

The use of X-ray fluorescence (XRF) analysis in predicting the alkaline hydrothermal conversion of fly ash precipitates into zeolites

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Abstract

The use and application of synthetic zeolites for ion exchange, adsorption and catalysis has shown enormous potential in industry. In this study, X-ray fluorescence (XRF) analysis was used to determine Si and Al in fly ash (FA) precipitates. The Si and Al contents of the fly ash precipitates were used as indices for the alkaline hydrothermal conversion of the fly ash compounds into zeolites. Precipitates were collected by using a co-disposal reaction wherein fly ash is reacted with acid mine drainage (AMD). These co-disposal precipitates were then analysed by XRF spectrometry for quantitative determination of SiO₂ and Al₂O₃. The [SiO₂]/[Al₂O₃] ratio obtained in the precipitates range from 1.4 to 2.5. The [SiO₂]/[Al₂O₃] ratio was used to predict whether the fly ash precipitates could successfully be converted to faujasite zeolitic material by the synthetic method of [J. Haz. Mat. B 77 (2000) 123]. If the [SiO₂]/[Al₂O₃] ratio is higher than 1.5 in the fly ash precipitates, it favours the formation of faujasite. The zeolite synthesis included an alkaline hydrothermal conversion of the co-disposal precipitates, followed by aging for 8 h and crystallization at 100 °C. Different factors were investigated during the synthesis of zeolite to ascertain their influence on the end product. The factors included the amount of water in the starting material, composition of fly ash related starting material and the FA:NaOH ratio used for fusing the starting material. The mineralogical and physical analysis of the zeolitic material produced was performed by X-ray diffraction (XRD) and nitrogen Brunauer–Emmett–Teller (N₂ BET) surface analysis. Scanning electron microscopy (SEM) was used to determine the morphology of the zeolites, while inductively coupled mass spectrometry (ICP-MS), Fourier transformed infrared spectrometry (FT-IR) and Cation exchange capacity (CEC) [Report to Water Research Commission, RSA (2003) 15] techniques were used for chemical characterisation. The heavy and trace metal concentrations of the zeolite products were compared to that of the post-synthesis filtrate and of the precipitate materials used as Si and Al feed stock for zeolite formation, in order to determine the trends (increase or decrease) and ultimate fate of any toxic metals incorporated in the co-disposed precipitated residues.

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1. Introduction

The disposal of fly ash (FA) and acid mine drainage (AMD) in South Africa has received much attention lately due to the harmful effects of these pollutants on the environment.

The development of innovative technologies to reduce the harmful effects of these pollutants is constantly being investigated, including ways to promote fly ash utilisation. South African FA contains relatively high concentrations of SiO₂, Al₂O₃ and CaO, with CaO considered as a liming agent to

neutralise AMD [3]. The possibility was explored to employ a co-disposal reaction, firstly to neutralise AMD by co-disposing it with FA, and secondly to collect the precipitates of the reaction for zeolite synthesis.

Zeolites have been obtained by hydrothermal treatment of fly ash [4–6]. Zeolites have important industrial applications such as in catalysis, sorbents for removal of ions and molecules from wastewaters, radioactive wastes and gases, and as replacements for phosphates in detergents [4,7].

XRF analysis of FA or FA-related precipitates is important as the results from this analysis can serve as indices for the alkaline hydrothermal conversion of the fly ash compounds into zeolites. If the [SiO₂]/[Al₂O₃] ratio is higher than 1.5 in the fly ash precipitates, it favours the formation of faujasite zeolitic material by the synthesis method of Rayalu et al. [1].

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Different instrumental methods are available for the analysis of major, minor and trace elements in samples of FA and FA precipitates. Although some techniques can be used for solid materials, in most of the methods the sample needs to be placed in solution, which involves ashing, fusion, decomposition and dissolution [8].

In selecting the method of analysis for a given application it is a compromise between the accuracy required and the time consumed. Since a large number of elements are routinely analysed, a multi-element technique, capable of determining elements in a solid sample is preferable. One such a technique is X-ray fluorescence (XRF) spectrometry. There are two main approaches to the analytical use of XRF spectrometry: wavelength dispersive and energy dispersive XRF spectrometry. The former is in general more sensitive and requires more expensive equipment [8].

The aim of this work was to investigate whether fly ash and acid mine drainage can be co-disposed to form precipitates at a near neutral pH. Secondly to analyse the co-disposal precipitates by XRF spectrometry, to determine its appropriateness for hydrothermal zeolite synthesis. Thirdly to synthesize zeolites from the co-disposal precipitates followed by characterization of the adsorbent material [2,9].

2. Experimental

2.1. FA precipitate samples and sample preparation

The FA precipitates were collected by using a co-disposal reaction wherein fly ash is reacted with acid mine drainage in a specific FA:AMD ratio (e.g. 1:3.5, 1:4, 1:5). The readings for pH and EC of the co-disposal 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 co-disposal precipitates were dried in the oven at a temperature of 70 °C and then transferred into a plastic container.

The co-disposal precipitate samples were milled and ground with an agar mortar and pestle, to ensure that a powder of even particle size was obtained. The sample was further crushed in a Zibb mill to approximately 5 µm grain size [9].

2.2. Bulk elemental analysis using XRF

A Phillips 1404 XRF Wavelength Dispersive Spectrometer equipped with an array of six analyzing crystals and fitted with a Rh X-ray tube target was used. A vacuum was used as the medium of analyses to avoid interaction of X-rays with air particles.

Approximately 1 g of the sample was heated for 5 h at 110 °C. It was again weighed after heating to determine any adhesive water present. Each same sample was then heated for 5 h at 900 °C. It was then weighed to determine

any other volatiles present (e.g. S, C, N compounds) and presented in analysis as loss on ignition (LOI). This figure may be positive in the event of any oxidation, taking place during the time in the furnace at 900 °C. Approximately 0.28 g of the sample is weighed out of the 110 °C H₂O- and LOI-determined sample into a platinum crucible and thoroughly mixed with 1.5 g Norrish Spectroflux no. 105 (a mixture of 47% Li₂B₄O₇, 36.7% Li₂CO₃ and 16.3% La₂O₃ to enhance the fluxing process). It was then heated at 1000 °C for 5 h to start the melting process. Individual samples were then heated over a flame to melt completely and poured onto a carbon disc where they were pressed to produce a flat penny-shaped disc. Care was taken not to leave the sample over the flame for too long as the alkali elements (Na, K) may vaporize over direct heat. The disc was now ready for analyses by XRF [9].

The spectrometer was fitted with a Rh tube, six analysing crystals, namely: LIF200, LIF220, LIF420, PE, TLAP and PX1 and the detectors were a gas-flow proportional counter, scintillation detector or a combination of the two. The gas-flow proportional counter uses P10 gas, which is a mixture of 90% Argon and 10% Methane. Major elements were analysed on a fused glass bead at 50 kV and 50 mA tube-operating conditions. Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured. Standards that were used in the calibration procedures for both major and trace element analyses are as follows: AGV-1 (Andesite), BHVO-1 (Basalt), JG-1 (Granodiorite), JB-1 (Granodiorite), GSP-1 (Granodiorite), SY-2 (Syenite), SY-3 (Syenite), STM-1 (Syenite), NIM-G (Granite), NIM-S (Syenite), NIM-N (Norite), NIM-P (Pyroxenite), NIM-D (Dunite), BCR (Basalt), GA (Granite), GH (Granite), DRN (Diorite) and BR (Basalt) [9].

2.3. Zeolite synthesis

In the zeolite synthesis method the FA precipitates were 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 crystallisation at 100 °C for 24 h. The solid product was recovered by filtration and washed thoroughly with deionised water until the filtrate had a pH of 10–11. The product was then dried at a temperature of 70 °C [1].

The synthesized zeolitic material was then prepared for mineralogical, chemical and physical characterisation [9].

2.4. X-ray diffraction (XRD) analysis

The zeolite sample mineralogy was evaluated by conducting XRD spectrometry (Philips Analytical graphite monochromator and Cu K α radiation samples were scanned for 2 θ ranging from 7 to 70°). The data files presented by X'Pert Graphics & Identify data collection software

were used to identify the minerals present in the samples [9].

2.5. Scanning electron microscopy (SEM)

A Hitachi X-650 Scanning Electron Microanalyzer was used to take the micrographs of the samples. Samples were mounted on aluminium stubs using conductive glue and were then coated with a thin layer of carbon [9].

2.6. ICP-MS analysis

The presence of trace elements in the post-synthesis filtrate and acid digested zeolite samples was determined by inductively coupled mass spectrometry (ICP-MS) using a Perkin-Elmer Elan ICP-MS unit [9].

2.7. Fourier transformed infrared (FT-IR) spectrometry

Approximately 15 mg of the zeolite sample, plus 1 g of KBr was weighed out, milled and ground in an agate mortar and pestle for 5 min, until a fine smooth powder of even particle size was obtained. A quarter (~ 0.25 g) of the zeolite and KBr mixture was then pressed with a steel die at 10 t cm^{-2} into a pellet (or wafer). IR spectra of the zeolite samples were recorded on a Perkin-Elmer, Paragon 1000 PC, FT-IR Spectrometer, in the range between 4000 and 400 cm^{-1} [9].

2.8. Cation exchange capacity (CEC)

Approximately 5.0 g of the zeolite sample was weighed out and placed in a 100 ml polyethylene bottle. A 25 ml ammonium acetate solution was added and the mixture, kept at 25°C in a water bath, was shaken for 1 h. The supernatant was filtered directly into a 100 ml volumetric flask through filter paper, and care was taken not to pour any sample into the filter funnel. The extract was then made up to 100 ml with deionised water and the concentration of exchangeable cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) determined by ICP-MS analysis [9].

2.9. N_2 -BET surface area determination

The specific surface area of the zeolite samples was determined by using a Micromeritics, ASAP 2010, Micropore Analyser. Nitrogen adsorption isotherms were obtained at liquid nitrogen temperature. Prior to the determination of the adsorption isotherm, the sample was outgassed [9].

3. Results and discussion

3.1. Preparation of FA and AMD co-disposal precipitates

The co-disposal precipitates were collected at a near neutral pH by using a FA:AMD ratio of 1:3.5–1.5. The reactants

used were either Arnot or Matla FA co-disposed with one of Navigation or Brugspruit AMD [9].

3.2. XRF analysis of co-disposal precipitates

The co-disposal precipitates were analysed by XRF spectrometry for quantitative determination of SiO_2 and Al_2O_3 . From this data the $[\text{SiO}_2]/[\text{Al}_2\text{O}_3]$ ratio was determined.

The XRF results for the co-disposal precipitates are given in Table 1 [2,9].

Samples PptE3, PptE4 and PptE8 represent the co-disposal precipitates of the reaction between Arnot FA and Navigation AMD. Sample PptM1 was formed when Matla FA was reacted with Navigation AMD. From the results in Table 1 it can be seen that the $[\text{SiO}_2]/[\text{Al}_2\text{O}_3]$ ratio range from 1.4 to 2.5. Thus samples PptE3, PptE4 and PptM1 can be converted to faujasite, while sample PptE8 may produce a zeolite product, although not specifically faujasite [2,9].

3.3. Results of zeolite synthesis

Different factors were investigated during the hydrothermal zeolite synthesis steps. These factors included the amount of water in the starting material, composition of fly ash related starting material and the FA:NaOH ratio used for fusing the starting material. In the following paragraphs the results obtained from the XRD analysis of the different starting materials are discussed.

With the addition of different amounts of water to 1 g of the co-disposal precipitates, different or no zeolite products were synthesized. With the addition of 6 ml of deionised

Table 1
XRF results of co-disposal precipitates

Sample	SiO_2	TiO_2	Al_2O_3	Cr_2O_3
PptE3	57.03	1.30	23.52	0.02
PptE4	57.38	1.29	23.25	0.03
PptF8	35.37	1.37	25.35	0.03
PptM1	47.42	1.49	26.87	0.02
Sample	$\text{Fe}_2\text{O}_3\text{T}$	MnO	NiO	MgO
PptE3	5.70	0.16	0.02	2.61
PptE4	6.16	0.12	0.02	2.37
PptF8	6.04	0.07	0.02	2.45
PptM1	4.85	0.06	0.01	2.32
Sample	CaO	Na_2O	K_2O	P_2O_5
PptE3	6.22	0.00	0.59	0.24
PptE4	6.18	0.00	0.57	0.24
PptF8	7.22	0.00	0.58	0.36
PptM1	9.47	0.27	0.71	0.96
Sample	H_2O^-	LOI	Total	$\text{SiO}_2/\text{Al}_2\text{O}_3$
PptE3	0.49	1.99	99.90	2.42
PptE4	0.64	2.02	100.30	2.47
PptF8	2.30	12.29	99.05	1.40
PptM1	0.98	2.32	97.75	1.76

All concentrations in weight (%).

water to 1 g of co-disposal sample material PptE3, PptE4, PptE8 and PptM1, the following results were obtained. Samples PptE3 and PptE4 produced faujasite and sodalite as zeolite phases. No zeolite phase was present in the starting material from samples PptE8 and PptM1. The results therefore indicate that the co-disposal samples with a $[\text{SiO}_2]/[\text{Al}_2\text{O}_3]$ ratio higher than 2, were successful in delivering faujasite as zeolitic material.

The use of different fly ash related starting materials were also investigated to assess the influence of fly ash quality on the zeolite phases produced. The starting material included fresh fly ash, water-leached fly ash and HCl leached fly ash. The FA produced faujasite as zeolite phase, the water-leached FA produced zeolite A and the HCl leached FA produced sodalite or sodalite/faujasite mixtures as zeolite phases.

The third variable investigated was the use of different FA:NaOH ratios during fusion of the starting material. In the synthesis steps outlined by Rayalu et al. [1], a FA:NaOH of 1:1.2 was used. This ratio was changed to 1:1.1 and 1:1.5 to investigate the effect it had on the zeolite phase produced.

In using the co-disposal material PptM1, with different FA:NaOH ratios, the following results were obtained. The ratio of 1:1.1 produced faujasite and sodalite as products, while the ratio of 1:1.5 produced only faujasite as zeolite product, compared to no zeolite product for a ratio of 1:1.2.

A change in the FA:NaOH ratios of the water-leached FA had the following effect on the zeolite product formed. For both the ratios of 1:1.1 and 1:1.5 sodalite was produced as zeolitic material, compared to no zeolite product for a ratio of 1:1.2.

For the acid (HCl) leached FA, a FA:NaOH ratio of 1:1.1 produced no zeolite phase, with the ratios of 1:1.5 and 1:1.2 producing the same zeolite phases of faujasite and sodalite [2,9].

3.4. SEM studies of synthesized zeolitic material

Scanning electron microscopy was used to determine the size distribution and morphology of the zeolite crystals.

Fig. 1 shows the crystals of the faujasite phase obtained when the fly ash, HCl acid leached FA and co-disposal precipitates are subjected to alkaline hydrothermal conversion

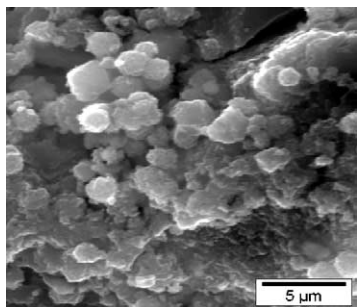


Fig. 1. SEM photomicrograph of faujasite.

into zeolites. The photomicrograph clearly shows the transformation of FA into a zeolite phase, as the morphology of single crystals look well defined [2,9].

3.5. Surface area determination of zeolitic material

The BET surface area and the pore volume of the synthesized zeolitic materials were determined for a range of starting material used.

The values of the surface areas for the zeolitic material prepared from the co-disposal precipitates range from 91 to $245 \text{ m}^2 \text{ g}^{-1}$. The highest value of $245 \text{ m}^2 \text{ g}^{-1}$ for the surface area was obtained for sample PptE4, which contains faujasite and sodalite as zeolitic material.

The pore volume for all the co-disposal precipitates was approximately the same and has an average value of $0.25 \text{ cm}^3 \text{ g}^{-1}$.

A very high surface area of $515 \text{ m}^2 \text{ g}^{-1}$ was obtained for the FA sample used as starting material in the zeolite synthesis. This sample contains faujasite as zeolitic material and also has the highest pore volume of $0.45 \text{ cm}^3 \text{ g}^{-1}$.

The results of the surface area for the water and HCl acid leached fly ash used in the zeolite synthesis range from 71 to $188 \text{ m}^2 \text{ g}^{-1}$. The values for the pore volume range from 0.16 to $0.33 \text{ cm}^3 \text{ g}^{-1}$ [2,9].

3.6. Cation exchange capacity (CEC) of zeolitic material

The CEC was determined for zeolitic material synthesized from the co-disposal precipitates, FA, and HCl acid leached samples. The results are shown in Table 2.

In Table 2 sample PptLFA represents the HCl acid leached FA, sample PptFA is the FA itself and sample PptE3 represents the co-disposal precipitate material. All three samples contained a mixture of faujasite and sodalite as zeolite phases.

The amount of exchangeable Ca^{2+} cations is far less for sample PptE3, compared to the other two samples, and the highest for sample PptLFA. Sample PptE3 has the lowest amount of exchangeable Mg^{2+} cations, with sample PptFA having the most, although the amount of Mg^{2+} cations that are exchanged for each of the three samples is not very high. For sample PptFA the amount of exchangeable K^+ is the lowest, while the highest value is obtained for the sample PptE3.

The amount of exchangeable Na^+ cations is higher for all the samples, when compared to the amount of exchangeable Ca^{2+} , Mg^{2+} and K^+ .

Table 2
CEC results of zeolitic material

Sample name	Exchangeable cations ($\mu\text{eq. per } 100 \text{ g}$)			
	Ca^{2+}	Mg^{2+}	Na^+	K^+
PptLFA	568.8	14.8	5931.6	115.9
PptFA	427.3	17.9	7208.3	98.5
PptE3	196.8	11.9	5878.5	123.6

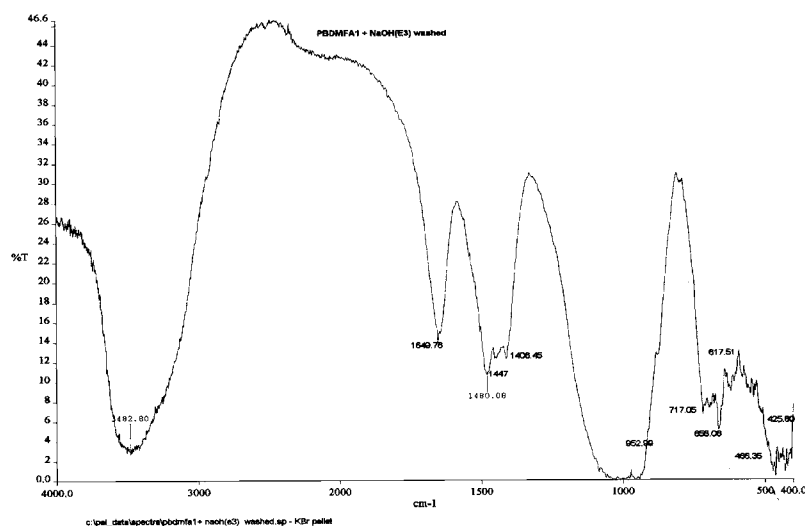


Fig. 2. FT-IR spectrum of co-disposal zeolitic material.

It also indicates that more Na^+ sites are available for cation exchange in the zeolite material, compared to the other cations. For samples PptLFA and PptE3 the amount of exchangeable Na^+ cations is approximately the same, while the highest amount of exchangeable Na^+ cations is recorded for sample PptFA.

These results therefore indicate, as with other zeolite materials, that mainly Na^+ is available for cation exchange with other more toxic ion and metal species [2,9].

3.7. FT-IR spectrometry results

In the FT-IR spectrum, the OH bands are observed as a single strong broad band occurring at approximately $3480\text{--}3500\text{ cm}^{-1}$. These results can be seen in Fig. 2, representing the FT-IR spectrum of sample PptE3.

These strong broad bands can thus be attributed to the presence of hydroxyls in the faujasite supercage and the hydroxyls in the sodalite cage. The faujasite supercage consists of sodalite cages as its building blocks and therefore its presence will be shown in the FT-IR spectrum [9–11].

The FT-IR spectrum also shows strong medium bands at 1646 and 1649 cm^{-1} respectively. These bands can be attributed to the H_2O deformation mode normally seen at 1650 cm^{-1} . The presence of the H_2O mode shows that complete dehydration has not been achieved for the zeolite samples [9,12].

3.8. Composition of post-synthesis zeolite filtrates

An ICP-MS study of the zeolite filtrates collected after zeolite synthesis was done, in order to gain a better understanding of the trace and heavy metal species contained in the filtrates, and also to determine which element species stays trapped in the zeolite sample and which are released.

In Table 3 the results of the ICP-MS analysis of the post-synthesis filtrates of samples PptE3 and PptLFA are shown. Sample PptE3 represents the zeolitic material prepared from the co-disposal precipitates, while sample PptLFA was prepared from the HCl leached FA.

Table 3
ICP-MS results of post-synthesis filtrates

Sample	Li	B	Na	Mg	Al
PptE3	1.87	35	174875	165	441
PptLFA	1.34	53.6	179239	15.5	326
Sample	Si	K	Ca	V	Cr
PptE3	30019	2770	775	31.1	34.6
PptLFA	21855	2103	426	46	58.4
Sample	Mn	Fe	Ni	Cu	Zn
PptE3	15.2	326	0.021	3.69	26.1
PptLFA	4.57	37.3	0.75	4.06	5.81
Sample	As	Se	Rb	Sr	Mo
PptE3	3.73	0.23	6.01	8.01	0.92
PptLFA	7.49	0.87	7.63	3.85	1.86
Sample	Cd	Sb	Cs	Ba	La
PptE3	0.19	0.14	0.25	5.16	1.01
PptLFA	0.093	0.21	0.47	1.25	0.075
Sample	Ce	Pr	Nd	Sm	Eu
PptE3	1.42	0.24	1.33	0.18	0.04
PptLFA	0.13	0.014	0.51	n.d.	n.d.
Sample	Gd	Tb	Dy	Ho	Er
PptE3	0.23	0.033	0.2	0.04	0.12
PptLFA	0.024	n.d.	0.011	n.d.	n.d.
Sample	Tm	Yb	Lu	Hg	Pb
PptE3	0.015	0.096	0.016	1.09	5.87
PptLFA	n.d.	n.d.	n.d.	0.32	3.59

n.d.: not detected.

The results in Table 3 show that the Al, Si and Na concentrations of the samples are relatively high. This can be expected for the Al and Si concentrations originating from the FA, as it provided the Al and Si building blocks for the zeolitic material. The concentration of Na is high due to the fusion step with NaOH during synthesis.

The concentrations of elements such as Hg, Pb, Cu, Ni, Cd and Se are relatively low, while higher concentrations for B and As are observed. However, these concentrations should not prove difficult to reduce with standard water treatment technologies [2,9].

In order to determine the fate of the heavy metals that may have been encapsulated in the zeolitic materials during synthesis, a study of the heavy metal content of the synthesized zeolites, by acid digestion of the solid zeolite materials was also performed.

The ICP-MS results for the metal content of the acid digested zeolites compared to the post-synthesis filtrates, shows that the concentrations of metal species Al, Fe, Ni, Cu, Zn, Ba and Hg are lower in the post-synthesis filtrates. On the other hand the concentrations of metal species Na, As, Cr and Pb are higher in the post-synthesis filtrates than in the zeolitic material, while mixed levels of concentrations were observed for metal species Se, Cd, Mn, K and Ca [2,9].

4. Conclusions

A co-disposal reaction between fly ash and acid mine drainage can be used to form precipitates at a near neutral pH, providing a source of Al and Si for zeolite synthesis.

Analysis of the co-disposal precipitates by XRF spectrometry for quantitative determination of SiO_2 and Al_2O_3 , provides an effective technique to determine its appropriateness for hydrothermal zeolite synthesis. A $[\text{SiO}_2]/[\text{Al}_2\text{O}_3]$ ratio higher than 2 for the co-disposal precipitates proves

to be successful in converting the precipitates into faujasite zeolitic material.

The results also show that a fusion method can convert South African fly ashes into faujasite, sodalite and zeolite A.

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