Pure, single phase, high crystalline, chamfered-edge zeolite 4A synthesized from coal fly ash for use as a builder in detergents

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Abstract

Single phase chamfered-edge zeolite 4A samples in pure form with a high crystallinity were synthesized by applying step-change of synthesis temperature during hydrothermal treatment of coal fly ash. The calcium binding capacity of these zeolite 4A samples (prepared from coal fly ash) and the commercial detergent grade zeolite 4A were tested for usage as a detergent builder. The results show that these zeolite 4A samples behaved similarly as the commercial one in removing calcium ions during the washing cycle. Moreover, from the leaching tests (evaluation of toxicological safety), the results show that these zeolite 4A samples leached the same elements (Sb, As, Se and Tl) as the commercial one with the concentrations in the same order of magnitude. This shows that the toxicological effect of the coal fly ash converted zeolite 4A was not worse than that of the commercial sample. Finally, economic and environmental aspects of converting coal fly ash to useful products were discussed.
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Keywords: Recycle; Zeolite 4A; Builder; Environmental; Cost analysis

1. Introduction

Eutrophication of natural water is a serious environmental problem that can cause the death of marine life. The use of STPP (sodium tripolyphosphate) in laundry detergents as a builder is known to be one of the prime sources for phosphate deposition in water [1]. The role of phosphates is to remove calcium and magnesium from water in order to favor the removing, solubilizing, emulsifying and suspending action of surfactants. Because of this harmful effect to the environment, zeolites have been successfully used as alternative builders in detergents to replace STPP [2]. Among the various zeolites, zeolite 4A has been extensively employed as detergent builders [3] and water softeners. Compared to phosphates, zeolites can additionally prevent the formation of poorly soluble (partially soluble) inorganic salts, which is a key factor in the formation of textile incrustations. At present, more than 1,000,000 tonnes of zeolites are used per annum in detergents and cleaning products world-wide [4]. Moreover, zeolite 4A has found widespread applications in both laboratories and industries. For these purposes, it has been manufactured industrially on a greater scale than any other zeolite [5].

Large quantities of coal fly ash are produced in electric power plants throughout the world every year. The amount of coal fly ash formed is approximately 500 million tonnes per year and is predicted to increase [6]. Efficient disposal of coal fly ash has been a worldwide issue because of the massive amount of ash produced and its harmful effects on the environment [7,8]. Coal fly ash contains a certain amount of metal oxides which will inevitably be released to the environment if coal fly ash is not converted into useful materials. As a technique for recycling coal fly ash, synthesis of zeolites from coal fly ash has received extensive attention over the last decade. By converting coal fly ash into zeolite, there is no additional burden on the environment. In addition, zeolite can also be reused after regeneration in certain applications. Many researchers have investigated the synthesis of zeolites from coal fly ash [9–33]. However, in many of these studies, the total conversion time was generally long (24–72 h or more) and the synthesis temperature was 90–225 °C. The synthetic zeolite products still contained a significant amount of residual fly ash. Moreover, the obtained zeolites, such as NaP1, sodalite, analcime, usually have a more condensed structure (low pore volume). The presence of non-zeolitic phases in the converted products limits the cation exchange capacity of the products and greatly hinders the potential applications of zeolites converted from coal fly ash. Thus, the applicability of synthetic zeolites from coal fly ash is greatly reduced.

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In spite of the large amount of studies focusing on the conversion of coal fly ash into zeolites, there are only a few studies [22,28,29] focusing on the production of pure form, single phase zeolite 4A from coal fly ash. Hollman et al. [22] adopted a two-stage synthesis method to synthesize pure form zeolites such as zeolite X, zeolite 4A (with some traces of sodalite) and NaP1. They adopted an extraction process to extract Si source from coal fly ash, and with the addition of Al source, to synthesize zeolites from the extracted solution. At a synthesis temperature of 90 °C, the reaction time was 48, 48 and 67–72 h for the synthesis of zeolite X, NaP1 and zeolite 4A (with some traces of sodalite), respectively. Chang and Shih [28] used a fusion method to synthesize zeolite A and the reaction time was 3 days at 60 °C. From these studies, synthesis of zeolites usually take a long time (24 h–3 days). Tanaka et al. [29] have synthesized pure form and single phase zeolite 4A from waste solutions. The reaction time was 24 h at 85 °C. These synthesized zeolite 4A samples were of a cubic shape which has little usage as a builder in detergents. For potential industrial applications, processes to synthesize pure form, single phase, highly crystalline zeolite 4A from coal fly ash that requires a shorter total synthesis time should be explored.

Recently, Hui and Chao [34] have successfully applied a temperature step-change method in synthesizing pure, single phase, highly crystalline, chamfered-edge zeolite 4A from coal fly ash with a reduced synthesis time (total synthesis time is around 4 h). This has enabled a wider use of coal fly ash converted zeolite products in various industrial and environmental protection activities [35]. In our previous work [35], the heavy metal ions could be removed by zeolite samples within 60–90 min of operation which is acceptable for applications in wastewater treatment. However, for domestic application of zeolite 4A as a detergent builder in laundry to remove calcium ions in the water, the operation time is short, usually within 16 min. Compared to the previous study [35], the current study investigates another potential application (as a detergent builder) of coal fly ash prepared zeolite samples. The main aim of the present work is to utilize pure, single phase, highly crystalline, chamfered-edge zeolite 4A samples (prepared from coal fly ash) to remove Ca^{2+} ions in water. Moreover, toxicological safety of zeolite 4A samples (prepared from coal fly ash) was also evaluated through the leachability of elements after the washing cycle, where a comparison of the elements leached by coal fly ash prepared and commercial detergent grade zeolite 4A samples was conducted. The economic and environmental aspects of converting coal fly ash to useful products were also addressed. It is hoped that the more applications of coal fly ash prepared zeolite sample explored, the more effort will be devoted to the conversion of coal fly ash into useful materials.

2. Materials and methods

2.1. Adsorbate and adsorbent

All the compounds used to prepare the reagent solutions were of analytic reagent grade. "Hardness water" containing 0.001 and 0.002 M $CaCl_2$ were prepared by dissolving a weighed quantity of the respective chloride salts in deionized water. A commercial detergent grade zeolite 4A (Valfor 100) from PQ Chemicals (Thailand) Limited and pure, single phase, chamfered-edge zeolite 4A (prepared from coal fly ash) were used. The coal fly ash prepared zeolite 4A samples were synthesized by the effect of step-change of synthesis temperature during the hydrothermal treatment. Generally, a mixture of 30 g of fly ash and 300 ml of 2 M NaOH solution in a 1 l sealed PP bottle was kept in an oil bath at 100 °C for 2 h under stirred condition (300 rpm). Then, the solution was separated from the mixture by a filtration process. The molar ratio SiO_2/Al_2O_3:Na_2O/SiO_2:H_2O/Na_2O in the solution was adjusted to 1.64:8.09:56.51 by adding 100 ml of aluminum solution. The purpose of the addition of 100 ml aluminum solution was to control the molar ratio of the solution for subsequent synthesis of pure zeolite 4A from the coal fly ash extracted solution. With the addition of the aluminum solution, it was shown that pure, single phase and highly crystalline zeolite 4A sample could be easily synthesized from coal fly ash. The solution was then stirred (500 rpm) for 30 min at room temperature (25 °C) and was synthesized at the first temperature of 90 °C for 1.5 h and subsequently at the second temperature of 95 °C for 2.5 h. The coal fly ash prepared zeolite 4A samples were then pretreated with 1 M NaCl for 24 h at 25 °C before running the calcium binding capacity experiment. The purpose of the pretreatment was to bring the zeolite 4A near homoionic form (Na-form) so as to increase its effectiveness in the uptake of Ca^{2+} ions. Detailed information about the synthesis of the adsorbents converted from the coal fly ash can be found in Ref. [34].

2.2. Characterization

The zeolite 4A samples prepared were characterized by various methods. The solid products were characterized by powder X-ray diffraction (XRD) using a Philips PW 1830 diffractometer with Cu Kα radiation (1.5406 Å). The accelerating voltage and current used were 40 kV and 20 mA, respectively. XRD was used to estimate the degree of crystallinity of zeolite 4A employing a quantitative analysis based on the 'peak summation' procedure [36]. Accordingly, the areas under the most intense peaks, corresponding to the crystallographic planes (1 0 0), (1 1 0), (1 1 1), (3 1 1), (3 2 1), (4 1 1) and (3 3 2) were evaluated by the Traces analytical software and summed. The sample showing the maximum value of total area (T90(1.5 h)–T100(8 h)) was selected as a reference for evaluating the percentage of crystallinity. The degree of crystallinity of other samples was evaluated with respect to this reference value. The reported crystallinity of the samples is a relative crystallinity as a reference to sample T90(1.5 h)–T100(8 h). SEM images of coal fly ash and the samples were obtained using JEOL-6300 coupled with energy dispersive X-ray analysis (EDAX). All samples were gold coated prior to measurement. All metal concentrations were analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Perkin-Elmer 3000 XL). The samples were usually diluted five times by deionized water. Therefore, the concentrations of metal ion solutions should be in the range of 0–60 mg/l. The calibration standards were prepared using

standard solutions which was certified by the supplier. Three calibration standards (20, 40 and 60 mg/l) and a blank solution were used to calibrate the equipment. A linear calibration curve was obtained after calibration. If the correlation coefficient R^2 were <0.999, the machine was re-calibrated to ensure the accuracy of results. The samples were automatically measured three times in one aspiration. If the standard deviation of the test results were >1%, the samples were measured again until the test results fulfilled the analysis requirement. All the instrumental conditions were optimized for maximum sensitivity as indicated by the manufacturer's manual. Although there are different methods to interpret the mean and the span of samples, they will give qualitatively similar results. Work of Koroglu et al. [37] provides a way to interpret the mean and the span of samples based on laser beam scattering technique. To ensure consistency in the method and for ease of comparison, the method used in our previous studies [34,35] was adopted in the current study. The particle size measurements were performed by laser beam scattering technique (Coulter LS230). From the particle size distribution (PSD) curves obtained, the sizes, of which 10, 50 and 90 vol.% of the particles in the samples were smaller, could be determined [37–40]. These particle sizes (by volume) were denoted by $d(0.1)$, $d(0.5)$ and $d(0.9)$, respectively. The particle size, of which 50% of the particles in the sample is smaller, represents the average crystal diameter. The size span of the zeoilte 4A samples were calculated by using the following equation:

$$\text{span} = \frac{d(0.9) - d(0.1)}{d(0.5)} \tag{1}$$

where span is a measure of the width of the size distribution and smaller span values were obtained when narrower distribution exists.

In the study of Kuhl and Sherry [41], it was shown that at room temperature (25 °C) the percentage of Mg^{2+} ions removed by zeolite 4A was limited. This is due to the strong salvation tendency of Mg^{2+} ions forming bulky complex ions with water molecules. In addition, in the study of Mao et al. [42], it was reported that at room temperature (25 °C), the percentage of Ca^{2+} ions removed by zeolite 4A was 3.8 times higher than that of Mg^{2+} ions. In our study, experiments were carried out at room temperature (25 °C) and a commercial detergent grade zeolite 4A was also used to compare the performance of the coal fly ash prepared zeolite samples in the treatment of hardness water. It is believed that the potential application of the coal fly ash prepared zeolite samples as a detergent builder could be addressed from the performance of removing Ca^{2+} ions in tested hardness waters [41–43]. The calcium binding capacity of the zeolite 4A samples was determined as follows. "Hardness water" containing 0.001 and 0.002 M $CaCl_2$ (corresponding to 100 and 200 mg/l $CaCO_3$ hardness, respectively) were used in the study. At 25 °C, 0.1 g zeolite 4A sample was stirred vigorously (500 rpm) for 16 min with 100 ml of the "hardness water". The zeolite 4A sample was removed immediately by filtration. The filtrate was collected, acidified and analyzed for calcium ions (in mg/l) by inductively coupled plasma atomic emission spectroscopy (ICP-AES). In order to obtain the calcium binding capacity, the amount of ions adsorbed per unit mass of adsorbent q_e (in milligrams of metal

ions per gram of adsorbent) was evaluated using the following expression:

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{2}$$

where C_0 is the initial metal ions concentration (mg/l), C_e the equilibrium metal ion concentration (mg/l), V the volume of the aqueous phase (l), and m is the amount of adsorbent used (g). The removal efficiency of metal ions by adsorbent is given as a percentage as

$$\text{removal efficiency} = \frac{C_0 - C_e}{C_0} \times 100 \tag{3}$$

The cation exchange capacity (CEC) of zeolite 4A was determined by measuring the net amount of Na^+ ions in the solution after 16 min. The CEC is defined as the net increase (mmol) of Na^+ ions in the solution per gram of sample, thus the unit mequiv/g, provided that equilibrium of the ion exchange reaction was attained.

3. Results and discussion

3.1. Characterization of the coal fly ash, the synthesized zeolite 4A samples and the commercial detergent grade zeolite 4A

Fig. 1 shows the XRD pattern of the coal fly ash. It was found that quartz (SiO_2) and mullite ($3Al_2O_3\cdot2SiO_2$) existed as crystalline substances in the coal fly ash, as identified by the sharp peaks. Trace phases of calcite, portlandite, anhydrite, hematite and gehlenite were also identified. The presence of these minerals in the fly ash may be from either the products of lignite combustion or the result of soaking the fly ash during its transportation by conveyor belt from the power plants to the ash disposal areas [44–46]. The presence of amorphous phases was identified by the presence of the broad diffraction peak (near $2\theta = 24°$). The coal fly ash used in this study was spherical and had a smooth surface (0.04–600 μm with a mean diameter of
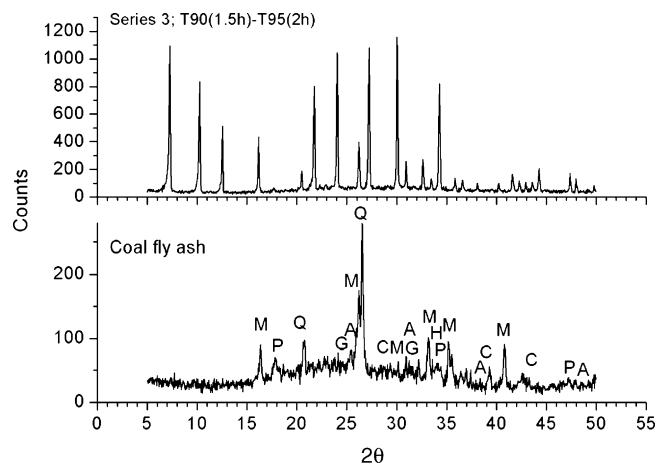

Fig. 1. XRD pattern of the coal fly ash and the representative zeolite 4A sample synthesized from the coal fly ash. M, Q, C, P, A, H and G represent mullite, quartz, calcite, portlandite, anhydrite, hematite and gehlenite, respectively.

20.7 µm). Fig. 1 shows the representative XRD pattern of zeolite 4A sample synthesized from coal fly ash. All zeolite 4A samples were identified as a single phase zeolite 4A (JCPDS card 43-0142). Fig. 2 shows the SEM picture of the synthesized zeolite

4A samples and the commercial detergent grade zeolite 4A. The morphology of synthesized zeolite 4A samples (Fig. 2a–g) and the commercial detergent grade zeolite 4A (Fig. 2h) were of a chamfered-edge shape. The mean diameters of synthesized zeo-
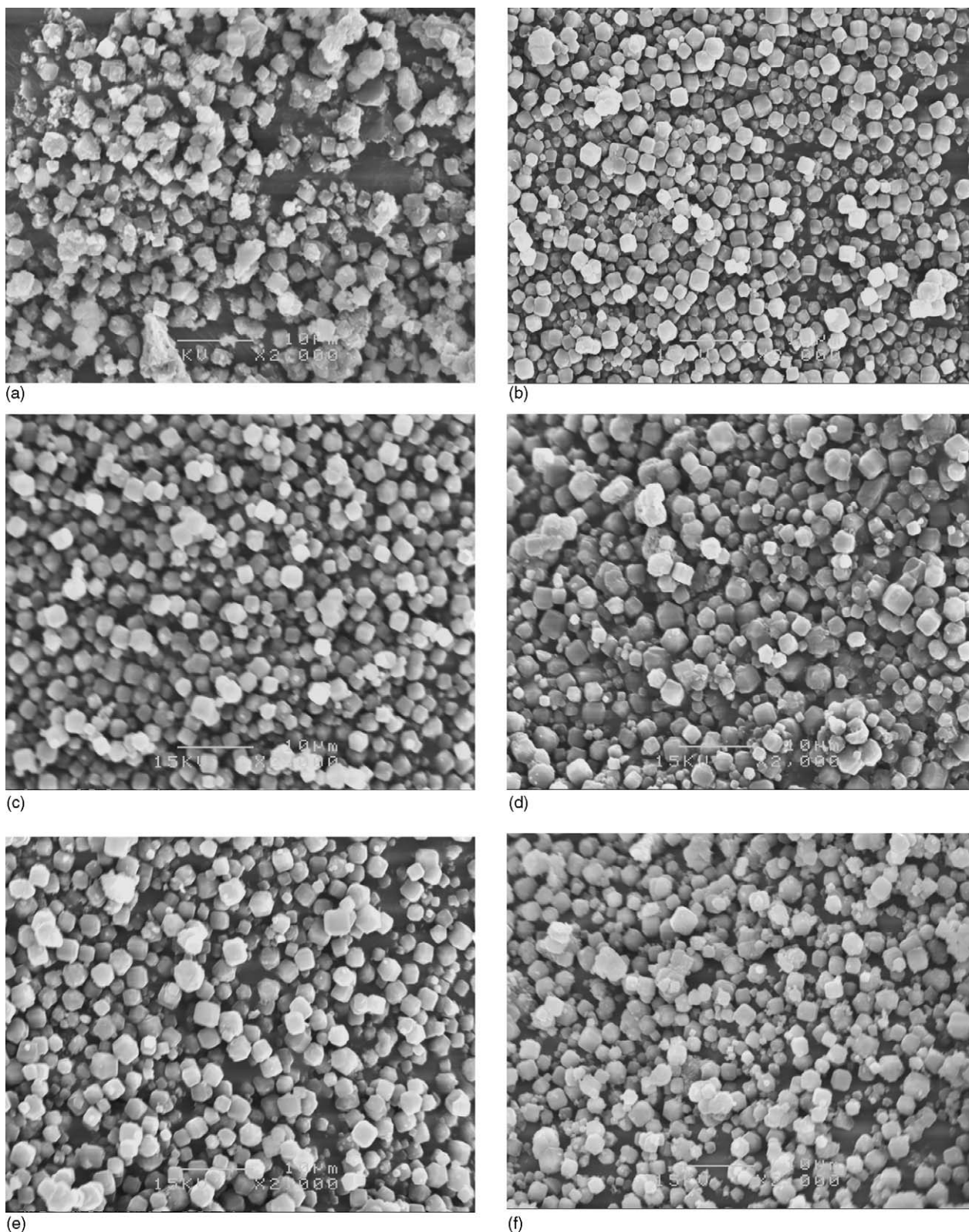

Fig. 2. SEM pictures of zeolite 4A samples. All images use the same scale bar and the length of the scale bar represents 10 µm. The sharp scale bar of (c) can be used as a reference.
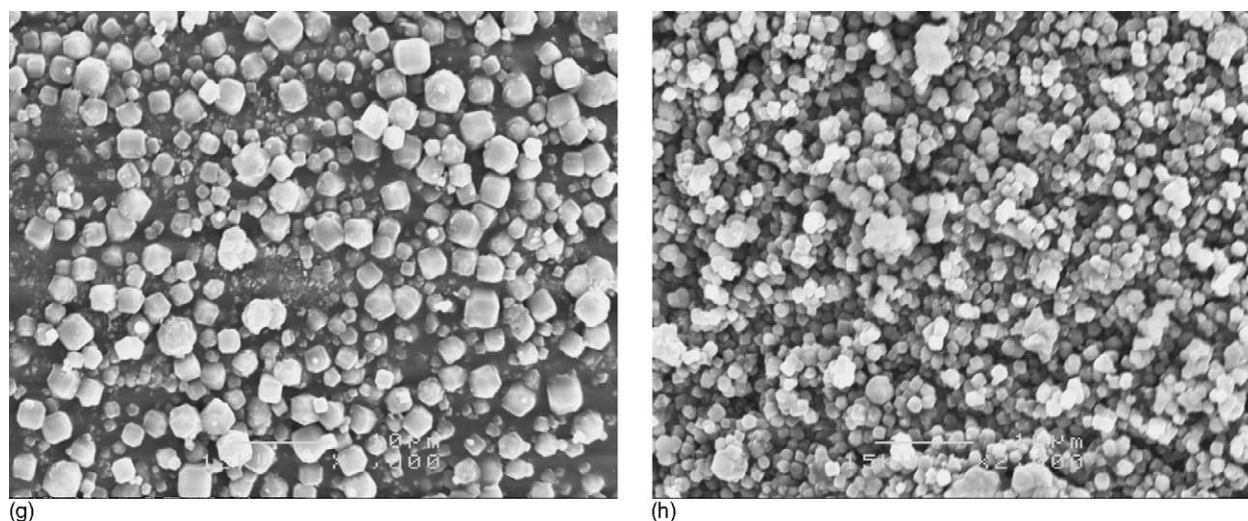
Fig. 2. (*Continued*).

lite 4A samples and the commercial detergent grade zeolite 4A were 2–4.5 and 2 μm, respectively. The main components of the coal fly ash and the synthesized pure, single phase, chamfered-edge zeolite 4A samples were oxides of Si and Al, and various metallic oxides as shown in Table 1. Apparently, the presence of impurities such as Fe, Ti, Mn, etc., in the synthesized zeolite samples may be due to the incorporation of these elements during crystallization. These elements were thought to be present as soluble oxides in coal fly ash and were expected to form oxyanions upon dissolution under alkaline conditions during the extraction of Si source from coal fly ash.

3.2. Calcium binding capacity of zeolite 4A samples

In the current study, all samples were identified as zeolite 4A. In addition, the particle sizes of these samples were similar showing the same order of magnitude. It is assumed that

the influence of various factors (nature of the material, crystal size, and the existence of surface Lewis base sites or Bronsted acidic, and Lewis acidic sites of the sample) on the ion exchange behavior of the samples will not be significant. It is hypothesized that the calcium binding capacity of the samples is mainly due to ion exchange taking place within the zeolite cavities. The $CaCO_3$ removal efficiency and calcium binding capacity (expressed in terms of $CaCO_3$), and CEC values of selected samples are depicted in Fig. 3. At 100 mg/l $CaCO_3$, all selected zeolite 4A samples attained 100% removal of Ca^{2+} ions, with a similar CEC value of 1.9. At 200 mg/l $CaCO_3$, removal of $CaCO_3$ was reduced to 82–94%, with CEC in a range from 3.1 to 3.6. The calcium binding capacity of zeolite 4A samples increased from 92.4–102.7 to 142.5–188.5 mg of $CaCO_3$ per gram of zeolite 4A when the initial water hardness was increased from 100 to 200 mg/l $CaCO_3$. This probably indicates that the maximum calcium binding capacity of zeolite 4A has not been

Table 1
Characterization of the coal fly ash, the synthesized zeolite 4A samples and the commercial detergent grade zeolite 4A

wt.%	Coal fly ash	1; T80(1.5 h)–T90(6.5 h)	1a; T80(1.5 h)–T95(5.5 h)	2; T85(1.5 h)–T95(4 h)	3′; T90(1.5 h)–T95(2.5 h)	3; T90(1.5 h)–T95(3.5 h)	4; T90(1.5 h)–T90(3.5 h)	5; T95(1.5 h)–T95(3.5 h)	Valfor 100
SiO_2	50.09	43.17	43.48	43.69	43.30	42.85	42.81	42.65	44.68
Al_2O_3	24.91	35.34	35.44	35.70	35.70	35.22	35.32	35.40	34.91
Na_2O	0.14	20.25	20.03	19.67	19.73	20.55	20.57	20.55	20.12
CaO	11.77	0.01	0.03	0.03	0.02	0.03	0.01	0.03	0.02
Fe_2O_3	7.6	0.46	0.62	0.62	0.79	0.90	0.77	0.85	0.03
MgO	0.4	0.30	0.10	0.15	0.21	0.22	0.27	0.28	0.18
TiO_2	1.17	0.01	0.01	0.02	0.02	0.02	0.01	0.02	0.01
K_2O	1.19	0.42	0.27	0.09	0.07	0.21	0.20	0.22	0.05
MnO	0.1	0.02	0.02	0.02	0.03	–	0.03	–	–
Si/Al mole ratio[a]	1.7	0.98	0.88	0.98	0.98	0.98	0.94	1.08	1.08
Span	n.a.	2.31	1.72	1.80	1.60	1.56	1.91	1.79	1.53
Crystallinity (%)	n.a.	78.7	94.9	85.8	65.8	54	60.8	58.6	86.1
BET surface area ($m^2 g^{-1}$)	1.38	60.32	62.12	64.54	65.64	63.87	64.12	64.56	71.41

n.a, Not available.
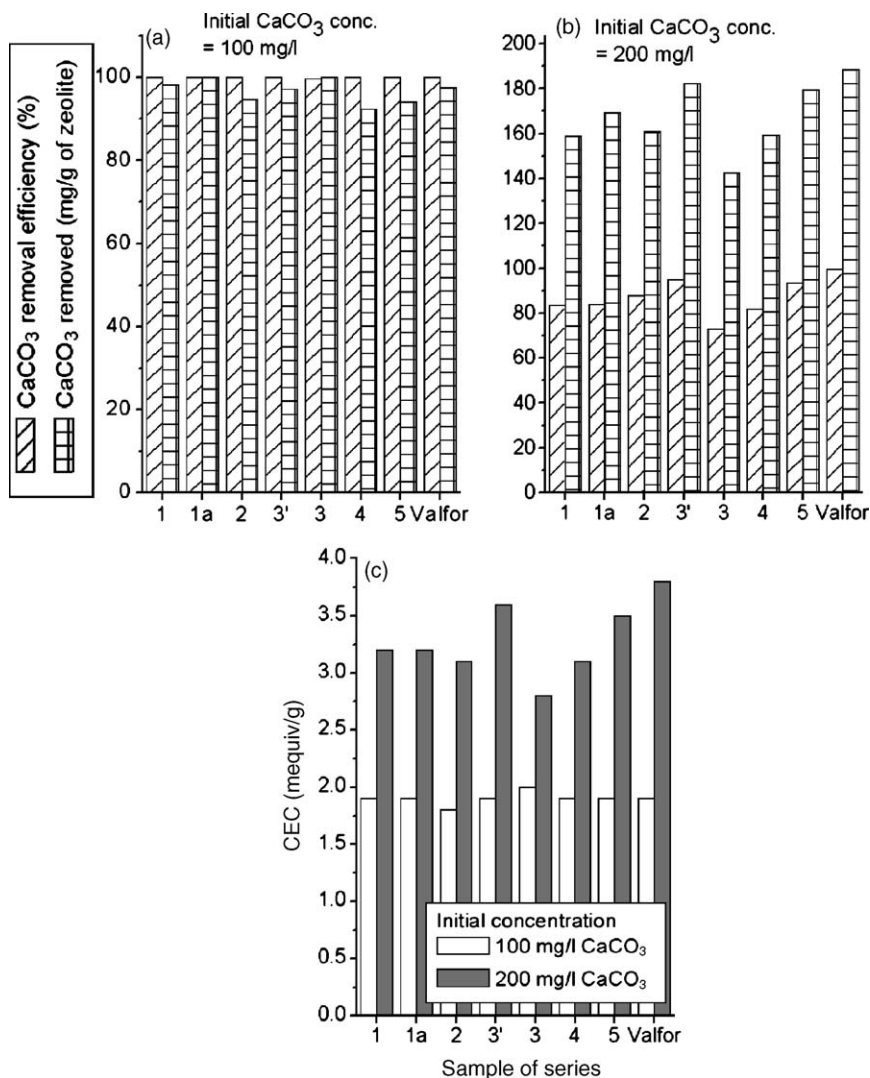[a] Values were determined by SEM-EDX.

Fig. 3. (a and b) Removal performance of CaCO$_3$ by zeolite 4A samples. (T, 25 °C; stirring speed, 500 rpm; time, 16 min; V, 100 ml; m, 0.1 g of zeolite 4A), (c) CEC of zeolite 4A samples (T, 25 °C; stirring speed, 500 rpm; time, 16 min; V, 100 ml; m, 0.1 g of zeolite 4A).

reached when the initial water hardness was 100 mg/l CaCO$_3$. It should be noted that metal precipitation (Ca(OH)$_2$) during the calcium binding capacity tests was virtually negligible as the pH of the solutions increased from an initial value of 5.78 to an equilibrium value of <9.79 which was well below the pH for minimum solubility (pH 12.91 for 40 mg/l of Ca^{2+} ions (100 mg/l CaCO$_3$), pH 12.76 for 80 mg/l of Ca^{2+} ions (200 mg/l CaCO$_3$)) [47]. As a result, the metal ion removal mechanism in this study was governed by the ion exchange and the adsorption processes. It is worth noting that series 3′ (sample (T90(1.5 h)–T95(2.5 h)), having the shortest overall synthesis time, achieved a relatively high calcium binding capacity in both hardness water cases. The prime function of the builder in laundry detergents is to remove the hardness ions, like Ca^{2+} ions, in the water so as to prevent the formation of poorly soluble inorganic salts which is a key factor in the formation of textile incrustations. In addition, it also ensures the effectiveness of the surfactants. The synthesized zeolite 4A samples can provide this function as they have a high calcium binding capacity which is comparable to commercial detergent grade zeolite 4A (Valfor 100).

3.3. Toxicological safety of zeolite 4A samples prepared from coal fly ash

Synthetic zeolite 4A from pure chemicals has undergone intensive toxicological studies and has been shown to be non-toxic to living organisms [48,49]. In particular, no allergenic or irritancy potential was identified upon skin contact or inhalation. Furthermore, zeolite 4A has no acute systemic toxic properties if swallowed. It has been demonstrated in controlled exposure tests with zeolite-based detergents [50] that potential residues of zeolite 4A on textile fibers pose no hazard to the consumer.

In order to investigate if there was any toxic element leached from the zeolite 4A samples (prepared from coal fly ash) during the washing cycle, a comparative study of the differences between the coal fly ash prepared zeolite 4A and the commercial detergent grade zeolite 4A was conducted. After the washing cycle (16 min), elements (such as Al, Sb, As, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Si, Ag, Tl, Zn and Ti) in the water were examined by ICP-AES. Fig. 4 shows the various trace
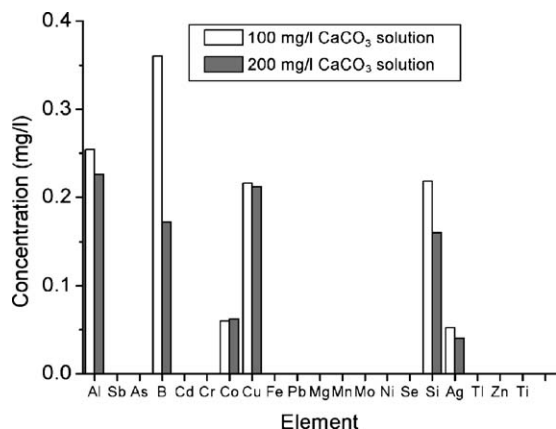
Fig. 4. Concentration of various trace elements in the synthetic hardness water solutions.

elements in the synthetic hardness waters (100 and 200 mg/l CaCO$_3$) used in this study. As can be seen, the synthetic solutions only contained very low concentrations of Al, B, Co, Cu, Si and Ag elements. Fig. 5 shows the only detected elements after the washing cycle by different zeolite samples. For the 100 mg/l CaCO$_3$ solution, the amounts of leached elements by zeolite 4A samples (prepared from coal fly ash) were: Sb, from 0.104 to 0.144 mg/l; As, from 0.124 to 0.212 mg/l; Se, from 0.01 to 0.144 mg/l; Tl, from 0.066 to 0.15 mg/l, whereas by commercial zeolite 4A, the amounts were 0.118, 0.114, 0.064 and 0.16 mg/l for Sb, As, Se and Tl, respectively. For the 200 mg/l CaCO$_3$ solution, the amounts of leached elements by zeolite 4A samples (prepared from coal fly ash) were: Sb, from 0.102 to 0.152 mg/l; As, from 0.118 to 0.19 mg/l; Se, from 0 to 0.1 mg/l; Tl, from 0.07 to 0.196 mg/l, whereas by commercial zeolite 4A, the amounts were 0.162, 0.134, 0.118 and 0.046 mg/l for Sb, As, Se and Tl, respectively. This shows that the amount of leached elements is dependent on the initial CaCO$_3$ concentration. In addition, the amount of leached elements by different zeolite samples is of the same order of magnitude. Apparently, the presence of leached elements Sb, As, Se and Tl after a washing cycle may be due to the incorporation of these elements in coal fly ash prepared zeolite samples during the crystallization. These elements were
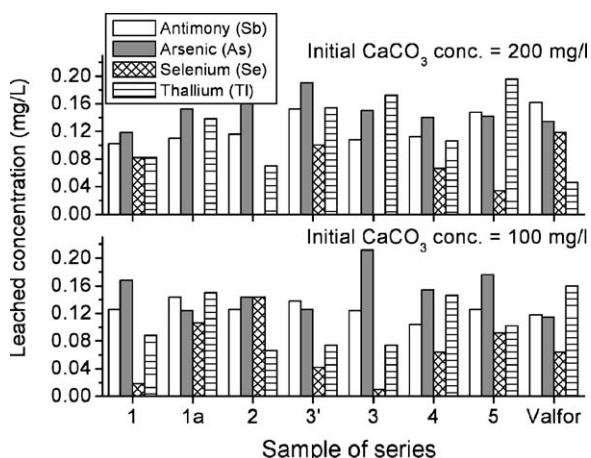
thought to be present as soluble oxides in coal fly ash and were expected to form oxy-anions upon dissolution under alkaline conditions during the extraction of Si source from coal fly ash. Regarding the release of these elements, the results show that the coal fly ash prepared samples do not pose any serious threat to the environment when compared with commercial grade zeolite 4A.

3.4. Economic and environmental aspects of recycling coal fly ash to produce useful products

Converting what was previously a waste material from an industrial process into a useful product has several important features from an economic perspective [51]. Taking coal-burning power industry as an example, coal is one of the major inputs in the electric power production industry competing with nuclear, oil, water, wind, and solar resources. Any method to turn the by-product of coal-based electricity generation, such as coal fly ash, into a useful commodity is bound to have a major impact on the economics of power generation and would affect other methods of power generation [52]. After combustion of coal, coal fly ash has to be hauled away and put into appropriately designed landfills resulting in costs to a power plant. All these costs are factored in when the company designs and operates its production processes, and consequently affect the prices of the products. However, when proper methods are developed and applied for the recycling/reuse of the coal fly ash, it may have a positive economic value which may result in increasing the profits of the company due to better utilization of the waste. Reuse of coal fly ash may provide a new source of revenue for the company and may offset expenses associated with its disposal. In the environmental aspect, the increased use of coal fly ash can reduce energy consumption, reduce the need for additional landfill space, and conserve natural resources. For example, a tonne of coal fly ash, compressed to 70 pounds per cubic foot, generally takes up approximately 28 cubic feet of landfill space and each tonne of coal fly ash used reduces the need for 1 tonne of virgin resources (e.g. limestone, gypsum, sand and soil) [53].

Generally, coal fly ash can be sold to industries such as highway construction [53] and land reclamation [54]. However, the demand for re-using coal fly ash in the mentioned projects is limited. Instead of dumping coal fly ash in landfill sites or lagoon, recycling of coal fly ash (conversion to zeolite products) may be a profitable approach, or can be used to offset dumping costs. In our previous studies, we showed that the coal fly ash could be converted to pure form zeolite 4A and the residuals from the conversion process could also be converted to adsorbents [35]. The yielding (quantity) of pure zeolite 4A is around 15–18% [34]. Compared with commercial zeolite 4A, these adsorbents performed in a similar manner in the removal of mixed heavy metal ions in synthetic wastewater [35]. In order to evaluate the feasibility of recycling coal fly ash from an economic point of view, a cost analysis was conducted. The marginal cost to produce zeolite products from 1 tonne of coal fly ash (production cost, P, HK\$/tonne of coal fly ash used) was calculated, where P should be lower than the dumping cost per tonne of coal fly ash (dumping cost, D, HK\$/tonne of coal fly ash dumped). Formula

Fig. 5. Elements leached after the washing cycle by different zeolite 4A samples.

on which the cost analysis is based is shown below:

profit from sale of pure form zeolite 4A + profit from sale of the residual adsorbents $> -D$

$$(HC - P)Y + (LC - P)(1 - Y) > -D$$
$$P < D + LC + (HC - LC)Y$$

where HC is the selling price of pure zeolite (HK\$/tonne of zeolite), LC the selling price of low quality zeolite (HK\$/tonne of zeolite), Y the percent of yield of pure zeolite. A cost analysis can be performed by using information from power generators in Hong Kong. In 2004, the combined annual production of fly ash from the two local power stations was 806,000 tonnes [55,56]. An amount of 719,000 tonnes of the fly ash was re-used, while the rest (87,000 tonnes) was dumped in landfills or lagoon. Although there is currently no charging scheme for dumping of coal fly ash in Hong Kong, the government has established a charging system so as to reduce the waste being disposed of. One example is the construction waste disposal charging scheme which was launched recently [57], and it is believed that other charging schemes would follow a similar logic and arrangement. It costs HK\$ 125 to dispose of 1 tonne of construction waste in landfill sites in Hong Kong. The amount is quite close to the dumping cost of 1 tonne of solid waste (HK\$ 183) calculated from another project conducted in the US [58]. In the cost analysis, $D = 200$ was selected which includes the cost of transportation of coal fly ash, HC = 8000, LC = 960 (these values are obtained from reference [59] which can reflect the prices of pure zeolite product and the residual adsorbents), $Y = 5\%$ (this is a conservative value compared with the lab-scale data). In order to make recycling of coal fly ash more economically feasible compared to dumping of coal fly ash, P needs to be smaller than HK\$ 1512/tonne of coal fly ash. The cost analysis shows that P increases with increasing Y, i.e. the more pure zeolite products produced the less restricted to the production cost P. The production cost P is related to the location, construction and maintenance of the zeolite synthesis plant, raw materials cost and labor cost. From the cost analysis, it shows that converting fly ash into pure zeolite and the residual adsorbents may be beneficial to the thermal power stations from both economic and environmental aspects.

4. Conclusion

The present study showed that the coal fly ash converted zeolite 4A samples were effective in removing calcium ions in water during the washing cycle compared with the commercial detergent grade zeolite 4A (Valfor 100). From a toxicological safety point of view, the coal fly ash converted zeolite 4A samples behaved in a similar manner to the commercial one. The synthesized zeolite 4A samples may be suitable for use as a builder in detergents considering its purity, crystallinity, morphology, particle size and ion exchange capacity. Economic and environmental aspects of recycling coal fly ash (conversion to zeolite products) were addressed. From an economic point of view, the marginal cost to produce zeolite products from 1 tonne of coal fly ash was suggested. It is hoped that the high quality of

zeolite 4A samples prepared from the coal fly ash by a novel recycling method could bring about a new and alternative approach for massive recycling of coal fly ash.

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