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# Synthesis of zeolite A from coal fly ash using ultrasonic treatment – A replacement for fusion step

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ABSTRACT

The synthesis of zeolites from fly ash has become an increasingly promising remedy to the crisis of coal fly ash production and disposal in South Africa. In recent studies, South African fly ash was proven to be a suitable feedstock for the synthesis of essential industrially used zeolite A. However, the process involves a costly energy intensive step whereby fly ash is fused at high temperatures, which may make the process economically unattractive on a large scale. The aim of this study is to investigate the possibility of replacing high temperature fusion with less energy intensive sonochemical treatment for the synthesis of zeolite A. Sonochemical treatment was first thought possible due to the violent cavitation caused by high intensity sonication. The results of the study showed that fusion can be replaced by 10 min of high intensity sonication. The incorporation of sonication also consequently reduced the crystallization temperature of the process making it possible to synthesize a pure phase zeolite A at lower temperatures and reduced times. This study effectively developed a novel process to replace the energy intensive fusion step with a short, easy and inexpensive treatment. Scale up of this synthesis approach may proffer a promising alternative option to the anticipated energy demand of the synthesis of fly ash-based zeolite with fusion method.



## 1. Introduction

The accumulation of fly ash from the combustion of coal during electricity generation is now an increasing environmental and/or economic burden to the power generating industry in South Africa. The disposal of coal fly ash requires large vacant land, which can be used to dump the ash or construct expensive ash dams. Moreover, these problems are more intense due to the large quantity of fly ash not being beneficiated. Until recently, in South Africa, the focus tends to be on economic growth through exports from mining activities rather than the management and utilization of the consequent wastes from these activities. With the growing economy and population, the demand for electricity has increased to unprecedented level. As a consequence, South Africa produced 36 Mt of coal fly ash from the generation of electricity only, excluding fly ash produced from the production of synthesis gas [1,2], only 5% of which was beneficially used while the surplus was usually disposed of in ash dams and dumps [2].

Till date, the use of fly ash is limited to it being an additive in building and construction materials (cement extension, lightweight aggregate). However, due to its diverse chemical, mineralogical and morphological properties, recent studies are investigating its use as a resource material in other applications such as acid mine drainage treatment, toxic element immobilization and as an adsorbent [3,4]. In addition, its high content of Si and Al makes it as a good resource for the production of zeolitic materials [5,6]. Although the larger quantities of Al and Si in fly ash are reported to be entrapped in the amorphous phase of the ash, the crystalline phases such as quartz, mullite, hematite and magnetite also contain significant quantities of these elements [7,8]. The first step in the synthesis of zeolites involves dissolution of the crystalline and amorphous phases of the ash in alkaline medium (NaOH or KOH) in order to make the Si and Al available for the formation of the zeolite framework during crystallization.

Although varieties of zeolites have been synthesized using different types of methods, such as hydrothermal, hydrothermal with fusion pretreatment, molten-salt methods, and methods applying microwave and ultrasound techniques [3,4,9–14], however the most robust approach to the use of fly ash as a feedstock in the synthesis of zeolites has been found to be high temperature fusion of the ash with NaOH, followed by hydrothermal synthesis of the

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zeolite products [11,15]. In the fusion process, the crystalline and amorphous Al/Si bearing phases are converted into sodium silicates and aluminosilicates which easily dissolve into solution [15]. In a recent study, zeolite A was synthesized from South African coal fly ash by use of the fusion pre-treatment step [16]. Zeolite A is of industrial importance, its of use in detergents making, polyvinyl chloride and in drying of gasses; However, its synthesis from South African coal fly ash is still limited to micro scale.

Even though the potential for the scale up synthesis of zeolite A from South African fly ash is promising, the fusion step is energy intensive and it may not be economically effective to operate purpose-built furnaces for this process on an industrial scale. Hence, it is important to investigate alternative treatment approaches to the fusion; one of such is the sonochemical treatment, which involves exposure to high intensity ultrasonic waves in the presence of a chemical. Ultrasound is a range of vibratory waves operating at frequencies greater than 16 kHz [17], when applied to liquid/slurry, a low pressure in the wave causes the formation of vapor bubbles which collapses violently causing a highly intense acoustic cavitation. This may result to hot spots or local temperatures greater than 5000 K and cooling rate greater than $10^7$ °C/s. The pressure and the high local temperatures, combined with extraordinarily rapid cooling, provide a unique means for dissolution and chemical reactions. The physics of this process has been described in details elsewhere [18–20]. It is the phenomena of cavitation that was speculated for the dissolution of the components of coal fly ash.

Musyoka et al. [16] reported significant reduction in the crystallization time for the synthesis of zeolite A when the filtrate from the solution of fused fly ash was sonicated prior to the hydrothermal treatment. The recent study by Bukhari et al. [21], which also involved application of an ultrasound to the filtrate from a fusion process was very similar to Musyoka et al. [16]. The authors obtained zeolite A at a temperature lower than the value reported by Musyoka et al. [16]. In a similar experiment, Belviso et al. [22] reported formation of zeolite-X at temperature of 25 °C. However, it appears from aforementioned studies that the energy of the cavitation during sonication process was not fully utilized, given that hot spots with temperatures greater than the fusion temperature can be achieved by sonication, which was supported by the report of Musyoka et al. [23]. It is hypothesized that zeolite A can be synthesized by replacing the fusion step with an ultrasound rather than application of ultrasound to the extract obtained from the fusion process as reported recently [21]. It is therefore the objective of this study to investigate the possibility of replacing a high temperature fusion step with high intensity ultrasonic treatment during the synthesis of zeolite A from South African coal fly ash. The view is to propose a less energy intensive process for the production of this material if a large full-scale synthesis would be considered.

## 2. Materials and methods

### 2.1. Materials and characterization techniques

Coal fly ash was obtained from a South African coal fired power station. Analytical grade sodium aluminate and sodium hydroxide was used for the adjustment of the Si/Al ratio and dissolution of fly ash respectively. The identification and quantification of mineral phases present in the raw materials and zeolite products were carried out using qualitative X-ray diffraction (XRD) and quantitative XRD (QXRD) techniques respectively. Each sample was oven-dried at 105 °C for 12 h to remove any adsorbed moisture prior to the analysis. For qualitative analysis, the mineralogy of the samples was analyzed using a Philips PANalytical instrument with a pw3830 X-ray generator operated at 40 kV and 25 mA. The samples were initially ground to a fine powder and later mounted onto sample holders. The samples were step-scanned in a range of $4° < 2\theta < 60°$ at intervals of 0.02° and counted for 0.5 s per step. Crystalline mineral phases present in the samples were identified with the help of Highscore Xpert software by comparing spectra with the standard line patterns from the powder diffraction file database supplied by International Centre for Diffraction Data (ICDD). For quantitative analysis, which includes the quantitative determination of crystalline and amorphous phases, each sample was first micronized in a McCrone micronizing mill. 20% Si (Aldrich 99.9%) was added and the sample was then prepared using a back loading preparation method. The analysis was done using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-K$\alpha$ radiation. The mineralogical phases were identified using X'Pert Highscore plus software. The relative phase amounts in weight% were estimated using the Rietveld method (errors were reported on the 3 sigma level in weight%). The morphology of both raw material and solid products was examined by the use of Scanning Electron Microscopy (SEM). While compositional analysis of fly ash material was carried out with X-ray fluorescence spectrometry (XRF), the composition of liquid samples was determined with inductively coupled plasma atomic emission spectrometry (ICP-AES). The functional groups and details of both fly ash raw material and solid products was uncovered using Fourier transform infrared spectroscopy (FT-IR).

### 2.2. Synthesis of zeolite A by means of high temperature ash fusion

In order to establish a basis for the study, results for the synthesis of zeolite A through pre-fusing the fly ash were reproduced by following the steps described by Musyoka et al. [9] Sodium hydroxide was ground into a fine powder and mixed with coal fly ash in a mass ratio of 1:1.2 (fly ash:sodium hydroxide). The mixture was transferred into a crucible and then placed in a furnace with the temperature set to 550 °C. The ash was allowed to fuse for 90 min after which it was ground into a powder and mixed with ultra pure water in a mass ratio of 1:5 (fused ash:water). The slurry was mixed for 2 h to allow extraction of the Si and Al species from the fused ash into solution. The slurry was then filtered and the Si/Al ratio of the clear solution was adjusted by adding sodium aluminate solution in a mass ratio of 5:2 (clear solution:sodium aluminate solution). The sodium aluminate solution was prepared by dissolving sodium aluminate powder in ultrapure water in a mass ratio of 20.84:1 (ultrapure water:sodium aluminate powder). The solution was then added to a 2.4 M sodium hydroxide solution in a volumetric ratio of 1:1 and stirred for 30 min with a magnetic stirrer. The resulting sodium aluminate solution was then added to the clear solution and stirred until a milky emulsion formed and then transferred into 250 mL glass bottles in a volume of maximum 100 mL per bottle. The bottles were placed into a hot air oven at a temperature of 100 °C and time duration of 2 h. The product was separated by filtration, washed with ultrapure water and dried over night at 70 °C.

### 2.3. Replacement of fusion with sonochemical treatment

Zeolite A was synthesized by replacing the fusion of ash with sonochemical treatment; 20 g of fly ash was mixed with 100 mL 5 M NaOH in a plastic sonication container. The mixture was subjected to sonication at 100% amplitude with a 600 W MISONIX S-4000 sonicator by LabPlanet USA. After sonication the solution was filtered and the Si/Al ratio of the clear filtrate was adjusted by following the steps described in the previous section. The adjusted solution was then transferred into glass bottles and