The use of a modified fly ash as an adsorbent for lead

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Abstract

Coal fly ash was modified by hydrothermal treatment with NaOH solutions of varying concentrations. During the modification the zeolites, Na-P1 and hydroxysodalite, were synthesised. Increasing base concentration led to hydroxysodalite being the preferred product. Elemental analysis revealed that the modification treatment preferentially leached Si from the fly ash at low base concentrations. Elevated base concentrations, however, resulted in Al also being leached as well as the inclusion of Na in the zeolitic product. The modification activated the fly ash significantly with respect to specific surface area (SSA) and cation exchange capacity (CEC). SSA increased from $1.0 \text{ m}^2 \cdot \text{g}^{-1}$ to a maximum of $62.7 \text{ m}^2 \cdot \text{g}^{-1}$ while CEC rose from 25 mmol/100 g to a maximum of 300 mmol/100 g. Metal sorption studies were performed with lead as the metal of choice. Adsorption experiments at pH = 5, revealed that all modified ash samples adsorbed significantly more Pb than the raw ash. The best adsorption was obtained for ash, modified with 3M NaOH. 3M NaOH-modified ash also proved the most effective sorbent when adsorption was determined as a function of pH.

Introduction

Large quantities of fly ash are produced during the combustion of coal in the production of electricity. Most of this ash is used in low level applications such as landfill. In South Africa, where high-ash content coal is used in power generation, 24×10^6 t of fly ash were produced in 1997. Only 5% of this ash was sold for reuse (Eskom, 1997). Increasing concerns about the environmental consequences of such disposal have led to investigations into other possible utilisation avenues. Furthermore, the conversion of a low-cost waste product into a higher level product would make the environmentally-friendly disposal of the remaining unused ash far more economically viable.

Fly ash is composed primarily of aluminosilicate glass, mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2). These materials provide a ready source of Al and Si, which is necessary for the synthesis of zeolites. Low Si/Al ratio zeolites have been shown to be excellent sorbents for the adsorption of transition metals because of their high cation exchange capacities (CEC) and large pore volumes (Höller and Wirschung, 1985; Flanigen, 1991; Querol et al., 1997b). Specific applications include the use of zeolites in nuclear waste processing (McFarlane et al., 1997). Thus, the conversion of fly ash into zeolites of this type might prove to be effective for removing such metals from wastewater streams cheaply and effectively owing to the low cost of the ash starting material.

Several authors have reported the conversion of a sizeable fraction of fly ash into zeolites by the treatment of ash with concentrated NaOH solutions at elevated temperatures and pressures (Höller and Wirsching, 1985; Henmi, 1987; Mondragon et al, 1990; Catalfarno et al., 1993; Lin and His; 1995, Park and Choi, 1995; Singer and Berkgaut, 1995; Amrhein et al., 1996; Querol et al., 1997a; Garde et al., 1999). Recently more sophisticated treatments including the use of microwave radiation (Querol et al., 1997b) and fusion with NaOH followed by hydrothermal treatment have been reported (Shigemoto et al., 1993; Chang and Shih, 1998).

The objective of this study was to investigate the conversion of fly ash into zeolites. The specific aims were to analyse the zeolitic products for zeolite type and surface characteristics such as specific surface area (SSA) and CEC. Furthermore the efficiency of the various products as far as the removing of lead was concerned, was also to be determined.

Most of the literature, detailing the synthesis of zeolites from fly ash, deals only with the actual synthesis and does not consider the applications thereof. Exceptions are the work of Singer and Berkgaut (1995) and Lin and Hsi (1995) who looked at metal adsorption. It was thus an aim of the present work to study the adsorption of metals from solution.

Lead was chosen as the adsorbate because of its known toxicity. It has been classified as a list II material by the European Community Directive on Dangerous Substances (Council of European Communities, 1976). The effectiveness of the zeolites produced from fly ash for the removal of lead from aqueous solution would be monitored and compared to other adsorbents such as natural zeolites (Kesraoul-Oukl et al., 1993) and sphagnum moss peat (Ho et al., 1996). The ash could hopefully prove to be a low-cost alternative to existing technologies, ideal for a developing country such as South Africa.

Experimental

Zeolite preparation

Samples of fly ash were obtained from Ash Resources (Pty) Ltd. These were a beneficiated high-silica ash known as Plasfill 5. The zeolite products were produced using a modification of the procedure of Henmi (1987). 100 g of fly ash was added to 1 000 ml of NaOH solution. The NaOH solutions varied in concentration from 1 M to 8 M. The slurries were then refluxed with overhead stirring under atmospheric pressure for 21 h. The product was collected by filtration, washed with hot distilled water and then dried at 90 °C for 48 h.

X-ray diffraction

The modified ash samples were shaken in hot distilled water to remove any possible remaining NaOH prior to X-ray diffraction (XRD) studies. After drying, powder XRD patterns were **obtained** using a Philips PW 840 X-ray diffractometer, using CuK, radiation (1.541 Å), set at 40kV and 25 mA. The files shown in the Joint Committee on Powder Diffraction Standards (JCPDS) were used to identify various crystalline zeolite phases and other minerals present.
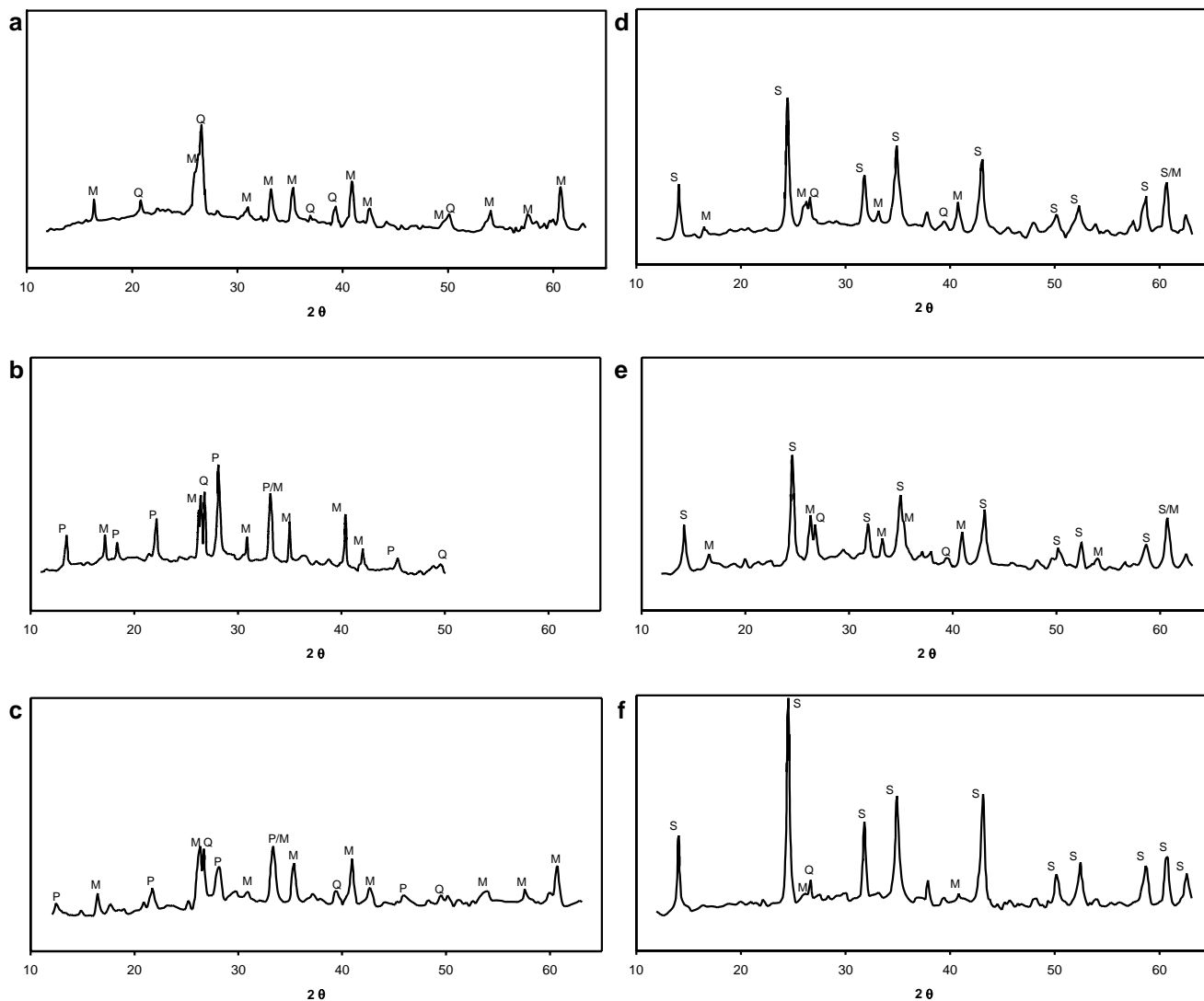
Figure 1

XRD patterns of unmodified and various treated fly ash samples. M = Mullite, Q = Quartz, S = hydroxysodalite, P = zeolite Na-P1.

a) XRD pattern of unmodified fly ash	*d) XRD pattern of 5M NaOH-treated fly ash*
b) XRD pattern of 1M-NaOH-treated fly ash	*e) XRD pattern of 6M NaOH-treated fly ash*
c) XRD pattern of 3M NaOH-treated fly ash	*f) XRD pattern of 8M NaOH-treated fly ash*

Morphological characterisation

The morphological changes that took place in the ash during the various modification procedures were studied by scanning electron microscopy (SEM). A Philips XL 30 scanning electron microscope was used. An EDAX DX4 energy dispersive X-ray analyser system (EDS) was coupled to the microscope, which allowed elemental compositions of the various products to be determined.

Surface area measurements

Surface area measurements were determined using a Micromeritics Flowsorb II 2300 single-point analyser and nitrogen gas was used as adsorbent.

Cation exchange capacity

CECs were determined using the procedure of Hesse (1972). 1 g of ash sample was shaken with 30 mℓ of 1.0 mol·ℓ^{-1} sodium acetate for 5 min. After centrifugation the procedure was repeated twice on the same sample. The solids were then shaken with 30 mℓ of 95% ethanol three times. Replacement of Na$^+$ was then carried out with NH$_4^+$ by shaking the solids three times with 30 mℓ of 1.0 mol·ℓ^{-1} ammonium acetate. The three sodium extracts were collected, diluted to 100 mℓ and analysed for sodium content by flame photometry using a Jenway PFP7 flame photometer.

Lead adsorption experiments

Lead adsorption experiments were carried out in a series of batch experiments. Firstly the adsorption of lead onto different modified ashes was carried out at pH = 5. Approximately 1 g of ash was shaken up with 125 mℓ of a Pb^{2+} solution (solutions varied from 0.5 g·ℓ^{-1} to 2 g·ℓ^{-1} Pb^{2+}). After 15 min the solution reached a constant pH, at which point the pH was adjusted with base/acid to pH = 5 as necessary. The solution was placed in a waterbath at 25°C and shaken for 4 h using a mechanical shaker. The ash was separated from the solution by gravitational filtration. The concentration of lead in the solutions was then determined, using inductively coupled plasma (ICP) spectrophotometry (on a Shimadzu ICPS-
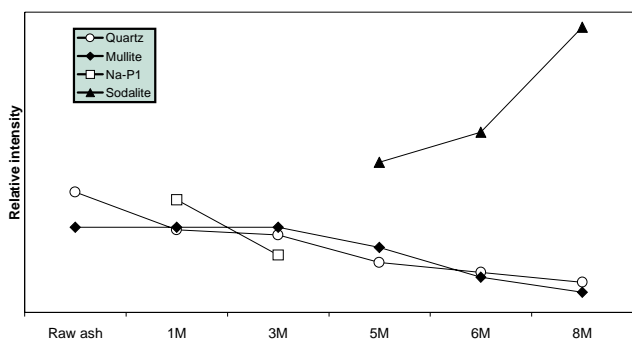
Figure 2
Intensities of XRD reflections of mullite (26.3° 2θ), quartz (26.6° 2θ), zeolite Na-P1 (28.1° 2θ) and hydroxysodalite (24.5° 2θ) for unmodified ash and various treated ash samples

1000#). Adsorption was determined by the difference between the initial and the final concentration of lead in solution.

To study the effect of pH on adsorption, 0.3 g of ash sample (original, 1M, 5M and 6M NaOH-modified ash) was added to 150 mℓ of a 0.2 g·ℓ⁻¹ Pb²⁺ solution. After 15 min the solution reached a constant pH, at which point the pH was adjusted with base/acid to an appropriate pH (adsorptions were carried out in the pH range 2 to 8). The solution was placed in a waterbath at 25°C and shaken for 4 h using a mechanical shaker. The ash was separated from the solution by gravitational filtration. The concentration of lead in the solutions was then determined using ICP, and the final pH of the solution was recorded.

Results and discussion

XRD

The XRD patterns for the untreated, 1M NaOH-, 3M NaOH-, 5M NaOH-, 6M NaOH- and 8M NaOH-treated ashes can be seen in Figs. 1a, b, c, d, e and f respectively.

The crystalline phases that can be identified in the unmodified fly ash are quartz and mullite ($Al_6Si_2O_{13}$). These are also present in all the modified ash samples. A secondary phase comprising zeolite Na-P1 ($Na_6(Si_{10}Al_6O_{32})\cdot12H_2O$) was formed during the modification process and can be seen in the 1M NaOH and 3M NaOH-treated samples.

At higher NaOH concentrations the zeolite, hydroxysodalite ($Na_6(Si_6Al_6O_{24})\cdot8H_2O$), can be identified. Similar observations were made by Singer and Berkgaut (1995), Lin and Hsi (1995), and Querol et al. (1997b) who found that zeolite Na-P1 formed at low base concentrations (<3.5 M) and hydroxysodalite at higher base concentrations. Under the reaction conditions, it was found that this phase formed in greater quantities at higher NaOH concentrations. This is reflected in Fig. 2. The intensities of the hydroxysodalite peaks in the XRD pattern increase with increasing NaOH concentration whereas those for quartz and mullite decrease. This concurs with the findings of Lin and Hsi (1995). The hydroxide acts as a strong mineralising agent, which forces the reactants into solution. The greater the OH⁻ concentration, the greater the concentration of reactants in solution and thus the greater the rate of crystal growth (Jansen, 1991).

Singer and Berkgaut (1995) also noted a decrease in the intensity of the quartz peaks in the XRD pattern as a result of zeolitisation. These authors observed that mullite was relatively stable under alkaline treatment. They, however, performed their modification procedure using 3.5 M NaOH. Figure 2 indicates that at higher NaOH concentrations, mullite is in fact digested. Similar

results were observed by Querol et al. (1997a). According to Singer and Berkgaut (1995), zeolite Na-P1 would be the first zeolite to form, but it would be replaced gradually with increasing reaction time by hydroxysodalite (a Na-P1 derivative). It is expected that increasing the base concentration speeds up the rate of this conversion process.

Morphological changes

Figure 3 shows the scanning electron microscope (SEM) images of various treated ash samples. When the various treated ash samples are compared with the untreated ash, a marked change in surface morphology can be observed. The untreated ash comprises smooth spherical particles. During alkaline treatment the surface becomes progressively rougher and broken. Cracks can also be seen developing in the spheres.

The covering of the spherical particles with small crystallites becomes apparent after the modification process. It is believed that in the case of the samples treated with higher NaOH concentration solutions (>5M), these crystallites are hydroxysodalite crystals. Large crystals are not observed. Instead, many small crystallites can be seen (the majority of which are less than 1 μm in length). This is consistent with nucleation occurring rapidly on the particle surface. Jansen (1991) has shown that the presence of impurities in the reactants may affect the crystal form and chemical properties of the zeolite formed. In particular, impurities lead to the formation of many small crystallites. This is because these impurities increase nucleation at the expense of crystal growth. Because fly ash is not pure quartz and mullite, but comprises a large amount of other materials, it is not surprising that nucleation proceeds at the expense of crystal growth during zeolite formation. Increasing the base concentration produced better defined and larger crystallites.

Figure 4 illustrates how the elemental composition of the samples varies with alkaline treatment. Lin and Hsi (1995) also observed an initial decrease in the Si/Al ratio in the treated ash. This indicates that the Si compounds are more reactive in the NaOH than in the Al compounds. This is confirmed by the XRD results. For NaOH concentrations less than 5M, the intensities of the quartz peaks decrease whereas those of mullite do not (see Fig. 2). The increase in the Si/Al ratio at higher NaOH concentrations results because mullite (which contains Al) was digested in the 5M, 6M and 8M treatments.

It is also clear from Fig. 4 that the alkaline treatment leads to the inclusion of sodium in the zeolite. Since Na is a constituent of both Na-P1 ($Na_6(Si_{10}Al_6O_{32})\cdot12H_2O$) and hydroxysodalite ($Na_6(Si_6Al_6O_{24})\cdot8H_2O$) zeolites, it is necessary that Na be taken up from solution during the zeolitilisation process. This is reflected in the increased Na/Si ratio.

Surface area measurements

Figure 5 illustrates the variation in specific surface area with modification treatment. The hydrothermal treatment of fly ash with base clearly increases the surface area of the ash. This is most significant with the 1M-modified ash whose surface area was measured to be 62.66 m²·g⁻¹. This is significantly higher than the surface area of the raw ash (1.05 m²·g⁻¹). Further treatment of the ash decreased the surface area again. We ascribe the initial increase in surface area to the formation of zeolite-P. The decrease in surface area reflects the conversion of zeolite-P to hydroxysodalite. Lin and Hsi (1995) found a similar increase in SSA although they found the surface area to peak at 3.5M NaOH treatment. The different origins of the ash samples and the time length of the treatment process, however, can explain the differences observed.
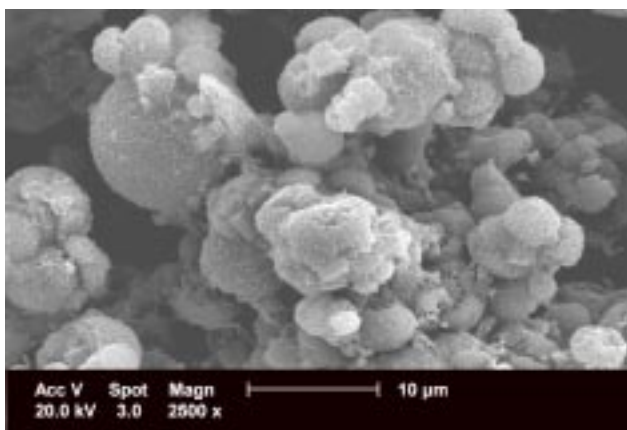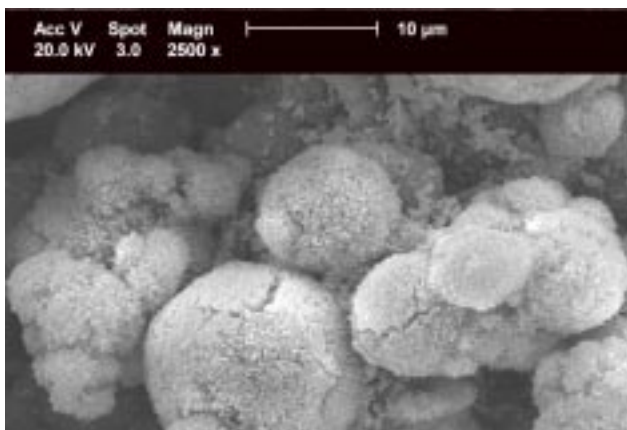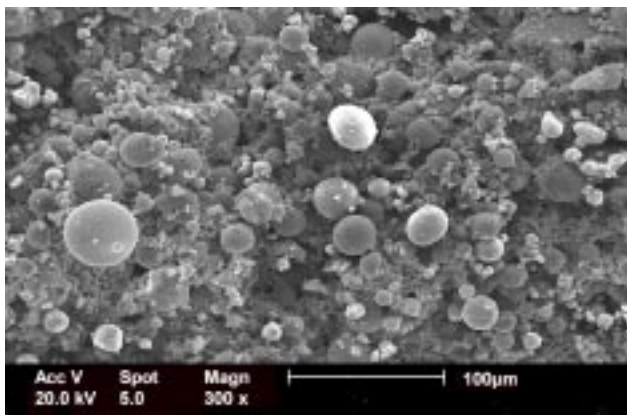
Figure 3
SEM images of the different treated fly ash samples
a) SEM image of unmodified fly ash.
b) SEM image of 1M NaOH-modified fly ash
c) SEM image of 8M NaOH-modified fly ash

Figure 4
Si/Al and Na/Si ratios in the different treated ash samples as determined by EDS

Figure 5
Variations in the specific surface area and cation exchange capacity for the different treated ash samples

Figure 6
Isotherms for the adsorption of lead onto various modified ash samples at pH = 5

Chang and Shih (1998) prepared zeolite-P with a surface area similar to ours (54.4 m²·g⁻¹).

CEC

Figure 5 indicates that the fly ash is activated with respect to cation exchange capacity during the modification procedure. The CEC rose from 25 mmol/100 g solid to a maximum of 300 mmol/100 g for the 3M NaOH-modified ash. The CEC does not follow the pattern observed for the surface area. This is in contrast to the results of Lin and Hsi (1995). The exchange capacities for the
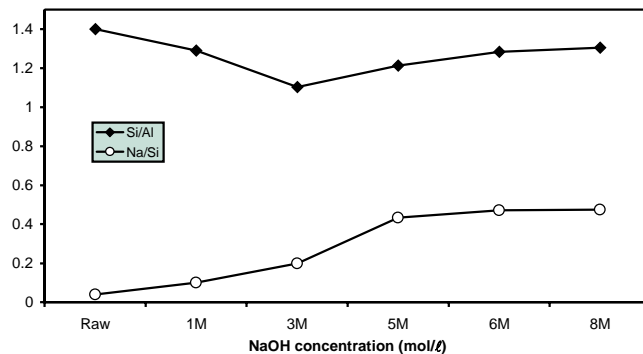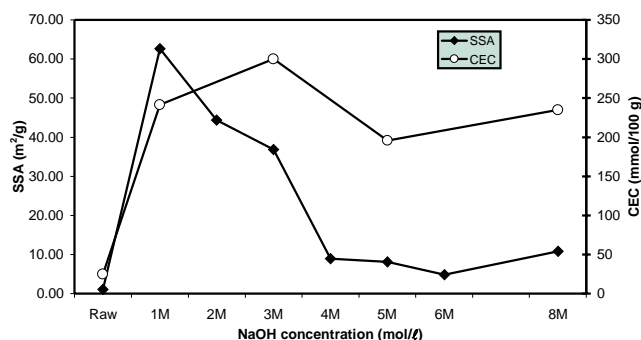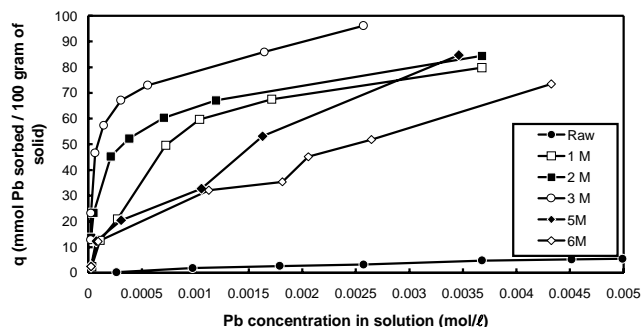
modified ash sample are similar to those of Singer and Berkgaut (1995), but higher than those obtained by Chang and Shih (1998) (151 to 186 mmol/100 g) and the maximum of 210 mmol/100 g observed by Lin and Hsi (1995).

Singer and Berkgaut (1995) reported that the CEC for synthetic zeolite Na-P1 was 580 mmol/100 g. From this we can estimate that approximately 42% and 52% of the 1M and 3M-modified ash samples have been converted into fly ash respectively. The CEC for synthetic hydroxysodalite (Singer and Berkgaut, 1995) is reported to be 590 mmol/100 g. This means that 33% and 42% of the fly ash in the 5M and 8M NaOH-modified ash samples have been converted to zeolite. Since zeolite Na-P1 is converted to hydroxysodalite, the low value for the 5M NaOH modification does not correspond with the observed phase changes. However, cation exchange in hydroxysodalite is restricted at room temperature

(Singer and Berkgaut, 1995) which may lead to low values. This may also explain the very low CECs reported by Lin and Hsi (1995) for sodalite-containing zeolites.

Pb adsorption isotherms

Constant pH = 5

Figure 6 illustrates the adsorption of Pb^{2+} from solution at pH = 5. The figure shows that the modified ash samples adsorb significantly more lead than the unmodified fly ash. The diagram indicates that the 3M NaOH-modified fly ash has the greatest affinity for lead. This is indicated by the steep increase in adsorption at low lead concentrations. It would also appear that the mode of adsorption for the sodalite-containing ash samples (5M and 6M) differs from the Na-P1 zeolites because the shape of their isotherms is much flatter. The shape of the isotherms suggested that the adsorption behaviour could be modelled using the Langmuir isotherm.

$$q = \frac{KCN_{max}}{1 + KC} \qquad (1)$$

where:

q is the amount per gram of solid of Pb adsorbed
C is the concentration of Pb in solution at equilibrium
K is the Langmuir adsorption constant
N_{max} is the total number of sites available for adsorption on the solid surface.

The Langmuir equation can be linearised either as:

$$\frac{C}{q} = \frac{1}{KN_{max}} + \frac{C}{N_{max}} \qquad (2)$$

or as:

$$\frac{1}{q} = \frac{1}{KN_{max}C} + \frac{1}{N_{max}} \qquad (3)$$

Eq. 2 has been criticised because it displays an induced correlation in C (Langmuir, 1997). Although both linearisations gave straight lines ($R^2 > 0.95$) for the experimental data, different values for K and N_{max} were obtained. This is because each linearisation weights each data point differently. Consequently, the experimental data was fitted directly to the untransformed Langmuir equation (Eq. 1) using non-linear regression.

The Langmuir parameters determined for the various ash samples are contained in Table 1. The data indicate that the 3M NaOH-modified ash has the strongest affinity for lead (evidenced by a large K value). The values of N_{max} indicate that in all cases the affinity of the solid material has been enhanced relative to unmodified ash. It is also apparent from the values of N_{max} that the modified ash samples could be divided into two groups: those with $N_{max} \approx 0.90$ mmol·g^{-1} and those with $N_{max} \approx 1.70$ mmol·g^{-1}. The former consists of the low base concentration modified ash samples and the latter consists of those modified with stronger base. This coincides with the observation, using XRD, that the former include Na-P1 zeolites and the latter include hydroxysodalite crystals.

It is significant that the values for N_{max} are less than the cation exchange capacities, except for the unmodified ash samples. Closer analysis of the experimental data reveals that the experimental data do not flatten off at higher lead solution concentrations as would be expected from the Langmuir isotherm. In fact, it actually appears

TABLE 1
Langmuir parameters determined for various ash samples at pH=5 using non-linear regression

Ash sample	N_{max} (mmol/g)[†]	K (L/mmol)[†]	R^2
Unmodified ash	0.217 (0.041)	0.070 (0.019)	0.998
1M NaOH-modified ash	0.985 (0.051)	1.293 (0.183)	0.998
2M NaOH-modified ash	0.812 (0.045)	5.591 (1.244)	0.966
3M NaOH-modified ash	0.911 (0.040)	12.10 (2.386)	0.956
5M NaOH-modified ash	1.759 (0.600)	0.254 (0.139)	0.986
6M NaOH-modified ash	1.628 (0.572)	0.183 (0.098)	0.989

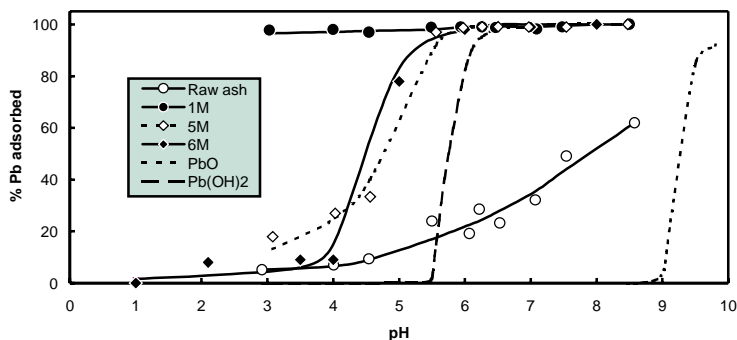† Numbers in brackets are standard deviations of the best fit estimates

Figure 7
Adsorption edges for the adsorption of Pb onto different ash samples as a function of pH

to increase linearly. This is especially true for the 1M, 2M and 3M NaOH-modified ash samples. Good correlation was obtained with the Langmuir isotherm at low solute concentrations, but at higher concentrations deviations occur. This could partially be so because ion exchange is restricted in some zeolites as reported by Singer and Berkgaut (1995). This may be especially true of lead rather than sodium, which could explain some of the deviations in N_{max} from the CEC.

Since the ash samples are, in fact, multi-phase materials, it is possible that the shape of the adsorption isotherms is the result of a strong binding site (dominant at low Pb concentrations) and a weaker binding site, which adsorbs lead at higher concentrations. Attempts were made to perform non-linear regression, assuming multiple Langmuir binding sites. This, however, proved to be unsuccessful.

The lead adsorption capacity measured here was higher than that observed for natural zeolites such as clinoptilolite (Kesraoul-Oukl et al., 1993). However, the cation exchange capacities of those zeolites (approximately 150 mmol/100 g) were also found to be lower than the CECs reported here for modified fly ash samples. Kesraoul-Oukl et al. (1993) found similar adsorption capacities to those reported here for another natural zeolite, chabazite (1 mmol/g). The maximum capacities reported here are significantly greater than other readily available materials which have been proposed for lead removal such as various clays (0.0015-0.4 mmol/g) (Farrah et al., 1980; Yadava et al., 1991) and for various types of moss peat (0.1-0.2 mmol/g) (Mcllellan and Rock, 1988; Ho et al., 1996)

Variable pH

Figure 7 illustrates the adsorption behaviour of various modified ash samples as a function of pH. It is apparent that in all cases the

percentage of lead adsorbed increased as pH increased. This is likely to be via an ion-exchange mechanism where the Pb^{2+} cations replace H^+ ions in the zeolite structure:

$$\equiv Z\text{-H} + Pb^{2+} \qquad \equiv Z\text{-Pb}^+ + H^+$$
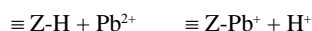
where $\equiv Z$- represents an exchange site in the zeolite framework. As pH increases this exchange equilibrium is pushed to the right in accordance with Le Chatelier's principle as competition from H^+ for exchange sites decreases. Figure 7 illustrates that the equilibrium lies far to the right for the Na-P1 containing modified ash (1M NaOH) at all pH values whereas the sodalite containing ashes (5M and 6M NaOH) are effective above pH 4.5. This is consistent with the batch studies performed at pH = 5 where the Na-P1 zeolites were more effective than sodalite. Both, however, remain more efficient than unmodified ash. Lin and Hsi (1995) found similar activation of fly ash after modification for the adsorption of Cu and Cd.

Figure 7 also contains curves for the theoretical precipitation of amorphous $Pb(OH)_2$ and litharge (PbO). These curves were generated using MINEQL+ (Schecher and McAvoy, 1991). The curves are included to determine whether the adsorption of Pb occurred via a precipitation mechanism rather than ion-exchange. The pH edges for the modified ash samples lie to the left, which indicates that an ion-exchange mechanism is more likely to have occurred. In the case of unmodified ash, no precipitation of $Pb(OH)_2$ could be observed.

Furthermore, the adsorption onto raw fly ash increases over a wide pH range which indicates that there are a variety of exchange sites on the ash surface with a range of acidities. This is to be expected since the ash is not a pure compound but a mixture of different solids.

Conclusions

Na-P1 and hydroxysodalite zeolites have been prepared from coal combustion fly ash by a hydrothermal treatment of the ash with NaOH. By varying the concentration of the NaOH, control over the type of zeolite formed was achieved. The resultant modified ash samples exhibited much greater specific surface areas and cation exchange capacities than the unmodified ash. The adsorption of lead from aqueous solution by these modified ashes was found to occur readily. Na-P1 zeolites were more effective at removing Pb than hydroxysodalite, but both were much improved when compared to the original ash. The synthesised products show a greater adsorption capacity than similar cheap materials such as clay or moss peat.

It is envisaged that this modification procedure can convert fly ash into a beneficial product, which would prove effective in removing heavy metals such as lead from contaminated effluent streams. Further studies on the leaching behaviour of such materials need to be performed since this will determine the final disposal of the material.

Acknowledgements

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