

Alkaline Hydrothermal Conversion of Fly Ash Filtrates Into Zeolites 2: Utilization in Wastewater Treatment

Vernon Somerset,¹ Leslie Petrik,² and Emmanuel Iwuoha¹

¹Sensor Research Laboratory, Department of Chemistry, University of the Western Cape, Bellville, South Africa

²Inorganic Porous Media Group, Department of Chemistry, University of the Western Cape, Bellville, South Africa

Filtrates were collected using a codisposal reaction wherein fly ash was reacted with acid mine drainage. These codisposal filtrates were then analyzed by X-ray Fluorescence spectrometry for quantitative determination of the SiO_2 and Al_2O_3 content. Alkaline hydrothermal zeolite synthesis was then applied to the filtrates to convert the fly ash material into zeolites. The zeolites formed under the experimental conditions were faujasite, sodalite, and zeolite A. The use of the fly ash-derived zeolites and a commercial zeolite was explored in wastewater decontamination experiments as it was applied to acid mine drainage in different dosages. The concentrations of Ni, Zn, Cd, As, and Pb metal ions in the treated wastewater were investigated. The results of the treatment of the acid mine drainage with the prepared fly ash zeolites showed that the concentrations of Ni, Zn, Cd, and Hg were decreased as the zeolite dosages of the fly ash zeolite (FAZ1) increased.

Key Words: Acid mine drainage; Cation exchange capacity; Fly ash; Hydrothermal synthesis; Metal ions; Wastewater; XRD; Zeolites.

INTRODUCTION

With most of the coal-fired power stations in South Africa operating on the coal combustion principle, large quantities of fly ash (FA) are produced annually. Despite the many environmental issues associated with coal combustion, it

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Address correspondence to Vernon Somerset, Sensor Research Laboratory, Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa; E-mail: vsomerset@uwc.ac.za

will remain a major source of electrical power generation for many years to come. It has therefore become necessary to look at methods that can be used to produce or manufacture value-added products from FA.

Another persistent environmental problem also encountered in South Africa is acid mine drainage (AMD), an unavoidable by-product of the mining and mineral industry. AMD forms when pyrite and other sulfide minerals associated with coal seams are exposed to water and oxygen. AMD are waters with typical high concentrations of dissolved heavy metals and sulfate and can have a pH as low as 2.^[1–3]

When AMD is discharged untreated, it can pollute receiving streams and aquifers, and the resulting overall effect on streams and waterways can be very dramatic. Some of the harmful effects of AMD on the environment include the disappearance of all aquatic life, the coating of river bottoms with layers of rust-like particles, and the decrease in pH of the water and streams. It is therefore essential that methods are in place to treat mine drainage to limit its negative effect on the environment.^[1]

South African FA contains relatively high concentrations of SiO_2 , Al_2O_3 , and CaO , with CaO considered as a liming agent to neutralize AMD.^[4] The possibility was explored to use a codisposal reaction, first to neutralize AMD by codisposing it with FA and second to collect the filtrates of the reaction for zeolite synthesis.

Studies^[5–7] on zeolite synthesis have shown that zeolites can be obtained by hydrothermal treatment of FA. Zeolites have important industrial applications, such as in catalysis, sorbents for removal of ions and molecules from wastewater, radioactive wastes and gases, and as replacements for phosphates in detergents.^[5,8]

In this work, the codisposal FA filtrates and fresh FA were converted into zeolite by alkaline hydrothermal treatment with sodium hydroxide (NaOH).^[9] The difference in zeolite product obtained from using different FA-derived samples in the synthesis was investigated. The ability of the different zeolites to remove metal ion species from solution, as compared with a commercial synthetic zeolite, was also investigated. The metal ion concentrations of specific elements, Ni, Zn, Cd, As, and Pb, were investigated as different dosages of the zeolite were added to AMD. The ultimate aim was to investigate whether the synthesized zeolite can lower these metal concentrations as an increased dosage of the zeolite was added to the AMD.

MATERIALS AND METHODS

Sample Preparation

The codisposal filtrates were collected by using a codisposal reaction wherein FA was reacted with AMD in a specific FA/AMD ratio (e.g., 1:3.5, 1:4,

1:5). The readings for pH and electrical conductivity (EC) of the codisposal reaction mixture were taken at regular time intervals until a near-neutral pH of 7 was obtained. Solids and liquids were separated using filter paper. The codisposal filtrates were dried in an oven at a temperature of 70°C and then transferred into a plastic container.^[10]

Fresh FA as well as codisposal filtrate samples were prepared for chemical analysis and zeolite synthesis. The FA and codisposal filtrate samples were milled and ground with an agar mortar and pestle to ensure that a powder of even particle size was obtained.^[10]

Zeolite Synthesis

FA and codisposal filtrates were subjected to alkaline hydrothermal zeolite synthesis. Each sample was fused with sodium hydroxide (NaOH) in a 1:1.2 ratio at 600°C for about 1–2 h. The fused product was then mixed thoroughly with distilled water, and the slurry was subjected to aging for 8 h. After aging, the slurry was subjected to crystallization at 100°C for 24 h. The solid product was recovered by filtration and washed thoroughly with deionized water until the filtrate had a pH of 10 to 11. The product was then dried at a temperature of 70°C and prepared for characterization.^[11]

Characterization

The chemical composition of the raw FA and codisposal filtrates was evaluated with X-ray Fluorescence spectrometry. The zeolite samples were characterized in terms of mineralogy (by x-ray diffraction), surface area (BET analysis), and cation exchange capacity.

Decontamination Experiments

The decontamination tests were performed using AMD samples to which different dosages of zeolite (commercial and synthesized from FA material) were added. Batch experiments were carried out at room temperature, with continuous stirring in PVC containers. Aliquots of 100 mL of each water sample and zeolite powder doses from 0.5 to 2 g/100 mL were used. After 1 h, the mixtures were filtered and the pH values and concentrations immediately measured. Major and trace element contents were determined by ICP-mass spectroscopy.

RESULTS AND DISCUSSION

Zeolite Synthesis

Near-neutral codisposal filtrates were collected by reacting a known mass of FA (e.g., 100 g) with a fixed volume of AMD (e.g., 350 mL) for a specific

Table 1: XRF analysis-chemical composition of the fresh FA and co-disposal filtrate samples (10).

Oxide (wt%)	Samples	
	FA	Codisposal filtrate
SiO ₂	51.49	57.03
TiO ₂	1.45	1.30
Al ₂ O ₃	26.37	23.52
Cr ₂ O ₃	0.03	0.02
Fe ₂ O ₃ T	5.03	5.70
MnO	0.06	0.16
NiO	0.01	0.02
MgO	2.52	2.61
CaO	7.83	6.22
Na ₂ O	0.53	0.00
K ₂ O	0.65	0.59
P ₂ O ₅	0.38	0.24
H ₂ O ⁻	0.11	0.49
Total	99.0	99.9
Si/Al	1.95	1.95

FA/AMD ratio (e.g., 1:3.5). The chemical composition of the AMD is shown in Table 2. This was done to investigate the rate of neutralization and the effect of mixing time on the pH and electrical EC measurements. An FA/AMD ratio of 1:3.5 to 1:5 resulted in an end pH of near neutral during the codisposal reaction, enabling the collection of the codisposal filtrates.^[10]

XRF spectrometric analysis of the codisposal filtrate and fresh FA samples was done for quantitative determination of the SiO₂ and Al₂O₃ content of the samples. From these data the [SiO₂]/[Al₂O₃] ratio was determined. The results for the XRF analysis are shown in Table 1, indicating that both samples are

Table 2: Chemical composition of AMD.⁽¹⁰⁾

	Li	B	Na	Mg	Al
AMD (ppb)	281	2916	10703	81246	93.6
	Si	K	Ca	V	Cr
AMD (ppb)	146653	2852	65338	1.23	105
	Mn	Fe	Ni	Cu	Zn
AMD (ppb)	8891	70161	10.6	341	143
	As	Se	Rb	Sr	Mo
AMD (ppb)	5.34	7.24	29.4	2183	2.25
	Cd	Sb	Cs	Ba	La
AMD (ppb)	8.81	0.55	1.92	8.17	0.69
	Ce	Pr	Nd	Sm	Eu
AMD (ppb)	0.75	0.072	0.28	0.13	0.10
	Gd	Tb	Dy	Ho	Er
AMD (ppb)	0.12	0.031	0.13	0.051	0.11
	Tm	Yb	Lu	Hg	Pb
AMD (ppb)	0.13	0.18	0.036	18.5	4.79
	U				
AMD (ppb)	0.11				

Table 3: Crystalline phases, surface area, and exchangeable cation values for raw and treated fly ash and codisposal filtrate material.^(10,15)

Sample material	Crystalline phases present	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Exchangeable cations (meq/100 g)
Raw FA	Quartz, mullite	1.05	—	—
AFAZ1 (FA zeolite)	Faujasite	515	0.449	7.752
Raw codisposal filtrate	Quartz, mullite	1.58	—	—
FAZ1 (co-disposal filtrate zeolite)	Faujasite, sodalite, zeolite A	245	0.245	6.211

relatively rich in SiO₂ and Al₂O₃. The relatively high amount of calcium oxide (CaO) accounted for the neutralization potential of the FA in the codisposal reaction.

The hydrothermal treatment of the FA and codisposal filtrates led to the formation of different zeolitic material, depending on the different starting material used. Table 3 shows the results for the crystalline phases formed, the surface area, pore volume, and amount of exchangeable cations present for the treatment of the fresh FA and codisposal filtrate samples.

The results in Table 3 show that the hydrothermal treatment of the raw FA and codisposal filtrate increased the surface area of both types of starting FA material over the untreated material. A higher surface area and pore volume was obtained for the FA zeolite compared with the codisposal zeolite. The results also indicate how the surface areas of the FA and codisposal filtrate increase after the hydrothermal treatment. This can be attributed to the fact that the agglomeration of fine zeolite crystals formed during the treatment process. Similarly, the results for the sum of the exchangeable cations (i.e., Na⁺, K⁺, Ca²⁺, and Mg²⁺) in the last column of Table 3 show that the amount of exchangeable cations present in the FA zeolite is higher than in the codisposal zeolite.

X-ray diffraction analyses indicated that the hydrothermal zeolite synthesis conditions led to the formation of faujasite for all FA sources used in this study. In the case of the codisposal filtrate, not only faujasite formed, but also crystalline phases of sodalite octahydrate and zeolite A were present. Figures 1 to 3 show the various crystalline phases present before and after the hydrothermal treatment process. Figure 1a shows that the predominant crystalline phases present in the FA are quartz (SiO₂) and mullite (Al₆Si₂O₁₃). After alkaline hydrothermal treatment, Figure 2 indicates that the crystalline phase faujasite has formed. For the codisposal filtrate, sample quartz and mullite are also present, as shown in Figure 1b. After alkaline hydrothermal treatment, the crystalline phases faujasite, sodalite, and zeolite A are present, as shown in Figure 3.

Comparison of FA and CDFiltrate

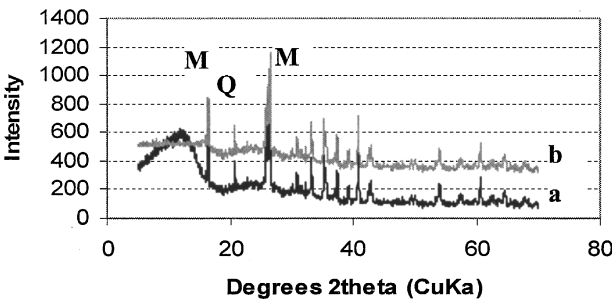


Figure 1: X-ray diffraction spectra for (a) raw FA and (b) codisposal filtrate samples.

FA Zeolite

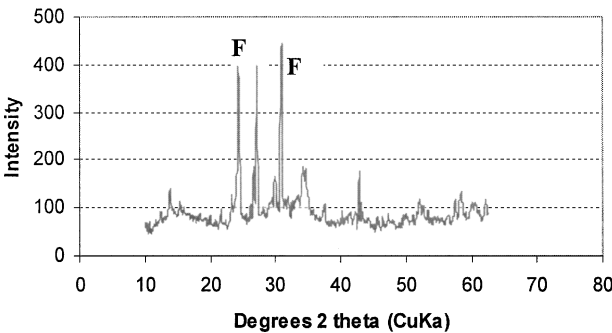


Figure 2: X-ray diffraction spectrum of fly ash zeolite sample, FAZ1.

Co-disposal filtrate zeolite

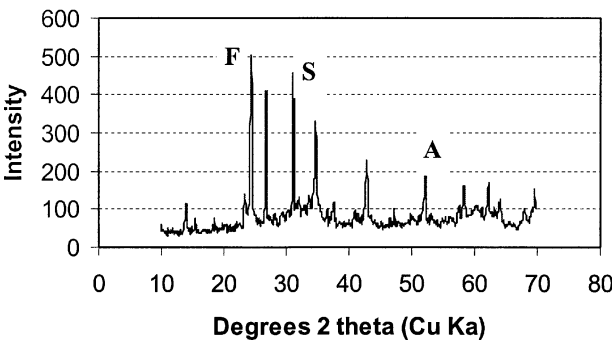


Figure 3: X-ray diffraction spectrum of codisposal filtrate zeolite sample, AFAZ1.

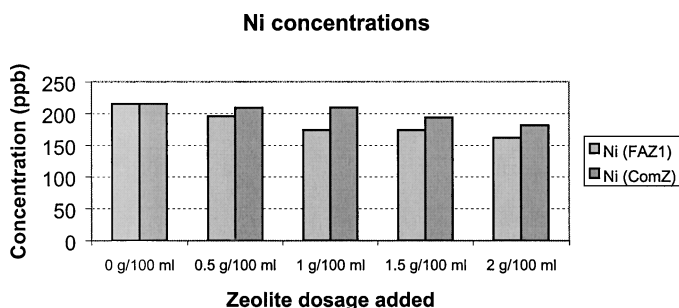


Figure 4: Ni concentrations of AMD after treatment with commercial zeolite (ComZ) and FA zeolite (FAZ1), respectively.

Wastewater Treatment with Synthesized Zeolites

The prepared zeolitic material was reacted with AMD in different doses (g/100 mL) during the investigation of laboratory scale experiments. This was done to observe whether any reduction in the concentrations of selected metal ion species could be observed after zeolite treatment of the wastewater.

In this method, the working hypothesis was that the use of a product containing a high proportion of zeolites (e.g., Faujasite (FAU), Sodalite (SOD), zeolite A), with a fraction of alkaline FA particles, could raise the pH and induce a favorable environment for ion exchange.^[7] In the experiments performed, AMD was treated with a commercial faujasite zeolite (ComZ) and the zeolite sample, FAZ1, prepared from FA material. The metal element removal experiments were carried out with aliquots of 100 mL of each water sample and zeolite powder doses of 0.5, 1, 1.5, and 2 g/100 mL were added to each sample.^[10]

The results obtained after ICP-mass spectroscopic analysis of the wastewater samples are illustrated in Figures 4 to 8. For the Ni concentrations shown in Figure 4, it was observed that the concentrations gradually decreased as

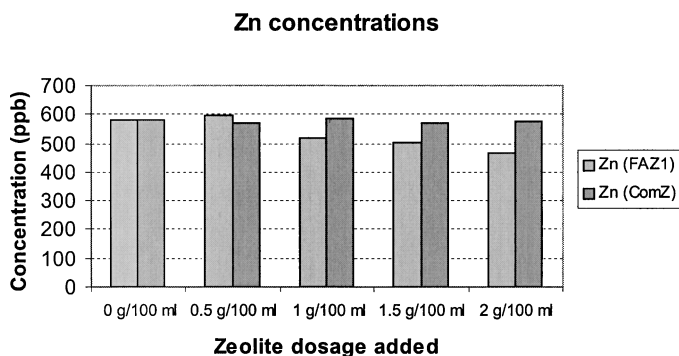


Figure 5: Zn concentrations of AMD after treatment with commercial zeolite (ComZ) and FA zeolite (FAZ1), respectively.

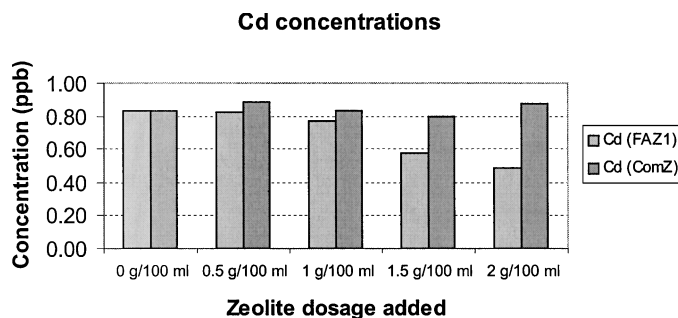


Figure 6: Cd concentrations of AMD after treatment with commercial zeolite (ComZ) and FA zeolite (FAZ1), respectively.

the ComZ zeolite dosage was increased and a lower final concentration was obtained. A relatively bigger decrease in the Ni concentrations with the addition of FAZ1 zeolite to the AMD was obtained than with the use of ComZ.

In Figure 5 the Zn concentrations after treatment of the AMD with zeolitic material are shown. In the treatment of the AMD with the FA zeolite (FAZ1), an initial increase was seen in the concentration after which it gradually decreased to a lower concentration than in the initial AMD, as the zeolite dosage was increased. With the use of the commercial zeolite (ComZ), the results show that the Zn concentrations remains relatively unchanged as the zeolite dosage was increased.

The Cd concentration also showed a decrease in the treatment of the AMD with increase dosage of the FAZ1 zeolitic material, as shown in Figure 6. Contrary to this, a higher final Cd concentration was obtained when the AMD was treated with increased dosage of commercial faujasite (ComZ).

As shown in Figure 7, there was again a decrease in the As concentration with increase in FAZ1 zeolite dosage, although the change was relatively small. A lower As concentration compared with the initial value was achieved for the

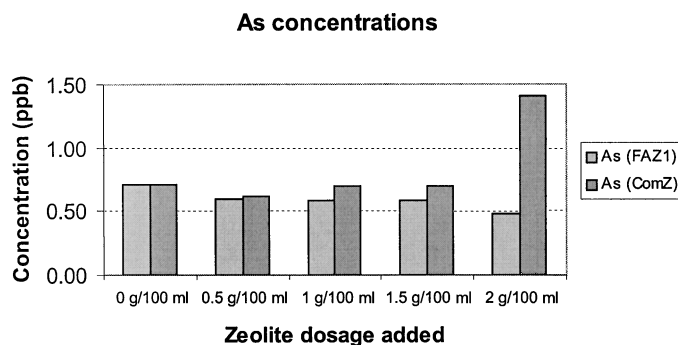


Figure 7: As concentrations of AMD after treatment with commercial zeolite (ComZ) and FA zeolite (FAZ1), respectively.

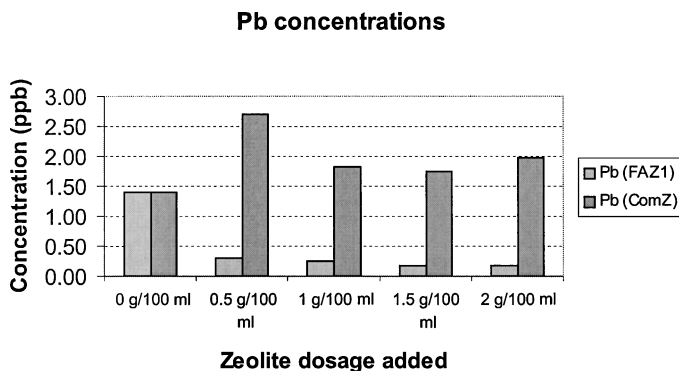


Figure 8: Pb concentrations of AMD after treatment with commercial zeolite (ComZ) and FA zeolite (FAZ1), respectively.

highest zeolite dosage added. Not so promising results were obtained for the commercial zeolite. As the zeolite dosage of ComZ was increased, an increase in As concentration for the AMD was detected.

Figure 8 shows the best results for the use of FAZ1 zeolitic material in terms of metal species removed from the AMD. A much lower Pb concentration than the initial one detected was obtained for the highest FAZ1 zeolite dosage added. For the use of the ComZ, zeolite increases in the Pb concentration occurred with the final Pb concentration at the highest zeolite dosage, being higher than initially detected.

CONCLUSIONS

The results of this study have shown that FA can be codisposed with AMD for the collection of codisposal filtrates at near-neutral pH. The FA and codisposal filtrates provide a rich source of SiO_2 and Al_2O_3 as feedstock for zeolite synthesis, which can be successfully converted into faujasite, sodalite, and zeolite A zeolitic material. These results were substantiated by the x-ray diffraction graphs obtained for the zeolitic material. The type of zeolite formed was dependent on the FA source, because it was also contributing to the physical and chemical characteristics of the resulting zeolites. It was further shown that the synthesized zeolites can be utilized for metal decontamination experiments on AMD. The results obtained for the treatment of AMD with FA zeolite (FAZ1) and commercial zeolite (ComZ) showed that for some metal species (e.g., Ni, Cd, Zn and Pb) the FA zeolite was a better zeolitic material for the removal of the cation species from the AMD compared with the commercial zeolite. Further work is required, however, to gather information on the stability of the synthesized zeolites and the mechanisms of metal ion removal.

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