightly less for use as detergent builder. Attempts have been made to improve the optical brightness (OB) of FAZ-A samples using pretreatment of fly ash (FA) through magnetic separation of iron, acid treatment and lime treatment to control colour development in zeolite sample. Treatment of FA and FAZ-A samples has also been attempted by EDTA chelation technique to control iron content. OB, iron content and cation binding capacity (CBC) in FAZ-A sample are crucial and diagnostic parameters for assessing their use as detergent builder. Treatment methodologies have therefore been standardized for improvement in OB as a trade-off between CBC and iron content depending upon the end use of zeolite-A.

Keywords: Zeolite-A, Fly ash, Optical brightness, Detergent builder

IPC Code: B 29 D 11/00

Introduction

Fly ash (FA) has been successfully used for synthesis of zeolite-A, zeolite-P and hydroxysodalite type zeolite were synthesised by treating lignite FAs with NaOH solution. Zeolite-A and zeolite-P have been synthesized from brown coal ash and silicic tuff and Kaolinitic tuff respectively. The formation of zeolite-P has been suppressed by investigating the effect of mechanical forces on zeolite-A synthesis. However, limited studies have been undertaken to improve the optical brightness (OB) of zeolite-A sample from FA.

The most popular detergent builders used are sodium tripolyphosphate (STPP) and tetra sodium pyrophosphate (TSPP), because of their effectiveness, reasonable cost, and safety for use with appliances, fabrics and human. However, their use is environmentally unsafe due to the excessive deposition of phosphates into water bodies that results into eutrophication. Zeolite can substitute phosphate builders since it fulfills most of the requirements of a good detergent builder. It removes hardness causing cations through ion exchange, has high sequestering power and exhibits phenomenon like soil antiredeposition and dye transfer inhibition. Zeolite-A crystals do not damage the fabric due to their cubic shape with rounded edges. Also, zeolites are toxicologically safe and do not contribute towards eutrophication. Fly ash zeolite-A (FAZ-A) has almost all physico-chemical characteristics comparable with commercial zeolite-A except for OB and iron content; which may prove to be detrimental for its proposed application as detergent builder. This paper attempts to improve OB of the FAZ-A by modifying the process of synthesis of zeolite-A from FA.

Materials and Methods

FA samples originating from bituminous coal (FASBC) were collected from Koradi Thermal Power Station (KTPS), Koradi, Nagpur. All the chemicals used were of analytical grade. The international grade standard zeolite-A was procured from Wako, Japan and Degussa, Germany.

Pretreatment

FA was subjected to sieving using sieves of different mesh size (170 µ and 53 µ). FA (50 g), after acid treatment with 8N HCl (250 ml) for 2 h, was filtered and washed with double distilled water till pH 7. Acid extract was neutralized by caustic soda (50%) and filtered by Whatman paper to separate the precipitate. This filtrate was proportionately used while preparing the sodium aluminate solution required during synthesis.
Using magnetic separation method, magnetic iron present in FA as an impurity was removed mechanically, whereas enough care was taken to avoid the loss of fine silica and alumina particles.

Fusion
FA samples with or without pretreatment were subjected to fusion with NaOH in a muffle furnace (Make, Micro Scientific Works; capacity, 4 kW; temp, up to 1000°C). Mixture was homogenized by grinding FA and NaOH in a definite ratio using domestic mixer (Sumit). The mixture was then heated (550-600°C) for 1 h.

Aging and Crystallization
Fused mass was cooled, milled and mixed thoroughly in distilled water with simultaneous addition of sodium aluminate. The slurry so obtained was then subjected to stirring and aging using jar testing unit (Phipps and Bird Model: 7790–402) for 8-10 h. It was then subjected to hydrothermal crystallization in a closed container in an oven (Tempo) at 100°C for 2-3 h.

Washing and Drying
After crystallization, the solid crystalline product was recovered by filtration using vacuum pump (Leovac). It was washed with double distilled water and dried in oven.

Methods of Characterization
Calcium Binding Capacity (CBC)
Synthesized zeolite-A sample (0.5 g) was weighed and dried for 1 h in an oven maintained at 110°C. It was then cooled to room temperature in a desiccator, precisely weighed again and poured into a beaker (1:1) containing 500 ml of 0.05% CaCl₂.2H₂O solution (pH, 10-11). A similar system was also prepared for standard zeolite-A sample (Degussa). Both these mixtures were agitated using jar-testing unit for 15 min at 120 rpm to facilitate the sample to perform exchange of calcium ions. The mixture was then filtered using Whatman paper No. 42. The filtrates and the original Ca²⁺ ion solution were titrated complexometrically by 0.01 M EDTA solution using murexide indicator showing sharp colour change from pink to violet. The CBC was determined as follows:

\[
CBC = \frac{(A - B) \times 0.1 \times 500 \times 100 \text{ meq. of Ca}^{2+} / 100 \text{g sample}}{20 \times 0.5 \times 25} = (A - B) \times 80 \text{ meq/100g}
\]

where \(A\) is the volume of 0.01 \(M\) EDTA required for original Ca²⁺ solution and \(B\) is the volume of 0.01 \(M\) EDTA required for solution after treatment with zeolite-A.

Sorption Capacity (SC)
Sample (1 g) was accurately weighed in a crucible, dried in oven for 1 h at 110°C and then weighed again. The crucible was then heated at 800°C for 1 h in preheated furnace, cooled on a metal plate for one min and then in desiccator, and weighed. The percentage weight loss gives the SC of zeolite, which is its characteristic property.

XRD Crystallinity
The values of interplaner d-spacing corresponding to Bragg’s reflections (2\(\theta\)) for zeolite-A (12.20 ± 0.20, 8.60 ± 0.20, 7.05 ± 0.15, 4.07 ± 0.08, 3.68 ± 0.07, 3.38 ± 0.06, 3.260.05, 2.96 ± 0.05, 2.73 ± 0.05, 2.60 ± 0.05) were used as a basis for identification and quantification of crystalline phase. The X-ray diffraction patterns were recorded at RSIC, Nagpur using X-ray diffractometer (Phillips: PW–1830). The operating target voltage was 35 kV and the current was 20 mA. The radiations of CuKα were generated using X-ray generator (Phillips: PW–1729) and the β radiation were filtered using monochromator. The samples were scanned for 2\(\theta\) range (5-60°). For quantification of crystalline zeolite-A phase in the FAZ-A sample, percentage crystallinity and degree of crystallization were calculated by comparing the sum of peak intensities for the characteristic ‘d’ values of zeolite-A, of FAZ-A with that of standard zeolite-A (crystallinity, 100%).

\[
\text{Crystallinity percentage} = \left( \frac{\text{Sum of peak intensities for FAZ-A}}{\text{Sum of peak intensities for standard zeolite-A}} \right) \times 100
\]

Optical Brightness
OB of a sample is the ratio expressed as percentage of the radiation reflected by a body to that reflected by a perfectly reflecting diffuser measured at an effective wavelength (457 nm) with Carlzeiss Photoelectric Reflection Photometer using BaSO₄ as standard. The reflectance at 570 nm is also measured and the difference between these values is termed as “yellowness”.

[Note: The original document contained more content, but it was cut off at this point.]
Results and Discussion
The yellow shade of FAZ-A samples is due to the incorporation of colouring impurities (organic matter, ferruginous minerals) in FA, which influence the zeolite brightness. During the fusion step, free and structural Fe is oxidized to coloured Fe compounds, thus reducing the brightness. There is further decrease in brightness during the stirring and aging step and during hydrothermal crystallization, which can be attributed to the liberation of partially soluble Fe hydroxide/oxide during the reaction with alkali.

FAZ-A synthesized so far have OB of about 58.2 percent. Hence, to improve the OB, it is essential to remove the iron oxide impurities by giving pretreatments like sieving, magnetic separation and acid treatment to the FA samples. In addition, sodium aluminate was prepared by refluxing the slurry [Na$_2$O, 20.2%, Al$_2$O$_3$, 18.4% (SA VI)] for 1 h to precipitate the iron hydroxide. The sodium aluminate was kept standing for some time and the supernatant sodium aluminate was taken for synthesis. ZA-1 (Table 1) was synthesized without following any pretreatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-treatment (s)</th>
<th>Sodium-aluminate composition</th>
<th>Sodium-aluminate ml</th>
<th>Seeding</th>
<th>Crystallization time h</th>
<th>Sorption capacity %</th>
<th>CBC meq/100g</th>
<th>Crystallization %</th>
<th>OB %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA-1</td>
<td>None</td>
<td>Na$_2$O: 50.3 Al$_2$O$_3$: 39.0</td>
<td>20</td>
<td>+Ve</td>
<td>3.0</td>
<td>19.1</td>
<td>430</td>
<td>100</td>
<td>58.2</td>
</tr>
<tr>
<td>ZA-2</td>
<td>Sieving by 170 µ</td>
<td>Na$_2$O: 50.3 Al$_2$O$_3$: 39.0</td>
<td>20</td>
<td>+Ve</td>
<td>3.0</td>
<td>21.8</td>
<td>500</td>
<td>100</td>
<td>60.2</td>
</tr>
<tr>
<td>ZA-3</td>
<td>Sieving by 170 µ</td>
<td>Na$_2$O: 50.3 Al$_2$O$_3$: 39.0</td>
<td>20</td>
<td>+Ve</td>
<td>3.5</td>
<td>21.5</td>
<td>510</td>
<td>90</td>
<td>60</td>
</tr>
<tr>
<td>ZA-4</td>
<td>Sieving by 53 µ</td>
<td>Na$_2$O: 50.3 Al$_2$O$_3$: 39.0</td>
<td>20</td>
<td>+Ve</td>
<td>3.0</td>
<td>21.0</td>
<td>470</td>
<td>100</td>
<td>65</td>
</tr>
<tr>
<td>ZA-5</td>
<td>Sieving by 170 µ</td>
<td>Na$_2$O: 50.3 Al$_2$O$_3$: 39.0</td>
<td>20</td>
<td>+Ve</td>
<td>3.5</td>
<td>21.0</td>
<td>540</td>
<td>100</td>
<td>65</td>
</tr>
<tr>
<td>ZA-6</td>
<td>Sieving by 53 µ</td>
<td>Na$_2$O: 50.3 Al$_2$O$_3$: 39.0</td>
<td>20</td>
<td>+Ve</td>
<td>3.0</td>
<td>22.4</td>
<td>520</td>
<td>85</td>
<td>68</td>
</tr>
<tr>
<td>ZA-7</td>
<td>Acid Reflux in 8 N HCl for 2 h</td>
<td>Na$_2$O: 50.3 Al$_2$O$_3$: 39.0</td>
<td>20</td>
<td>+Ve</td>
<td>3.0</td>
<td>21.8</td>
<td>490</td>
<td>88</td>
<td>65</td>
</tr>
<tr>
<td>ZA-8</td>
<td>Magnetic separation</td>
<td>Na$_2$O: 50.3 Al$_2$O$_3$: 39.0</td>
<td>20</td>
<td>+Ve</td>
<td>3.0</td>
<td>20.2</td>
<td>500</td>
<td>98</td>
<td>70</td>
</tr>
<tr>
<td>ZA-9</td>
<td>Magnetic separation</td>
<td>Na$_2$O: 20.2 Al$_2$O$_3$: 18.4</td>
<td>112</td>
<td>+Ve</td>
<td>3.0</td>
<td>21.0</td>
<td>540</td>
<td>100</td>
<td>72</td>
</tr>
<tr>
<td>ZA-10</td>
<td>Acid treatment with H$_2$SO$_4$</td>
<td>Na$_2$O: 20.2 Al$_2$O$_3$: 18.4</td>
<td>42</td>
<td>+Ve</td>
<td>3.5</td>
<td>-</td>
<td>500</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>ZA-11</td>
<td>Sieving by 53 µ Magnetic separation</td>
<td>Na$_2$O: 20.2 Al$_2$O$_3$: 18.4</td>
<td>42</td>
<td>+Ve</td>
<td>3.0</td>
<td>-</td>
<td>480</td>
<td>-</td>
<td>88</td>
</tr>
<tr>
<td>ZA-12</td>
<td>Sieving by 53 µ Magnetic separation</td>
<td>Na$_2$O: 50.3 Al$_2$O$_3$: 39.0</td>
<td>20</td>
<td>+Ve</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>85</td>
</tr>
</tbody>
</table>

CBC: Calcium binding capacity
OB: Optical brightness
The most suitable treatment appears to be the most suitable treatment method for improving OB. A combination of sieving and magnetic separation also gives reasonably good results. EDTA treatment of FA has not given encouraging results; whereas lime treatment gives encouraging results for controlling discoloration but has comparatively low CBC and crystallinity, which is not desirable from the point of view of its proposed application as detergent builder.

Conclusions

Attempts were also made to further improve OB by employing the pretreatment steps of sieving, magnetic separation and acid treatment. The as-synthesized sample shows significant improvement in OB (88%) using sodium aluminate of composition [Na₂O, 20.2%; Al₂O₃, 18.4% (ZA-11)]. Almost similar results in OB were obtained for sample with increased crystallization time (3.5 h, ZA-12) and variation in sodium aluminate composition [Na₂, 50.3%; Al₂O₃, 18.4% (ZA-12)]. As a trade off between CBC, crystallinity and OB, this particular combination of treatment steps improves OB sufficiently for its proposed application as detergent builder. Some additional treatments were also explored to improve the OB. FA was subjected to EDTA treatment in addition to sieving and magnetic separation (ZA-13). However, no significant change in OB in comparison with ZA-8 was observed. Therefore, the mode of treatment is not feasible for improving colour.

The colour development in zeolite-A from FA is attributed to the intense coloration of ferric hydroxide, which is precipitated with zeolite resulting in its coloration. Attempts were also made to control discoloration through lime treatment wherein ferric hydroxide complexes with lime to form ferro calcium complexes, which are not coloured. In this mode of treatment, no significant change was observed in colour improvement, in fact there was decrease in CBC, which is not desirable.

Acknowledgements

Authors thank Dr S Devotta, Director, NEERI, Nagpur for permitting to publish this paper. They also thank Dr N Labhsetwar and Mr R B Biniwale,
Scientist, NEERI for useful suggestions, and Dr D G Garway, Scientist, Regional Sophisticated Instrumentation Centre, for XRD analyses.

References