TREATMENT OF COAL FLY ASH FOR CATION EXCHANGE CAPACITY IMPROVEMENT

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ABSTRACT

Previously, utilizations of coal fly ash as an absorbent for the removal of heavy metals from wastewater have not been successful because of it's low cation exchange capacity (CEC). Many attempts have been made to improve the properties of fly ash. In this study we refluxed coal fly ash with 1.0 M NaOH for 24 hrs. As a result the CEC of the treated fly ash increased by a factor of 24 to almost 200 meq/100 g compared to untreated fly ash. Porosity and crystallization of the treated fly ash also increased and it was converted into zeolite Na-P and sodalite octahydrate. The concentration of Na_2O in treated fly ash was 6 times higher than in untreated fly ash.

KEYWORDS: adsorbent, CEC, treated fly ash, heavy metals, zeolite

1. INTRODUCTION

Every day 35,000 tons of lignite are burnt at the Mea-Moh electric power plant in the North of Thailand, resulting with generation of 7000 tons of fly ash per day [1]. More than 50 % of the fly ash is disposed in landfills, a method that is getting increasingly expensive. Besides the high costs, disposal in landfills also poses environmental problem as its content of heavy metals such as As, B, Ba, Cd, Cr, Pb, Hg, Mo and Se, may cause contamination of the ground water. There have been several attempts to find alternative uses for fly ash such as in agriculture [2], as an additive for cement [3], for the removal of dye [4], mixed with concrete for the Pakmoon Dam construction [5] or as adsorption media for heavy metals from water [6].

To increase the value of fly ash, the utilization of fly ash as an adsorbent for the removal of heavy metals has been reported [7-9]. A disadvantage using the fly ash as an adsorbent is its low CEC. However, by heating suspended fly ash in 3.5 M NaOH at 80-90 °C for 24 hrs, Henmi [10] was able to increase the CEC of fly ash from 140 $mmol_c\ kg^{-1}$ to 3600 $mmol_c\ kg^{-1}$. From XRD analysis he found that the fly ash had undergone a phase transformation to sodalite.

Similar phase transformation has been reported also for other materials that have compositions similar to fly ash. When basaltic glass was heated in the NaOH solution to 150-250 °C [11] it was found that zeolites, chabasite, phillipsite and analcime were formed. Also synthetic basaltic glass, which has a composition similar to fly ash, was transformed to

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analcime, zeolite ZK-19, zeolite P_1 and tobermorite when heated in the alkali solution [12]. Singer and Berkgaut [13] treated fly ash with 3.5 M NaOH at 100 °C for 2-48 hrs. As a result, zeolite P and hydroxysodalite with a CEC of 2.5-3 meq/g were formed.

Zeolite possesses a high CEC. It therefore has been used in a wide range of applications, e.g., improvement of soil, paper manufactory, as a detergent, catalyst and for water treatment. In the future it can be expected that the demand of zeolite will increase. Currently most zeolites are synthesized from silica gel and aluminium salts by hydrothermal crystallization in alkali solution [14].

The objective of this study was to investigate the influence of the base concentration and reaction time on the CEC in the treatment of fly ash. The type of zeolite formed, its CEC and the chemical and physical properties before and after the treatment were to be determined.

2. MATERIALS AND METHODS

2.1 Effect of base concentration and reaction time on the CEC

Samples of fly ash used in this study were collected from the Mea-Moh electric power plant in the North of Thailand.

Only the fraction of fly ash, with a particle size smaller than 63 μm was used. The fly ash was refluxed with NaOH solution at a ratio of 1:8 using 0.5, 1.0, 1.5, 2.0, 3.5, 4.0 and 5.0 M NaOH. For each base concentration, the fly ash was refluxed for 6, 15, 24, 48 and 72 hrs respectively. The treated fly ash was cooled down to room temperature, separated from the basic solution by centrifugation, decantation and washed four times with D.I. water. After the washing process the sample was dried at 60 °C for 48 hrs.

The CEC of treated fly ash was determined by Ammonium Acetate Method. 5 grams of treated fly ash were saturated overnight with 30 mL of 1 M NH_4OAc in a 50 mL centrifuge tube. The solution was then centrifuged for 5 minutes and decanted. The residue was shaken two times for 5 minutes with 30 mL of 1 M NH_4OAc each centrifuged and decanted. The product was washed three times with 30 mL alcohol. To ensure that the treated fly ash was saturated with Na^+, it was shaken three times with 30 mL of 10 % acidified NaCl for 5 minutes and decanted. The supernatant was collected into a 100 mL volumetric flask and filled with 10 % acidified NaCl to the mark. 20 mL was pipetted into a Kjeldahl flask and a few milliliter of 1 M NaOH were added. Distillation was carried out for 2 minutes and the distillate was collected in 2 % mixed indicator. For the determination of NH_4^+, the solution was titrated with 0.05 M H_2SO_4[15].

2.2 Physical and chemical properties of fly ash

The particle size distribution of untreated and treated fly ash were examined with the help of a laser particle size analyzer (Mastersizer X, Malvern). The morphology was examined with the help of a scanning electron microscope (Jeol, JSM 6400). Determination of composition of untreated fly ash and treated fly ash was achieved by using an X-ray fluorescence spectrophotometer (Fison, ARL 8410). The powder XRD patterns of untreated and treated fly ash were recorded with an X-ray diffractometer (Jeol, JTDX-8030). For successive structural determination, a fourier transform infrared spectrometer (Nicolet, Impact 1400) was used.

All reagents used in this research were analytical reagent grade.

3. RESULTS AND DISCUSSION

3.1 Physical and chemical properties of fly ash

The chemical composition of both untreated and treated fly ash was determined by X-ray fluorescence method. The results are shown in Table 1.

Table 1. Chemical Composition of Untreated Fly Ash and Treated Fly Ash

	Element (wt %)					
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	Fe_2O_3
Untreated Fly Ash	38.16	21.11	16.64	2.94	1.65	11.78
Treated Fly Ash	38.12	23.08	13.92	2.09	9.93	8.72

The treatment process leads to a drastical increase in the Na_2O concentration in the fly ash. As a result, suspensions of treated fly ash in D.I. water show a higher pH than those of untreated fly ash (pH 8) due to the leaching of Na^+ of the treated fly ash. This higher pH makes suspensions more suitable to adsorb heavy metals from aqueous solutions.

The particle size distribution of untreated fly ash and treated fly ash, show clear differences (Figure 1). In untreated fly ash the particle size distribution ranges from 0.5 to 68.33 μm with a maximum at approximately 25 μm. After the treatment process no particles with a size larger than 38 μm can be found. Also the number of particle with less than the 10 μm decreases due to conglomeration effects. Approximately 75 % of the particles in treated fly ash can be found in the range of 10 to 38 μm with a maximum at 21 μm.

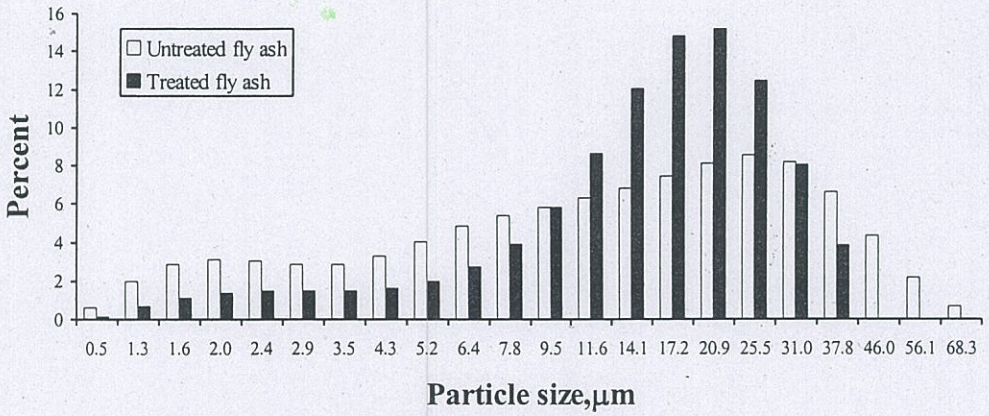

Figure 1. Size distribution of untreated fly ash and treated fly ash.

3.2 Effect of base concentration and reaction time on the CEC

The CEC of treated fly ash depends both on reaction time and base concentration (Figure 2.). The maximum CEC of about 200 meq/100 g is achieved with a solution of 1.0 M NaOH. Immediately after the beginning of the treatment process, the CEC increases rapidly reaching its maximum after 24 hrs. A longer reaction time does not lead to a further improvement of the CEC. For 0.5 M NaOH the increase in CEC starts slower, reaching a maximum of 136 meq/100 g after 72 hrs reaction time. At concentration above 1.0 M NaOH, the CEC does not improve after a rapid increase within the first 20 hrs. The resulting CECs are 83, 60, 50 and 43 meq/100 g for 2.0, 3.5, 4.0 and 5.0 M NaOH respectively.

3.3 Phase transformation of fly ash

SEM analysis (Figure 3) of untreated and treated fly ash show that during the treatment process the fly ash undergoes a phase transformation. Untreated fly ash has a spherical structure and smooth surface. After the treatment with 1.0 M NaOH for 24 hrs a glassy and rough surface with needle-like shaped crystals prevail. With increasing NaOH concentration the ruggedness of the surface increases.

XRD analysis of the treated fly ash shows that the treatment process has transformed the untreated fly ash to zeolite. In untreated fly ash quartz peaks at 20.76, 26.56, 35.56, 40.84 and 43.16 (2θ) (Figure 4A) indicate that quartz is the major constituent.

After treatment with 1.0 M NaOH for 24 hrs these quartz peaks almost disappear and new peaks appear at 12.40, 17.72, 21.60, 27.92, 33.20 and 45.80 (2θ) indicating that the fly ash is transformed to zeolite Na-P which consists mainly of $Na_6[(AlO_2)_6(SiO_2)_{10}]$. $15H_2O$ (Figure 4B). Further increase in NaOH concentration leads to another phase transformation. Figure 4C and 4D demonstrate that at concentrations of 3.5 and 5.0 M NaOH the main product is zeolite sodalite octahydrate, $Na_6(Si_6Al_6O_{24}).8H_2O$ as indicated by the peaks at 13.96, 24.28, 29.12, 34.48, 37.04, 39.64 and 42.64 (2θ)[10,16].

In FT-IR increasing OH-peaks and H-O-H bending signals (Figure 5C-5E) confirm these phase transformations. The transformation of fly ash into zeolite sodalite octahydrate explains the increased Na-concentration in the fly ash after treatment as shown in Table 1. This Na^+ is exchangeable by other cations e.g. NH_4^+ resulting in a higher CEC.

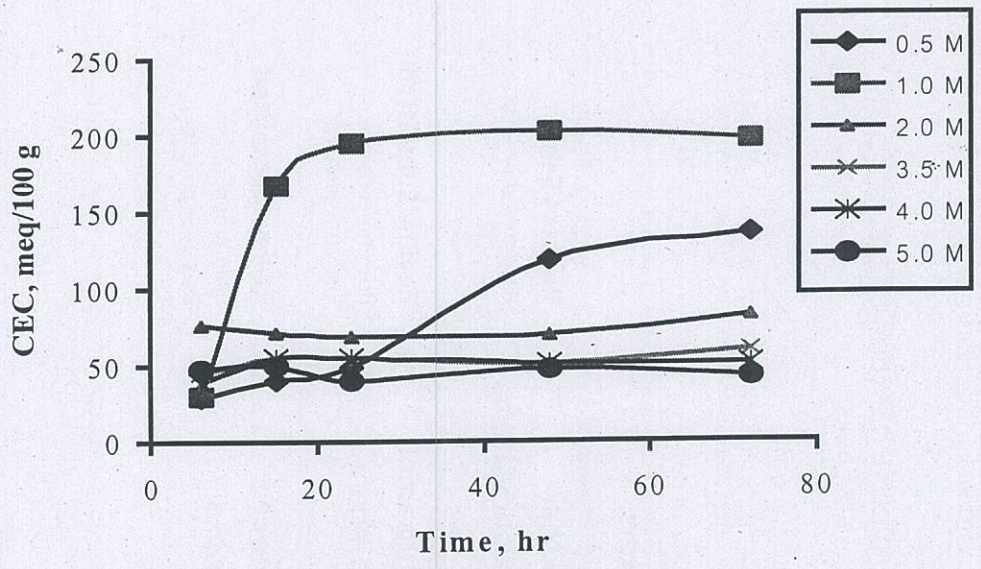

Figure 2. CEC of fly ash treated with 0.5-5.0 M NaOH related to treatment time.

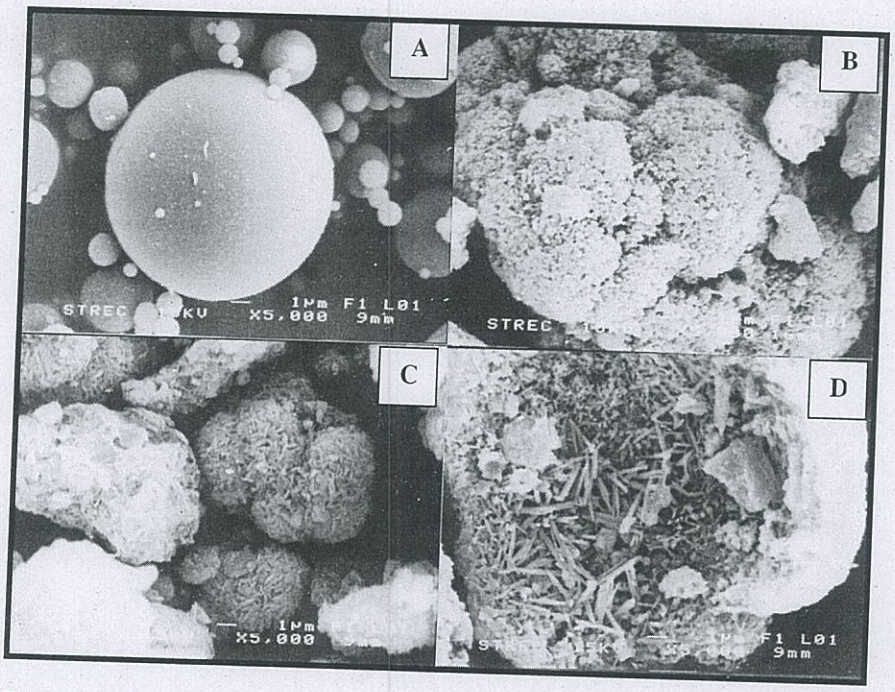

Figure 3. Scanning Electron Microscope image of A) Untreated fly ash and fly ash treated for 24 hrs with B) 1.0 M NaOH C) 3.5 M NaOH and D) 5.0 M NaOH.

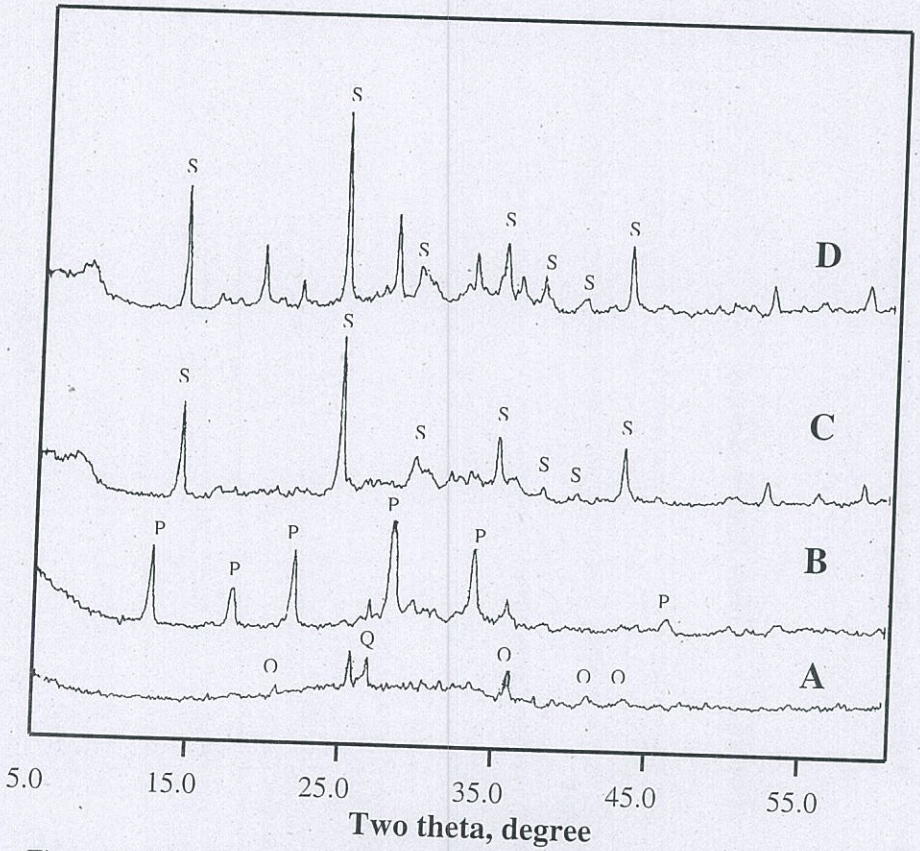

Figure 4. XRD patterns of A) Untreated fly ash and fly ash treated for 24 hrs with B) 1.0 M NaOH, C) 3.5 M NaOH and D) 5.0 M NaOH. (Q=quartz, P=zeolite-P, S=sodalite octahydrate).

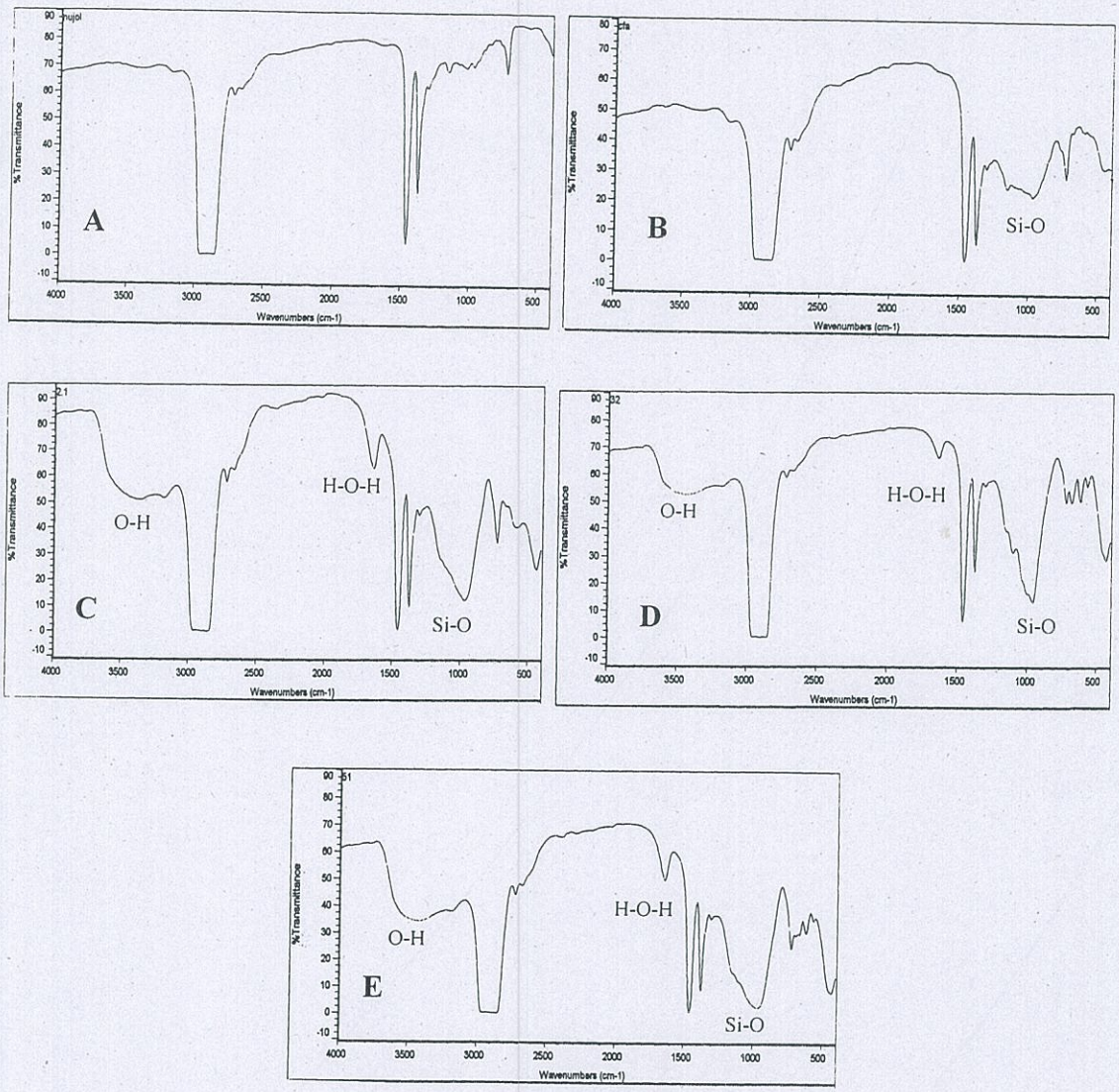

Figure 5. FT-IR spectra of A) Nujol, B) Untreated fly ash, and fly ash treated for 24 hrs with C) 1.0 M NaOH, D) 3.5 M NaOH and E) 5.0 M NaOH.
The increasing OH and H-O-H signals in C-E are characteristic for zeolite Na-P (C) and sodalite octahydrate (D and E).

4. CONCLUSION

The treatment of fly ash with NaOH (>0.5 M) for 24 hrs leads to the formation of zeolite with sodalite octahydrate being the main component. A larger surface area, increased ruggedness of the surface and a large amount of exchangeable Na^+ in the formed sodalite octahydrate lead to an increased CEC. With its higher CEC and the higher pH of its suspensions treated fly ash is more suitable to act as an adsorbent for the removal of heavy metals from water.

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