PREPARATION OF ZEOLITIC ADSORBENTS FROM WASTE COAL FLY ASH

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Abstract—Power plants burning coal generate a large amount of fly ash as waste matter. The objective of this study is to produce zeolitic adsorbents that possesses high adsorptive capacity for toxic cations. The sample was first pretreated with a High Intensity Magnetic Separator for the removal of iron and magnetic materials (mainly Fe_2O_3 and TiO_2). The zeolitic adsorbents were prepared under the various conditions of NaOH concentration (1-5 N), reaction time from 3 to 96 hours and at the various temperatures of 60, 80 and 100℃. The results of the experiment showed that the coal fly ash should be synthesized with 4 N NaOH for 48 hours at 100℃ in order to have good adsorptive capacity. The zeolitic adsorbents showed higher cation exchange capacity values than the natural zeolite in removing NH_4^+, Pb^{2+}, Ca^{2+} and Cd^{2+} ions.

INTRODUCTION

Power plants burning coal generate a large amount of fly ash as waste matter. It is estimated that 3 million tons of waste coal ash will be generated by burning 7.4 million tons of domestic anthracite coal for power generation by the year of 2001 in Korea. KCIPB [1992] reported that the development of an efficient utilization method of waste coal ash will be a vital factor for power generation of domestic anthracite coal and imported bituminous coal.

The coal fly ash has been mostly used for reclamation, as a raw material for cement and as a subbase material. Processing coal fly ash into a resource of high value has not substantially been practiced [Clean Japan Center, 1991]. In Korea, except being used as an additive to cement, coal fly ash has been disposed of, thereby creating environmental problems. The objective of this study was to produce zeolitic adsorbents that possess high adsorbency of toxic cations [Haruna, 1990].

Zeolites are naturally produced and typical natural zeolites include mainly mordenite and clinoptilolite. It has been known that they have ion-exchange properties. Therefore the natural zeolites are widely used as a drying agent, a deodorant, a freshness-holding agent, an ion exchange agent for waste water treatment and, a soil improvement (golf course, agriculture and horticulture) fertilizer additive [Clean Japan Center, 1991; Munson, et al., 1974].

Apart from the natural zeolites, zeolitic adsorbents are industrially produced from sodium hydroxide, colloid silica, sodium alumina, etc [Szostak, 1989; Barrer, 1982].

Synthetic zeolites are also called molecular sieves due to their special crystal structure, and the main applications of zeolitic adsorbents include detergent builders, adsorbents, catalysts, etc [Break, 1974].

One of the indicators for judging the quality of these zeolites is the basic exchange capacity which is an indicator to show how

many basic ions can be ion-exchanged. In this study, it is aimed to achieve 180 meq/100 g for CEC or more which is between natural zeolite and conventional zeolitic adsorbents.

EXPERIMENTAL

1. Materials

A coal fly ash sample was taken from the Samcheunpo power plant in Kyungnam, Korea. The total sample of 5 kg was mixed throughly and was split out. The sample was pretreated using the HIMS (high intensity magnetic separator) for the removal of iron and magnetic materials (mainly Fe_2O_3 and TiO_2) which are known as the undesirable components for the synthesis of zeolite [Tazaki et al., 1989; Natush et al., 1980]. This sample was dried and was used for the zeolite preparation.

2. Methods

A 100 g sample of the coal fly ash treated with 250 ml solution of various concentrations of sodium hydroxide (1, 2, 3, 4, 5 N) in a flask. The solid was then crystallized at different temperatures (60, 80, 100℃) for different periods of time (3-96 h). Then the product was washed with distilled water to eliminate the remnant sodium hydroxide, dried and stored in a desiccator for further use in the subsequent experiments.

The final product was analysed by various methods:

(1) X-ray powder diffraction, using copper Kα radiation and Ni-fil., full scale range 3,000 cps using Japan Rigaku Co. (model D/Max-1200), apparatus.

(2) The morphologies of the samples were looked into by scanning electron microscopy (JEOL Co., model JSM-5400).
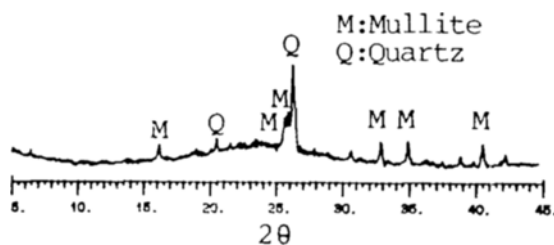
(3) Thermal analysis with 20 mg of sample and a heating rate of 10℃ min⁻¹ in air, using TG-DTA (Japan Rigaku Co., Thermoflex type).

(4) The measurement of cation exchange capacity (CEC : meq/100 g) [Shin et al., 1987] was carried out to determine the adsorptivity. Tests were repeated five times and the average value was taken.

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Table 1. Chemical analysis of coal fly ash

Comp.	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	TiO₂	Na₂O	K₂O	Ig.loss	CEC (meq/100g)
Ass. (%)	55.23	21.49	5.56	3 14	0.88	1.02	0.39	1.31	10.49	7.0
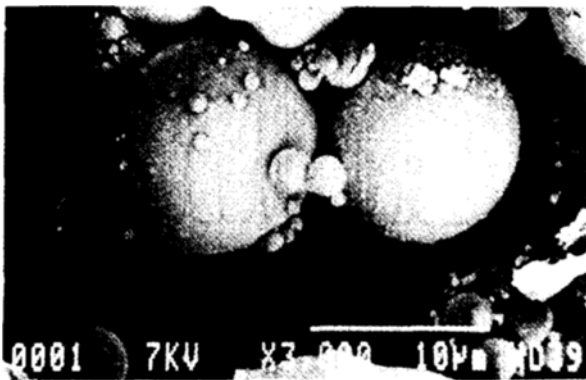
Fig. 1. Scanning electron micrograph of coal fly ash.

Fig. 2. X-ray diffraction patterns of coal fly ash.

Fig. 3. DTA curves of coal fly ash.

Table 2. The size distribution and calorie of coal fly ash

Size (mesh)	Direct.		Cumul.			
			finer		Coarser	
	Wt (%)	Calorie (Kcal/Kg)	Wt (%)	Calorie	Wt (%)	Calorie
+50	4.21	2956	100.00	603	4.21	2956
−50/+100	18.31	1499	95.79	499	22.52	1771
−100/+200	31.54	493	77.48	263	54.06	1026
−200/+400	20.85	119	45.94	105	74.91	773
−400	25.09	94	25.09	94	100.00	603
Total	100.00	603				

Table 3. The results of magnetic materials removal by using HIMS

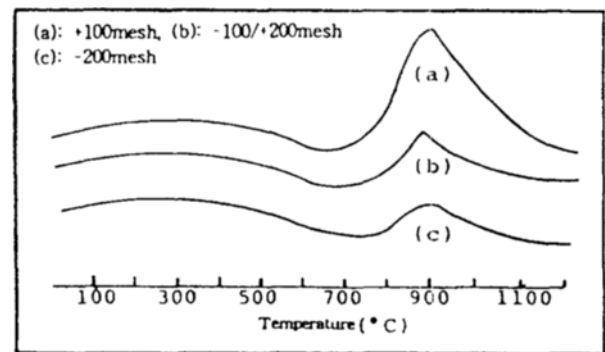| Magnetic field strength (gauss)	Product	Wt (%)	Fe₂O₃ (%)	Dist. (%)
6500	Conc.	94.03	4.20	71.16
	Tail	5.97	26.86	28.84
8000	Conc.	90.35	3.57	58.02
	Tail	9.65	24.19	41.98
10000	Conc.	90.05	3.53	57.14
	Tail	9.95	23.95	42.86
12000	Conc.	89.74	3.83	61.82
	Tail	10.26	20.69	38.18
15000	Conc.	89.22	3.86	62.06
	Tail	10.78	19.57	37.94

RESULTS AND DISCUSSION

1. Components and Composition

The original sample was chemically analysed and the result is listed in Table 1. It shows that coal fly ash consists of 55.23% SiO₂ and 21.49% Al₂O₃. It also contained 5.56% of Fe₂O₃ and 1.02% of TiO₂, which had to be removed before the synthesis, since these are undesirable components in the synthesis of zeolites [Fanor et al., 1990]. 10.49% of the sample is an ignition loss at 1000℃, which might be attributed to the burning of coal and organic matters.

Fig. 1 shows that the coal fly ash used is mainly spherical in morphology. Some of these are hollow (cenospheres) and some are filled with other spheres (pierospheres), which are the result of melting of the coal mineral matter and the evolution of gases such as N₂ and CO₂ etc, during the combustion process [Fisher et al., 1978]. Fig. 2 shows X-ray diffraction patterns of coal fly ash indicating common mineralogical phase, such as quartz, mullite [Falcone et al., 1984] and amorphous materials, formed during the combustion process. Metakaoline such as clay mineral is not detected by X-ray diffraction, probably due to its poor crystallization.

2. The Size Distribution and Calorie Measurement

The size distribution of the original sample was analysed. Each size fraction was analysed by using thermal gravimetry-differential thermal analysis, and calorimeter, and the results obtained are shown in Table 2. Table 2 shows that the minus 200 mesh size fraction of the coal fly ash is 46 wt%, and it has low calorie

of 105 kcal/kg. On the other hand, the 22.52 wt% plus 100 mesh size fraction has quite higher calorie up to 1771 kcal/kg. This result indicates that the coarse size fraction contains more unburned coal.

Fig. 3 shows the results of TG-DTA analysis on each size fraction and exothermic reaction peaks appear at 850-900℃. Coarse size fractions show higher peaks than do finer size fractions, and this result supports the data of Table 2.

3. The Pretreatments by HIMS

The removal of iron and magnetic materials was carried out by using HIMS as the pretreatment process [Willy 1988]. The intensity of magnetic field was varied from 6,500 to 15,000 gauss. Table 3 shows that by increasing the intensity of magnetic field
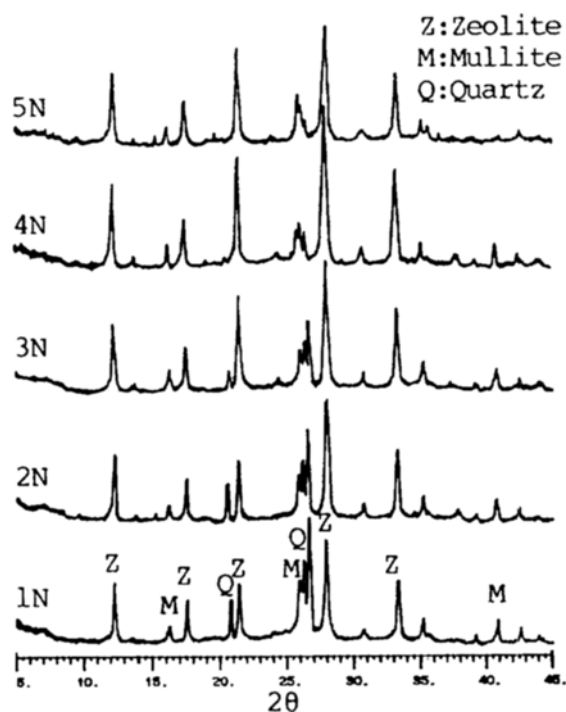
Fig. 4. X-ray diffraction patterns of zeolitic adsorbents obtained at various concentrations of NaOH at 100°C and 48 hours of reaction time.

Fig. 5. X-ray diffraction patterns of zeolitic adsorbents obtained at various reaction times.

from 6,500 to 8,000 gauss, the percentage of Fe_2O_3 in the concentrate decreases but this result suggests that it is adequate for the coal fly ash to be pretreated with 8,000 gauss of magnetic separation.

4. The Synthesis of Zeolite

The synthesis of zeolite was carried out under the various conditions of NaOH concentration (1-5 N), reaction time from 3 to 96 hours, at different temperatures of 60, 80 and 100℃, respectively.

Fig. 4 shows the results of the X-ray diffraction patterns of zeolitic adsorbents which were obtained by various concentrations of NaOH at 100℃ and 48 hours of reaction time. The main peaks of zeolitic adsorbents are at the following angles (2θ); 12.5, 21.7, 28.15 and 33.5. These patterns are very similar to N-B type synthetic zeolite (2θ angles; 12.6, 21.7, 28.1 and 33.5, 35.7) [Szostak, 1989]. It can be seen that the peaks of the zeolitic adsorbents increase with increasing the concentration of NaOH up to 4 N but rather slightly decrease at 5 N NaOH. The peaks of mullite at the 2θ angles of 16.5, 26.0, 31.0 and 33.3 decrease with the increasing concentration of NaOH. These results definity indicated that the coal fly ash could be effectively treated to zeolite by increasing the concentration of NaOH.

The X-ray diffraction patterns of zeolitic adsorbents obtained at various reaction times (3-96 h) when the temperature and concentration of NaOH were 100℃ and 4 N respectively are shown in Fig. 5. It can be seen that increasing the crystallization time from 3 hours to 48 hours increases and the intensity of peaks of zeolitic adsorbents. The highest peak is seen at 48 hours of crystallization time, but the peaks decrease and another small new peak seems to appear at 96 hours of crystallization time. Even though these new small peaks are not been able to be iden-
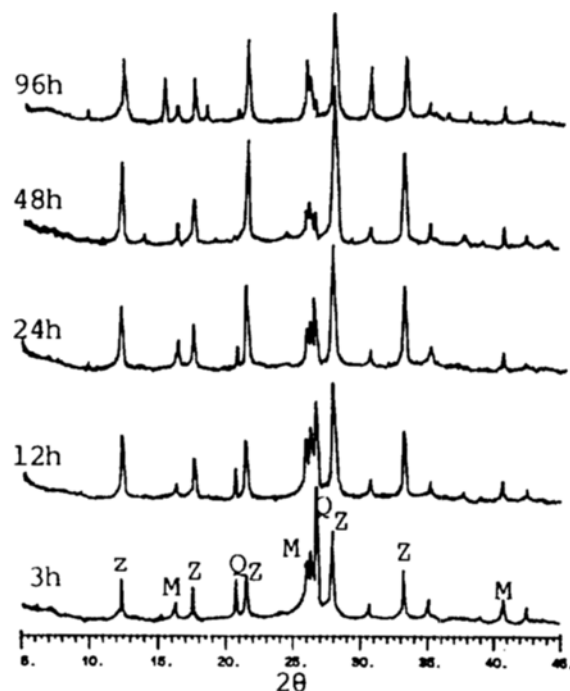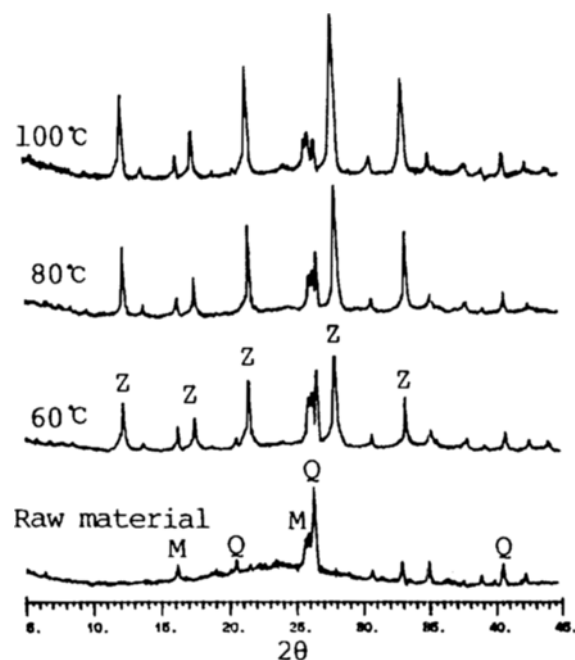

Fig. 6. X-ray diffraction patterns of zeolitic adsorbents obtained at various temperatures.

tified properly, it seems to be due to another new crystal form.

The temperature is known as a very important factor in the crystallization of zeolite. The X-ray diffraction patterns of zeolitic adsorbents obtained at various temperatures (60, 80 and 100℃) are shown in Fig. 6. The zeolitic adsorbents peaks at 100℃ are much higher than those of 60℃ and 80℃. Concurrently quartz
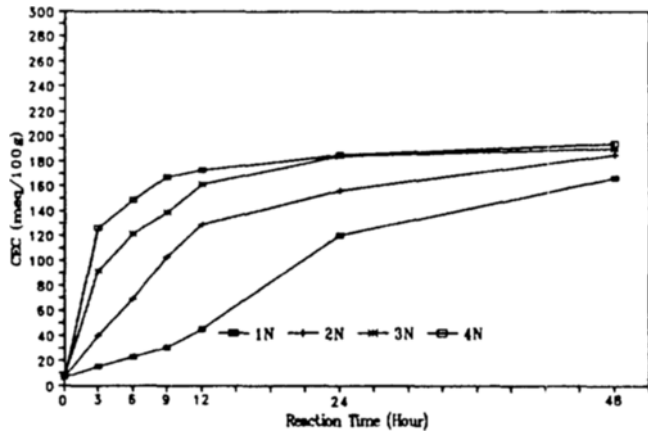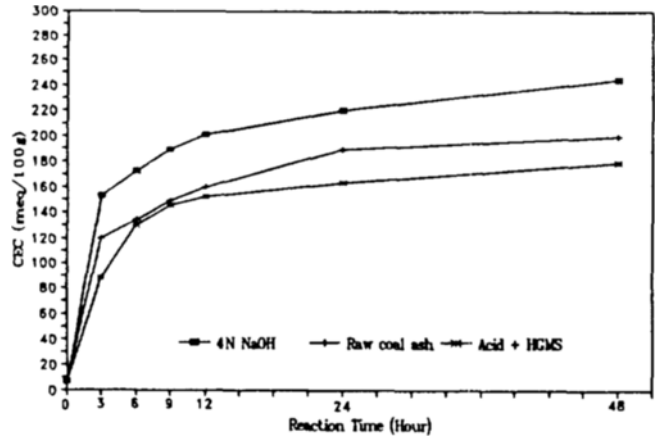
Fig. 7. The CEC vs. reaction time at 80°C.

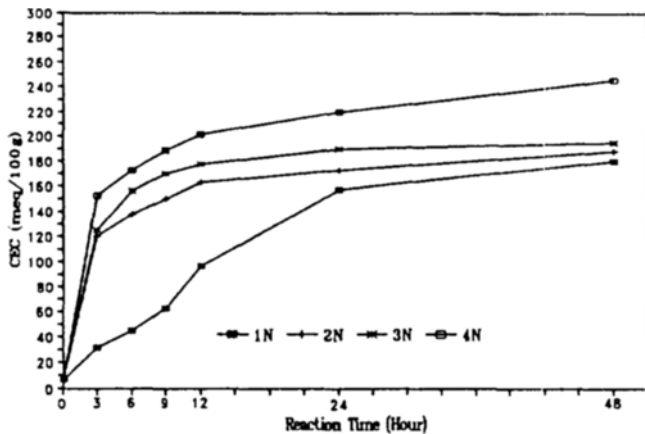Fig. 9. The CEC vs. reaction time with 4 N NaOH at 100°C with differently pretreated samples.

Fig. 8. The CEC vs. reaction time at 100°C.

Fig. 10. Scanning electron micrograph of zeolitic adsorbents.

peaks disappeared with increasing temperature and reaction time. From the above results, it is concluded that optimum conditions to synthesize the zeolitic adsorbents are with 4 N NaOH at 100℃ and for 48 hours.

The ability of cation exchange is the most important factor for zeolite as an adsorbent. The synthesis conditions for a zeolite strongly affects its adsorptive capacity as well as other properties [Sand, 1968; Shepard et al., 1963]. The changes in CEC of zeolitic adsorbents as the reaction time increases at 80℃ is shown in Fig. 7 and that at 100℃ is shown in Fig. 8. Fig. 7 shows that CEC increases with increasing reaction time and the concentration of NaOH. In the case of 1 N NaOH, CEC is very low at 45 meq/100g up to 12 hours reaction time, but it increases substantially at 24 and 48 hours and shows 120 and 166 meq/100g, respectively. More than 170 meq/100g of CEC is obtained at 4 N NaOH and above 12 hours of reaction time.

Fig. 8 shows the results at 100℃. The CEC at 100℃ is much higher than that at 80℃ (Fig. 7) and the highest value is 245 meq/100g at 48 hours of reaction time. It was learned that the results from Fig. 7 and 8 correspond with the results of X-ray diffraction patterns from Fig. 4, 5 and 6. These results indicate
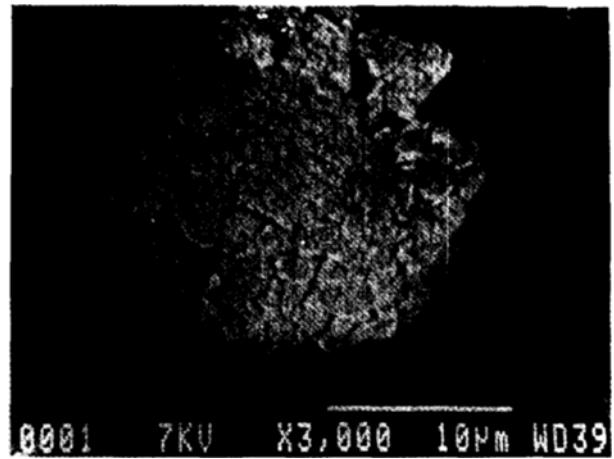
that the temperature is a very important factor in the synthesis of zeolite from coal fly ash.

Another experimental work was carried out to compare the above results (coal fly ash treated with HIMS) with the results from the coal fly ash which is treated with HIMS and 1 N H_2SO_4, and the original coal fly ash which is not pretreated. The results are shown in Fig. 9. The CEC of the coal fly ash treated with only HIMS is much higher (245 meq/100g) than that (180 meq/100 g) of coal fly ash treated by HIMS and acid and also the original coal ash (195 meq/100g). Therefore it can be concluded that acid treatment on the coal fly ash is not needed to synthesize the zeolite.

Fig. 10 shows the morphology of the zeolitic adsorbents product. Comparison of Fig. 1 and 10 show the transformation of the spheres of the original ash into porous crystalline materials. Also, the zeolitic adsorbents were chemically analysed and the result showed in Table 4. This result indicates that the amount of Na_2O and CEC were more increased than those of Table 1. On the

Table 4. Chemical analysis of zeolitic adsorbents

Comp.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	Ig.loss	CEC (meq/100g)
Ass. (%)	36.61	36.65	2.99	1.46	0.47	1.02	8.04	0.52	10.66	245

Table 5. The removal amount of ammonia by the zeolitic adsorbents

Amount of zeolitic adsorbents	0.0g	0.5g	1.0g	2.0g	3.0g
Ammonia ions (ppm)	1.51	0.64	0.57	0.51	0.45
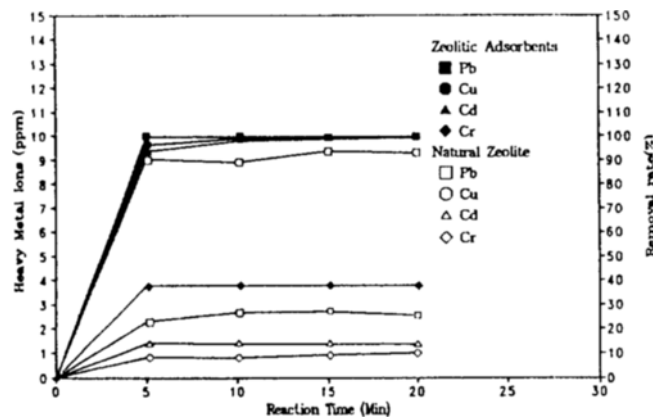
Fig. 11. Adsorption of heavy metal ions by the zeolitic adsorbents and natural zeolite.

other hand, the amount of SiO_2 was decreased.

APPLICATION OF THE ZEOLITIC ADSORBENTS TO WASTE WATER TREATMENT

The removal of heavy metal ions from waste water by using natural zeolites occur via an ion-exchange mechanism [Shin et al., 1982]. This removal property results from the selective ion exchange capacity according to the entrance size of pores and the cation exchange capacity of natural zeolites [Hara et al., 1975]. Shin et al., [1987] and Jorgensen et al., [1974] reported that zeolite was applicable to the removal of ammonia from waste water.

The 0.5-3.0 g of zeolitic adsorbents were added to 100 ml of river water having 1.51 ppm ammonia and agitated for 20 min. The supernatant solution was taken and analysed for ammonia. Table 5 shows that 1.51 ppm of ammonia is reduced to 0.64 ppm, which is 40% removal with only 0.5 g of zeolitic adsorbents in 100 ml of water. Ammonia could be reduced below 0.5 ppm which was the standard value for drinking water, with 3.0 g of zeolitic adsorbents.

Another test was carried out for the purpose of the removal of heavy metal ions using 1.0 g zeolitic adsorbents in 100 ml of sample solution which contained 10 ppm of Pb^{2+}, Cu^{2+}, Cd^{2+} and Cr^{3+} ions. The amount of adsorbed ions were calculated from the data obtained by atomic absorption spectrophotometic analysis.

Fig. 11 shows the adsorption amounts of heavy metal ions on the natural and zeolitic adsorbents with each 1.0 g according to contact time. The removal rates of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions by the zeolitic adsorbents are much higher than those by natural zeolites. However, the removal rate of Pb^{2+} ions by natural zeolite is only slightly lower than that by zeolitic adsorbents. It can also be seen that the adsorption removal rate of heavy metal ions is in the order of $Pb^{2+} \geq Cu^{2+} \geq Cd^{2+} > Cr^{3+}$. From these results, it is evident that the zeolitic adsorbents is very effective in remov-

ing either ammonia or heavy metal ions from waste water.

CONCLUSION

The coal fly ash consists of 55.2% SiO_2 and 21.5% Al_2O_3 are mainly quartz, mullite and clay mineral. It also contains 5.6% of Fe_2O_3 and 1.0% of TiO_2 which are undesirable components in the synthesis of zeolites. Ignition loss was 10.49% which might be due to the burning of coal and organic matters. The minus 200 mesh size fraction of the coal fly ash is 46 wt%, and it has low calorie as 105 kcal/kg. But the plus 100 mesh size fraction with 22.52 wt% has quite higher calorie up to 1,771 kcal/kg. And with increasing the intensity of magnetic field from 6,500 to 8,000 gauss, the percentage of Fe_2O_3 in the concentrate decreases but it increases slightly above 8,000 gauss.

The CEC of the coal fly ash treated with only HIMS is much higher (245 meq/100 g) than that (180 meq/100 g) of coal fly ash treated by HIMS and acid and also the original coal ash (195 meq/100 g). The optimum conditions to synthesized the zeolitic materials are with 4 N NaOH at 100℃ and for 48 hours and its CEC value is 245 meq/100 g.

From this result, the zeolitic adsorbents as N-B type synthetic zeolite are very applicable to removing either ammonia or heavy metal ions such as Pb^{2+}, Ca^{2+} and Cd^{2+} ions in waste water.

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