ACID MINE DRAINAGE TRANSFORMATION OF FLY ASH INTO ZEOLITIC CRYSTALLINE PHASES

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SUMMARY

The development of a system for the utilization of fly ash produced at coal-fired power stations to treat acid mine drainage (AMD) resulting from coal mining activities was investigated. It involved a neutralization process, in which the pH of the AMD solution was raised from 2–3 to neutral pH when reacted with an appropriate amount of fly ash. The residual solids from the co-disposal reaction were processed and fused with sodium hydroxide at 600 ºC to produce zeolites including faujasite, which have useful applications as ion exchangers. Zeolites were characterized by X-ray diffraction (XRD) spectrometry and scanning electron microscopy (SEM).

KEYWORDS: Fly ash, acid mine drainage, co-disposal reaction, hydrothermal synthesis, zeolite, faujasite.

INTRODUCTION

The ever-increasing demand for electricity in modern society has resulted in the burning of large quantities of coal. Many of the coal-fired power stations in South Africa operate on the pulverized fuel principle. Two ash fractions are produced during combustion: bottom ash and fly ash (FA). FA forms the fine portion of residues removed from the flue gases. It ranges in size from 0.5 to 200 μm and is composed primarily of Si, Al, Fe, Ca, plus unburned carbon portions [1, 2]. Furthermore, FA can contain up to 50 trace elements, a number of which are very toxic to the environment. Due to its high CaO content, the ash produced in South Africa tends to be highly alkaline, and pH values reach 10 or more in the leachate [3].

The formation of acid mine drainage (AMD) is of great environmental concern at coal mining sites. It occurs when sulphide minerals (mainly pyrite) are associated with coal seams and, therefore, oxidized by contact with water and oxygen. AMD is characterized by low pHs and high concentrations of sulphate and heavy metals. It is essential to treat AMD before it is discharged, in order to limit its negative impact on the receiving streams and aquifers. This can be done by active or passive treatment systems [4, 5].

Despite the numerous environmental issues associated with its combustion, coal will remain a major source of electrical power generation in South Africa for years to come. It has, therefore, become necessary to look for methods to obtain value-added products from fly ash, such as zeolites [6–8]. In this article, attention is given to the possible use of FA as a neutralizing agent in the treatment of AMD and the synthesis of novel products (ion exchange adsorbents in the form of zeolites) from the solid residues collected after the co-disposal reaction of FA and AMD.

MATERIALS AND METHODS

Fly ash was collected from the Eskom power station of Arnot (South Africa), while the acid-mine drainage was sampled from the Navigation plant at the Anglocoal colliery of Landau (South Africa). The solid residues used as zeolite feedstock were prepared by reacting FA with AMD in specific FA:AMD ratios (e.g. 1:3, 1:5). The pH and electrical conductivity of the reaction mixture were measured at regular time intervals until a nearly neutral pH was obtained. A Mettler Delta 350 pH-meter, with automatic temperature correction at 25 ºC, was used for pH measurements. The EC was measured using a Hanna Instruments HI 991301 portable pH/EC/TDS/temperature-meter.

When neutral pH was reached, solid and liquid phases were separated by filtration. The co-disposal solid residues were recovered, dried in an oven at 70 ºC, then milled and ground with an agate mortar and pestle, until a powder of even particle size was obtained. Finally, the powder was further crushed in a Zibb mill to approximately 5 μm grain size.

Zeolite was synthesized according to a hydrothermal process [8]. The dried co-disposal solid residues were mixed with sodium hydroxide (NaOH) in a residue:NaOH ratio

of 1:1.2. The mixture was homogenized by grinding with an agate mortar and pestle, and then fused at 600 ºC for about 1-2 hours. The milled fused product was mixed thoroughly with distilled water, and the slurry was aged for 8 hours at room temperature. After ageing, the slurry was hydrothermally treated at 100 ºC for 24 hours. The solid product was filtered, washed with deionised water until the leachate had a pH of 10, and dried at 70 ºC.

The mineral content and crystallinity of this product were evaluated by XRD spectrometry, with a Philips analytical graphite mono-chromator. Cu-Kα radiation samples were scanned for 2θ ranging from 7 to 70º. The X'Pert Graphics & Identify data collection software was used to identify the minerals present in the samples. SEM was used to determine the size distribution and morphology of the synthesized crystals. A Hitachi X-650 scanning electron micro-analyser was used to take micrographs of the samples, which were mounted on aluminium stubs using conductive glue, and then coated with a thin layer of carbon.

RESULTS AND DISCUSSION

The pH and conductivity measured during the AMD neutralization experiment at an FA:AMD ratio of 1:2 are shown in Figure 1. Within the first 30 min of the experiment, the pH of the reaction mixture increased from 2.8 to 6, and the conductivity decreased from 10.8 to 7.5. This initial high reactivity was followed by a further decrease of conductivity, reaching 4 mS/cm after 240 min, whereas the pH remained constant. These results provide evidence that FA is a rapid and efficient neutralizing agent of AMD.

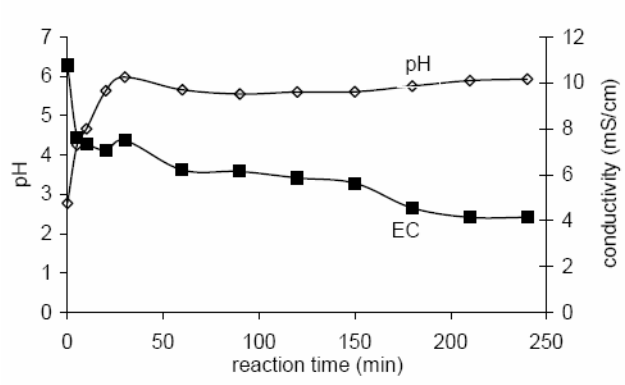

FIGURE 1 - pH and conductivity measurements during the co-disposal reaction of FA and AMD.

The neutralization of AMD is commonly achieved by the addition of chemicals, such as CaO, $Ca(OH)_2$, $CaCO_3$, NaOH and Na_2CO_3. The neutralization potential of FA is due to significant quantities of alkalinity in the form of CaO, MgO, K_2O and Na_2O. Furthermore, FA has a very high surface area but small particle size, resulting in a relatively high reactive surface area [2, 9-11]. FA may, therefore, be a substitute for limestone or lime treatment in the neutralization of AMD.

The XRD analysis indicates that several crystalline phases were present in the material obtained from the hydrothermal fusion of co-disposal solid residues. The phases were identified to be faujasite, sodalite and zeolite A phases, when accounting the zeolitic nature of the fused material. The nature of the synthesized products varied, i.e. different zeolitic phases were obtained, when different co-disposal solids were used as feedstock material.

The photomicrographs show the transformation of FA into a zeolite phase (faujasite), and the morphology of single crystals looked well-defined (Figure 2). For the faujasite, sodalite and zeolite A phases, the size of individual crystals varied from 1 to 5 μm.

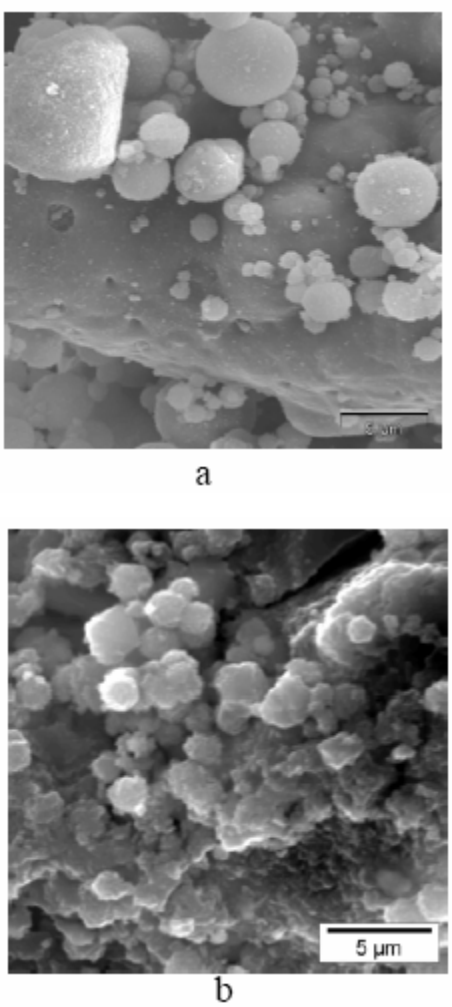

FIGURE 2 - Scanning electron photomicrograph of the FA (a) and the faujasite synthesized from FA:AMD co-disposal solid (b).

In the co-disposal process, pollution control of both coal mining and coal powered utility waste streams is shown to be possible through a reaction between two waste products, namely AMD and FA. The neutralization of AMD is achieved by reaction with FA. The results further indicate that high capacity ion-exchange adsorbents, such as the zeolites faujasite, sodalite and zeolite A, can be prepared from the co-disposed solid residues. Previous studies [11-

13] have shown that zeolite can be obtained by hydrothermal treatment of FA. The co-disposal process utilizing South African FA can be considered as a suitable method to achieve low-cost treatment of coal mine-derived AMD, the delivery of relatively cleaner process water at a circumneutral pH (suitable for further treatment), and production of zeolitic adsorbents by post-process synthesis from co-disposal solid residues.

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