REMOVAL OF TOXIC ELEMENTS FROM BRINE USING ZEOLITE NA-P1 MADE FROM A SOUTH AFRICAN COAL FLY ASH

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ABSTRACT

Presently, there are several strategies for the utilisation of fly ash available but most of them are leading to low volume of fly ash usage in South Africa. The cost implications, especially those associated with transportation, make it logistically difficult for fly ash to compete with other traditional raw materials in various applications. Synthesis of zeolites from coal fly ash with specific focus such as applications in water treatment could act as a more value-added high technology utilisation of fly ash to overcome this barrier. Previous studies have shown that the quality of zeolites synthesized is a major determinant in the efficiency of toxic element removal from waste water. It is therefore necessary to optimize the zeolite synthesis process to obtain high purity zeolites with high surface area and cation exchange capacity.

The present study optimized synthesis conditions used to prepare zeolite Na-P1 from South African fly ash for the purpose of removing trace elements from brine. The variables that were evaluated during the optimization process of zeolitsation were; hydrothermal treatment time (12 - 48 hours), temperature (100 – 160°C) and addition of varying molar quantities of water during the hydrothermal treatment step ($H_2O:SiO_2$ molar ratio ranged between 0 - 0.49). The most pure phase was achieved when $NaOH/Si_2O$ molar ratio was 0.59 at an aging temperature of 47 °C for 48 hours and a hydrothermal treatment temperature of 140 °C for 48 hours. The molar ratio of chemical composition of the optimum synthesis matrix was 1 SiO_2 : 0.36 Al_2O_3 : 0.59 NaOH : 0.49 H_2O. The cation exchange capacity of the product was 4.11 meq/g.The optimized process of zeolite Na-P1 was efficient in removing a large percentage of B, V, As, Mn, Ni, Pb, Fe, Zn, Mo, Sr, Ba, Mg, Cd and Se from a brine concentrate resulting from water treatment via reverse osmosis.

Key words: Coal fly ash, zeolite Na-P1, brine, toxic element removal, hydrothermal treatment.

1. INTRODUCTION

Millions of tonnes of fly ash are generated worldwide every year to satisfy the large demand for energy. Some of the adopted strategies for the utilisation of fly ash are published elsewhere (Molina and Poole 2004; Yaping *et al.*, 2008; Holler and Wirsching, 1985; Shigemoto *et al.,* 1993; Querol *et al.,* 1997, Hollman *et al.,* 1999, Woolard *et al.,* 2000; Querol *et al.*, 2001; Somerset *et al.,* 2004; Petrik *et al.,* 2005; Gitari, 2006). Most of these approaches are either geared to utilize the ash beneficially in order to reduce the cost of disposal, or to minimize their environmental impact.

Utilization of fly ash as feedstock in zeolites synthesis is of major interest due to their many industrial applications such as; in catalysis, as sorbents for the removal of heavy metal ions and organic contaminants from waste waters, the encapsulation of radioactive wastes, gas separation, and as replacements for phosphates in detergents (Somerset *et al.,* 2004). By applying different synthesis methods, many researchers have synthesized various types of zeolites from fly ash (Querol et al., 2002) but few studies have been successful in conversion of fly ash into pure phase zeolites (Walek *et al*., 2008). Studies by Querol *et al* (2001) investigated synthesis of zeolites from fly ash at pilot scale using various Spanish fly ashes. They concluded that the optimization of the synthesis yields have to be determined for each type of fly ash due to differences in the mineralogical and chemical compositions. These findings also contributed to the motivation for this study since the same case can be applied to class F South African fly ashes, which differ considerably in composition from European class C fly ash and have not previously been used as feedstocks to make pure phase zeolites.

Moreover, the presence of heavy metals in the environment even in moderate concentrations is responsible for illnesses related to respiratory or dermal damage and even several kinds of cancers (Barceloux, 1999). It is therefore important to remove toxic metal contaminants from waste water prior to discharge as they are considered persistent and bio-accumulative. Use of zeolites synthesized from fly ash for applications in the removal of metal species from waste waters has been a subject of study for quite some time and various investigations have been made to find the appropriate, efficient and economical zeolite type (Lee *et al*., 2003).

Zeolite Na-P1 can be synthesized under mild hydrothermal synthesis conditions without using templates (Inada *et al.,* 2005; Hollman et al., 1999) which makes it potentially economically viable. It has also been reported that zeolite Na-P1 can be used to remove toxic elements from acid mine drainage (Petrik et al., 2007) and brine (Natalia *et al*., 2001; Sonqishe, 2008). Applications of zeolite Na-P1 in waste water treatment is due to its unique ion-exchange and water sorption properties which are brought about by the high porosity, surface area, cation exchange capacity and the unusual framework flexibility (Zholobenko *et al.,* 1998). Successful transformation of South African fly ash into impure zeolite Na-P1 (containing unconverted fly ash phases such as mullite, hematite and quartz) using the mild temperature method (100 ºC) was achieved by Petrik *et al*., (2007). Since the quality of zeolites synthesized from fly ash is a major determinant in the efficiency of toxic element removal from waste water (Hendricks, 2005), synthesis conditions for specific pure phase zeolite Na-P1 were investigated for achieving high removal of major and trace elements from high saline process brine solutions.

2. EXPERIMENTAL

Material Handling and Storage

Pulverized coal fly ash from a South African power station was used as a Si and Al feedstock. The raw fly ash samples were stored in sealed plastic container with an airtight lid. Containers were kept in dark cool rooms away from sources of moisture, out of direct sunlight and away from fluctuating temperatures. The brine samples were collected from stage three treatment section of a water reclamation plant situated in the Witbank coalfields of South Africa's Mpumalanga province. These samples were transported on ice and refrigerated at 4 ^{o}C as soon as they reached the destination. This was done to preserve their integrity (Klink, 2003). The refrigerated samples were unfiltered and not acidified in order to determine pH and EC before use. Before the use of the samples, they were filtered using 0.45µm membrane and pH and EC was determined, after which they were acidified with 1 ml concentrated HNO_3 for trace element analysis.

Synthesis Procedure

A two step process for the synthesis of zeolites from fly ash adopted from Hollman *et al.* (1999) was customised whereby a mixture of fly ash and alkaline solution was subjected to (1) the ageing step and (2) the hydrothermal treatment step. During the ageing, 20g of fly ash and 20g of sodium hydroxide pellets (Kimix cc, ≥ 97 wt %) were mixed together using 100 ml of ultra pure water in a 250 ml plastic sealable bottle. A magnetic bar was added to the mixture; the bottle was sealed and then placed on a magnetic stirrer. The speed of rotation was 800 rpm. A temperature probe was inserted through the lid to enable accurate digital control of the temperature. The ageing temperature and time was kept constant at 47 ^{o}C for 48 hours since previous studies had shown that these conditions were optimum for dissolution of quartz and other silicon and aluminium containg phases from fly ash (Petrik *et al*., 2007; Sonqishe, 2008).

After ageing, varying amounts of ultra pure water (expressed as H_2O:SiO_2 molar ratio of 0.20, 0.26. 0.39 and 0.49) were added to separate aliquots of the slurry while stirring and the resulting homogenous solution was transferred in aliquots of 10 ml into 23 ml Teflon lining of the Parr bombs. The hydrothermal synthesis was conducted by placing the filled and sealed Parr vessels in to a thermostated Memmert hot air oven. The crystallization temperature was controlled in the range of 100 – 160 ^{o}C at intervals of 20 ^{o}C while the hydrothermal treatment time was varied simultaneouldy from 12 to 48 hours at interval of 12 hours. After hydrothermal treatment, Parr bombs were removed from the oven and allowed to cool down to room temperature. The liquid phase was separated from the solid product; pH was measured and the supernatant solution was kept for compositional analysis while the solid product was thoroughly washed with ultra pure water until a filtrate of pH of 9 -10 was obtained. The solid product was dried overnight at 90 ^{o}C and then transferred into airtight plastic containers prior to characterization. Experiments were undertaken in duplicate.

Characterization Techniques

X-ray fluorescence spectroscopy (XRF) analyses were done on a Philips PW 1480 X-ray spectrometer. The samples were prepared by mixing 9g of fly ash or zeolitic material with 2 g of a binder (which was made up of 10 % C-wax binder and 90 % EMU powder). The mixture was then thoroughly shaken, poured into the mould and pelletized at a pressure of 15 tons for about 1 minute using a Dickie and Stockler manual pelletizer. Major elements were analysed at 40 kV and 50 mA tube operating conditions while trace elements analyses were on a powder briquette at 50 kV and 40 mA tube operating conditions. Loss on ignition (LOI) was measured by placing the samples in the furnace at 1000 degrees for at least 45 minutes.

The concentrations of ionic species in the aqueous solutions were measured by the use of inductively coupled plasma atomic emission (ICP-AES) and mass spectrometry technique (ICP-MS). Analysis of major elements was by an Varian Radial ICP-AES, while traces were done on an Agilent 7500ce ICP-MS, using a High Matrix Introduction (HMI) accessory and He as collision gas.

The qualitative mineralogy of fly ash and the synthesized zeolite products were determined by the use of a Phillips diffractometer with Cu-Kα radiation (1.5406 Å). The accelerating voltage and current used was 40 kV and 20 mA, respectively. After being ground to a fine powder, the samples were placed in the sample holder and were step scanned from 4^o to 60^o 2θ at 0.5^o 2θ steps and integrated at a rate of 0.1 s per step. The phase identification was performed by a search program using the data base of JCPDS (Joint committee of powder diffraction standards) for inorganic compounds. To quantify the mineral phases, 20 % Si (Aldrich 99 % pure) was added to each sample to aid in the determination of the amorphous content. The samples were then milled in a McCrone micronizing mill, and were prepared for XRD analysis using a back loading preparation method. The quantitative XRDanalysis was done using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-Kα radiation. The mineral phases were identified using X'Pert Highscore plus software while the relative phase amounts (weight %) was estimated using the Rietveld method (Autoquan Program).

The Cation Exchange Capacity (CEC) was determined following a procedure adopted by Amrhein *et al* (1996). 0.5 g of untreated fly ash was first saturated using three repeated rinsing steps with 25 ml of 1.0 M sodium acetate (pH 8.2) and this was later followed by four washings with 25 ml ultra pure water. The extracting of the cations was done with three aliquots of 25 ml of 1.0 M ammonium acetate (pH 8.2). As for the synthesized zeolite samples, 0.5 g of the washed samples were extracted with four 25 ml aliquots of 1.0 M ammonium acetate (pH 8.2). The zeolites were continuously shaken with the extracting solution for 15 min, centrifuged for 15 min, and then decanted. This was repeated in total of four times and the cumulative extract was brought to 100 ml. The concentrations of exchangeable cations (Na^+, Mg^{2+}, Ca^{2+} and K^+) in the final solution were determined by the use of an Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES).

The morphology of the fly ash and zeolites prepared in this investigation was examined using a Hitachi X-650 scanning electron microscope and microanalyser equipped with a CDU - lead detector at 25kV. Samples were mounted on aluminum stubs and coated with a thin film of gold to make them conductive.

Brine Treatment Experiments

The removal of toxic elements from the brine by the use of the zeolite Na-P1 synthesized from the fly ash was studied on a batch wise mode. Experiments were conducted in 50 ml glass flask using 0.5 g of the adsorbent in contact with 10 ml of brine solution at 26 ± 1 °C. The glass flasks were shaken in a mechanical shaker for one hour and the solutions were transferred to 50 ml centrifuge tubes where they were centrifuged for 15 minutes and later the solutions were filtered. After the initial treatment, the solid zeolitic products were reused twice following the same procedure. The major and trace elements were analysed by use of inductively coupled plasma atomic emission (ICP-AES) and mass spectrometry technique (ICP-MS).

3. RESULTS AND DISCUSSION

Chemical Composition of Fly Ash and Zeolitic Samples

The results of the elemental compositions of the fly ash and zeolitic material analysed using X-ray fluorescence spectroscopy (XRF) are presented in Table 1.

Table 1. XRF of fly ash and zeolitic samples.

Major oxides mean mass (%)	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	TiO_2	SO_3	LOI
Fly ash	50.91	30.91	3.46	0.02	1.48	6.2	0.10	0.60	0.56	1.65	0.24	3.85
Zeolite Na-P1	36.69	25.17	2.28	0.06	2.21	6.07	6.53	0.13	0.04	1.58	0.06	11.92

The average SiO_2/Al_2O_3 ratio of fly ash was found to be 1.65. This ratio is of importance since it governs both the Si/Al ratio of the zeolite product and also the incorporation of Al in the framework structure (Nagy *et al.,* 1998). The major elemental chemistry of the fly ash is found to be consistent with the typical composition of fly ashes from the combustion of bituminous coal from South Africa (Gitari *et al.*, 2005) whereby the total SiO_2, Al_2O_3 and Fe_2O_3 is ≥ 70%. The Loss-On-Ignition (LOI) was 3.85 mass % in the fly ash and this measured mainly the unburned carbon remaining in the fly ash which is an important chemical parameter.

The SiO_2/Al_2O_3 ratio for synthesized zeolitic products was found to be 1.45. The less amount of Si and Al in the zeolite compared to fly ash signalled that there was wastage of the feedstock. Na_2O in the zeolitic sample was higher than in the starting fly ash and this was because of the incorporation of Na as a charge balancing cation since NaOH was used as the alkaline solution. CaO in the zeolitic sample was almost similar to the content identified in the fly ash since Ca can also act as a charge balancing cation. The presence of elements, such as Fe, Mn, Mg, Ca, Ti, and K in the synthesized zeolite may be due to the dissolution of these elements from the fly ash under alkaline conditions, and may then be incorporated into framework structure of zeolites during hydrothermal treatment. Due to experimental constraints, trace elements were not analysed.

Morphological Transformation During the Synthesis Process

Figure 1 shows the scanning electron microscope (SEM) images of the fly ash matrix and the synthesized zeolite. The SEM image of the surface of the fly ash particles was observed to be smooth and spherical because the glassy phase covers the particle (Inada *et al.*, 2005). After the hydrothermal treatment, granular crystalline products could be observed and from the XRD analysis, it was identified to be zeolite Na-P1.

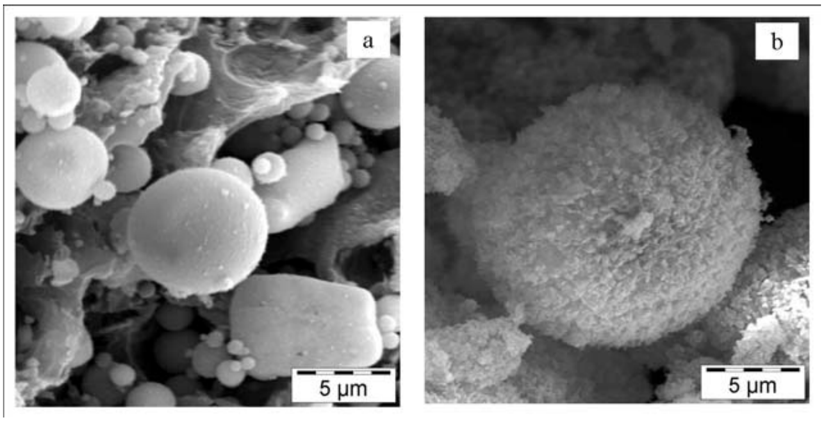

Figure 1. SEM images of a) fly ash and b) zeolitic sample synthesized from fly ash.

Mineral Composition of Fly Ash

The qualitative and quantitative X-ray Diffraction patterns of the fly ash are presented in Figure 2.

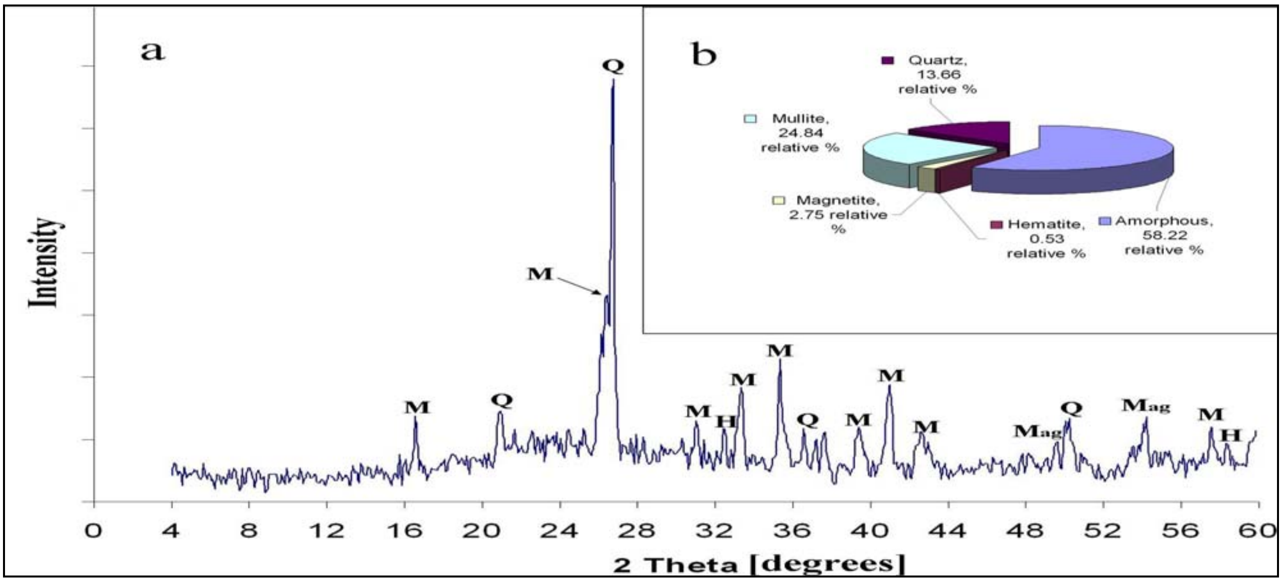

Figure 2. XRD of fly ash; a) Qualitative analysis b) Quantitative analysis
(Q = Quartz, M = Mullite, H = Hematite, Mag = Magnetite).

It was found that the predominant mineral phases in the fly ash were quartz (SiO_2) with major peak at 26.9 degrees 2θ, and less intense peaks also identified, mullite ($3Al_2O_3.SiO_2$), major peaks at around 26.4 degrees 2θ (as a shoulder on the quartz peak), magnetite, and hematite. The presence of amorphous phases are identified as a broad diffraction ‘hump’ in the region between 18 to 32 degrees 2θ (Inada *et al.*, 2005; Murayama *et al.*, 2002; Hui and Chao, 2006). The quantification results presented in Figure 2 (b) shows that the quantity of the phases identified were; Amorphous glassy phase (58.22 %) > Mullite (24.84 %) > Quartz (13.66 %) > Magnetite (2.75 %) > Hematite (0.53 %).

4. ZEOLITE SYNTHESIS

Effect of Variation of Hydrothermal Treatment Temperature and Time

The results of XRD patterns of products obtained at the hydrothermal synthesis temperature of 140 ^{o}C are presented in Figure 3.

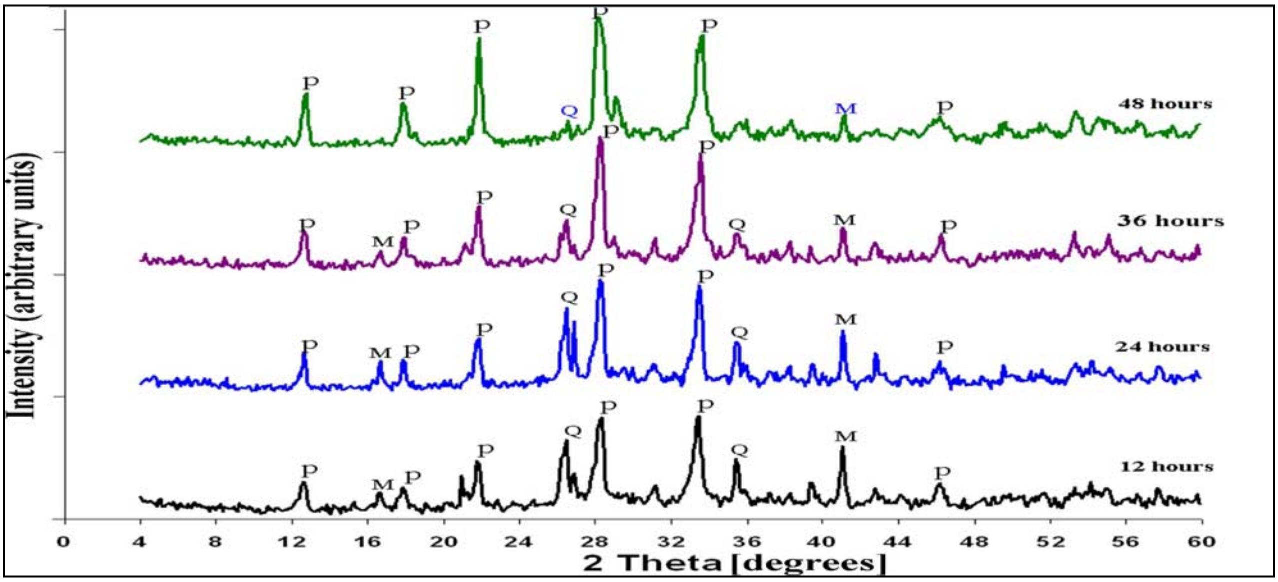

Figure 3. XRD patterns of products synthesized at 140 °C with variation of time; molar ratio of synthesis matrix was 1 SiO_2 : 0.36 Al_2O_3 : 0.59 NaOH : 0.39 H_2O. (P = Zeolite Na-P1, Q = Quartz, M = Mullite).

Variation of hydrothermal treatment temperatures from 100 °C to 120 °C (results not shown here), showed an appreciable presence of quartz, mullite and hematite that were only partially dissolved under these experimental conditions. As shown in Figure 3, when synthesis was carried out at 140 °C, there was almost a total utilisation of quartz and mullite phases meaning that they were progressively available as Si and Al feedstock for the zeolitisation process. Hematite peaks were not identified in the product meaning that it had been completely digested during the dissolution process. Zeolite Na-P1 in nearly pure phase was formed when hydrothermal treatment was prolonged from 12 to 48 hours. This can be observed from the progressive increase in the intensity of zeolite Na-P1 peaks, whilst peaks of other crystalline phases were minimized over the time of the experiment. When synthesis was done at 160 °C (not shown here), it was found that quartz and mullite were completely digested but an undesirable new phase (hydroxysodalite) was formed. Synthesis at 140 °C for 48 hours was thus found to be the best condition for the hydrothermal treatment process and was used for further investigations**.**

Effect of Variation of the Quantity of Water During Hydrothermal Treatment Process

Casci (2005) reported that the water content during zeolite synthesis impacts the purity and type of zeolitic material produced either directly through change of viscosity during mixing/agitation which in effect interfere with achievement of homogeneity of the synthesis slurry or indirectly by changing the compositional field that favours the formation of other zeolite types. The XRD of products obtained whilst varying the additional amount of water used during hydrothermal synthesis (at 140 °C and 48 hours) are presented in Figure 4. This additional water was added after aging since a constant volume of 100 ml had been used during the ageing process.

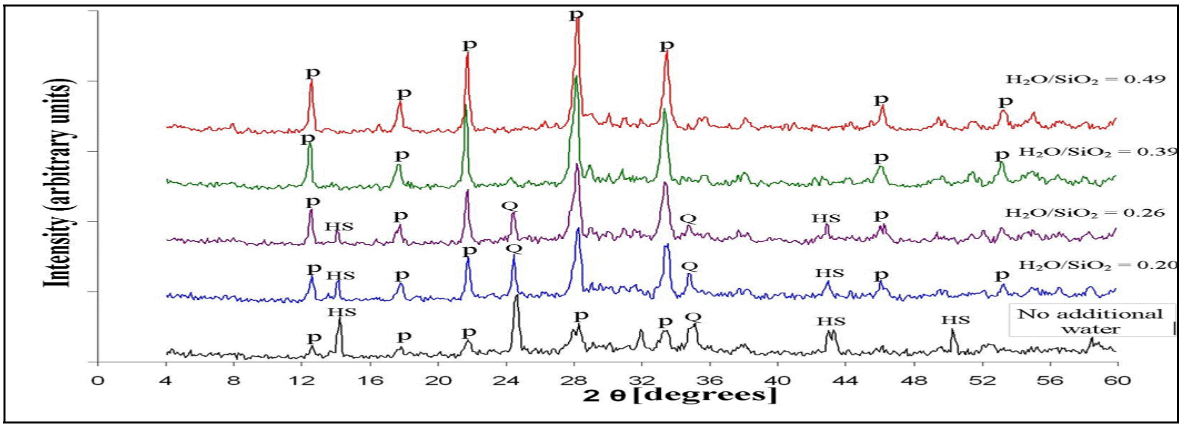

Figure 4. XRD patterns of products synthesized at 140 °C for 48 hours with variation of water content during the hydrothermal synthesis (P = Zeolite Na-P1, HS = Hydroxy-sodalite, Q = Quartz).

It was interesting to observe that addition water after ageing enabled the formation of a relatively pure phase zeolite Na-P1. This can be explained by the fact that during the ageing process, dissolution of fly ash takes place and this leads to saturation of ionic species in the solution which hinders further dissolution but on addition of more water it creates the conditions necessary for further dissolution of the fly ash matrix. Even though the highest quantity of water during the hydrothermal treatment step showed an improvement of the quality of zeolites, it is important to highlight that very high quantities of water can restrict production rates. Too much water can change the degree of supersaturation which will slow the crystallization kinetics. In addition, the use of excessive amount of water can also increase the cost of zeolite synthesis since there is a large amount of dilute supernatant that will require treatment before disposal. The CEC of fly ash was found to be 0.48 meq/g while that of zeolites synthesized at 100 ^{o}C and 140 ^{o}C for 48 hours was found to be 2.98 and 4.11 meq/g respectively. This trend correlated well with the XRD results. Comparing the CEC values obtained in this study with those obtained by other researchers, (Inada et al., 2005 = 3.0 and Querol et al., 2007 = 3.1), it can be seen that the value obtained in this study (4.11meg/g) was higher and this gives an indication that the zeolite Na-P1 is expected to show high ion exchange property. The value obtained was also close to the theoretical value of commercial zeolite Na-P1 (5 meq/g).

Brine Composition

The initial elemental composition of brine prior to the contact with adsorbent (zeolite Na-P1) is provided in Table 2 and 3.

	Ba	Ni	Al	Se	Zn	As	Fe	Pb	Mn	Co	Cr	V	Mo	Cu	Cd
Conc. (ppb)	300.83	67.85	48.38	45.90	35.46	25.77	22.81	20.45	11.19	13.53	10.14	9.92	8.87	5.4	0.2

Table 2. Major elemental composition of brine

Element	Na	K	Ca	Mg	Sr
Concentration (ppm)	5337.87	1390.91	477.49	252.73	9.93

Table 3. Trace elemental composition of brine

Removal of Toxic Elements from Brine

The percentage removal of toxic elements from brine during the preliminary study on application of the pure phase zeolite Na-P1 synthesized from fly ash was calculated using equation 1.

% removal = (Ci – Ce)/Ci * 100 ……………………………………. Eqn. 1

where Ci and Ce are initial and final concentrations of the metal ion in the solution.

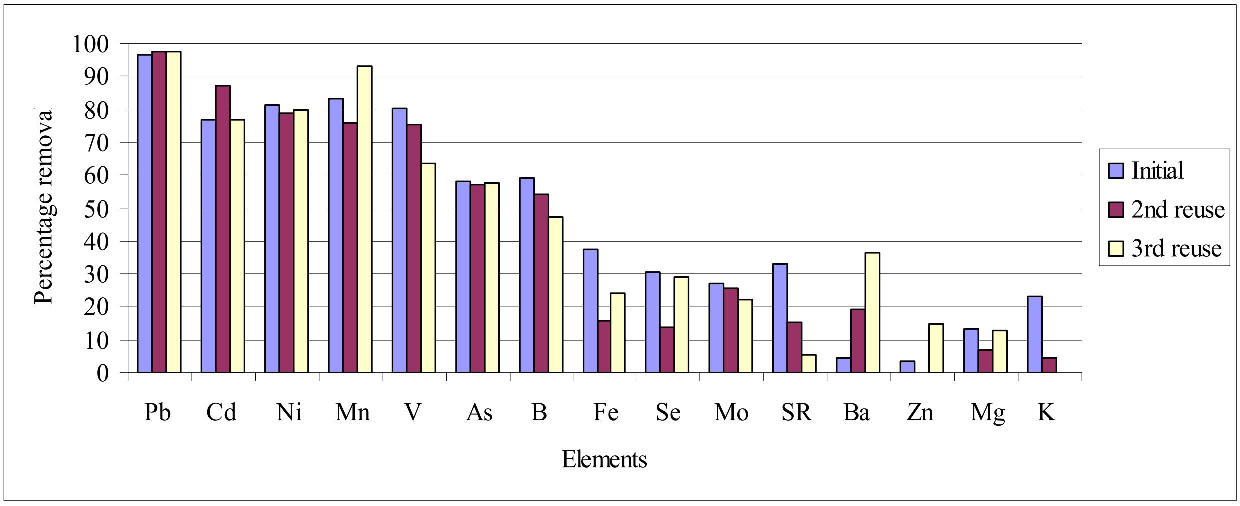

Figure 5. Percentage removal of trace elements from brine by a multiple use of zeolite Na-P1.

Figure 5 shows the percent toxic element removal obtained for Pb, Cd, Ni, Mn, V, As, B, Fe, Se, Mo Sr, Ba and Zn from brine by sorption on zeolite. It can be clearly shown that there is a good efficiency to remove toxic elements in brine for selected elements. It is also noted that the zeolite Na-P1 was reused up to three times while maintaining an almost similar capability for removal of toxic elements from brine. Experiments that were conducted by Petrik *et al.*, (2007) using the dosage (50g/l) of impure zeolite Na-P1 (with quartz, hematite and mullite phases still present) showed that some toxic elements such as Pb, Cd, Mn, Mo and Sr leached out from the zeolite Na-P1 into the solution. The same elements in this study were found to be adsorbed therefore implying that the purity of the zeolite improved the efficiency of removal of toxic elements.

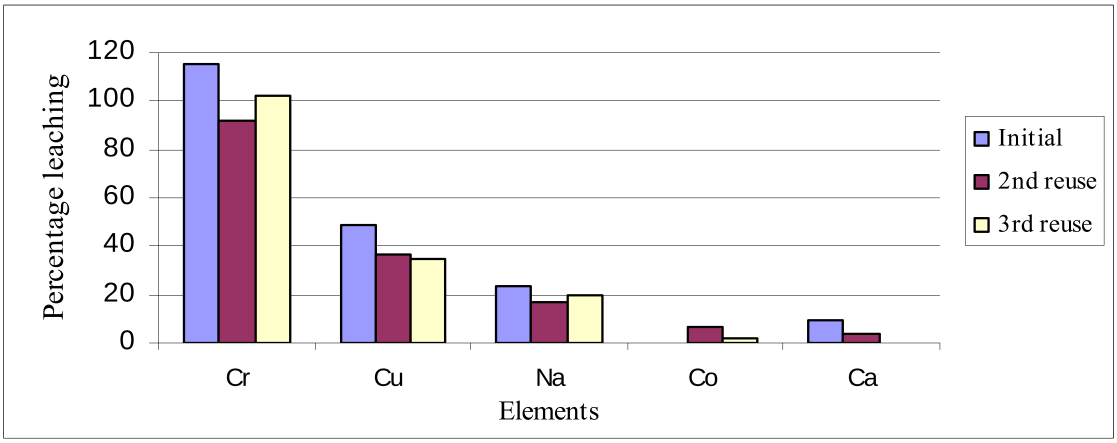

Figure 6. Percentage increase of trace elements concentration (in brine) relative to initial brine composition after treatment using zeolite Na-P1.

As shown in Figure 6, the concentration of Cr, Cu, Na, Co and Ca increased in the brine after treatment using zeolite Na-P1. The additional concentration of Na and Ca elements could have been due to ion exchange which occured during the removal of elements that are reported in Figure 5. It is also important to point out conclusion by Hendricks (2005) who reported that even though, cation exchange capacity is an important characteristic quality during the removal of undesired species from polluted effluents; it is not the only deciding factor in determining the zeolite's performance during ion exchange since there are other factors to be considered such as sorption. The high concentration of Cr and lower amounts of Cu and Co may be due to competitive desorption. It has been reported that unlike mono- and divalent metal ion, chromium removal behavior is more complex and is strongly influenced by the pH in aqueous solution (Deyi *et al.,* 2008).

5. GENERAL CONCLUSIONS

The study has shown that pure phase zeolite Na-P1 can be prepared from South African Class F fly ash because of its compositional dominance of aluminosilicate and silicate phases. The results also highlight that simple adjustment of reactant composition, presynthesis or synthesis parameters show a great improvement in phase purity and cation exchange capacity (4.11 meq/g) of zeolite Na-P1. The optimum synthesis conditions for preparing pure phase zeolite Na-P1 were achieved when the molar regime was 1 SiO_2 : 0.36 Al_2O_3 : 0.59 NaOH : 0.49 H_2O and at synthesis conditions such that ageing was done at 47 ^oC for 48 hours. The hydrothermal treatment time and temperature was 48 hours and 140 ^oC respectively. It was interesting to note that the water content added after the ageing step, expressed as H_2O/SiO_2 molar ratio played an important role in the hydrothermal conversion of fly ash to zeolites. The experiments done in this study using higher purity zeolite Na-P1 synthesized from fly ash showed a good toxic elements removal efficiency from brine solution and is expected to show further improvement when brine treatment procedure is optimized.

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