

# Modification of Synthetic Zeolite Pellets from Lignite Fly Ash A : The Pelletization

Chaiwat Rongsayamanont<sup>1</sup>, Khajornsak Sopajaree<sup>2</sup>

<sup>1</sup>Chiang Mai University, Department of Environmental Engineering, Muang, Chiang Mai, Thailand;

<sup>2</sup>Associated Professor, Chiang Mai University, Department of Environmental Engineering, Muang, Chiang Mai, Thailand

KEY WORDS : synthetic zeolite, coal fly ash, waste utilization, surface area, pore forming agent, Na-P1

## ABSTRACT

The possibility of the use of synthetic zeolites from coal fly ash as adsorbent in water purification has also been investigated in a number of studies but the development of its another form with more appropriate for real industrial application has not been clarified adequately. This study focuses on modification zeolite synthesized from coal fly ash in pellet form by simple ceramic technology. The XRD results showed that our zeolite, which was hydrothermally synthesized (1 M of NaOH solution at 110<sup>0</sup>C 1 atm 96 hr) from Mae Moh Coal Fired Power Plant in Thailand, were Na-P1 type (JCPDS 39-0219) which is the typical product by zeolitization of coal fly ash and preferable to achieve a high CEC values (2.49 meq/g). These pellets were prepared by wet granulation of zeolite Na-P1 with bentonite used as a binder and Poly(Vinyl) Alcohol (PVA) ,which play in 'pore forming agent' role, was added during the pelletization. For temperatures effect study, the heating temperatures was optimized through some physical properties after PVA burnout. When the temperature was increased, a mechanical strength was gradually increased until 800<sup>0</sup>C and had been rapidly increased after 800<sup>0</sup>C . While its apparent density had been rapidly decreasing at 800<sup>0</sup>C and then increased after that. For modifying pellet study, the specific surface area was increased with increasing PVA content after burnout at selected temp as 800<sup>0</sup>C (maximum 28.68 sq.m/g at 15% PVA content), due to leaving large pores behind. Moreover, the cation exchange capacity was increasing in the same tendency (maximum 0.55 meq/g at 15% PVA content). This may be implied that these artificial pore probably can be increasing ion accessibility. However this application still want to further study.

## 1.Introduction

The recent usage of coal, which has the largest amount of deposit as an energy source, is being reconsidered. A huge amount of coal fly ash has been discharged from electric power plants and dumped into reclaimed ground or landfill. Currently, the recycling process is an emergent subject in Thailand. The major application of

the coal fly ash is the use for concrete manufacturing due to its large amounts of silica and alumina. However this application is limited within the demand of construction materials, therefore, zeolite synthesis from coal fly ash by hydrothermal alkali treatment has been receiving a lot of attention. [1-3] The produced zeolite has high potential to be developed as a high efficient low cost adsorbent which can be applied to environmental technology for water and air purification, soil improvement, and so on. The possibility of the use of these zeolites as adsorbent in water purification has also been investigated in a number of studies [3-6] but the development of its another form with more appropriate for real industrial application has not been clarified adequately. The objective of this study was to develop synthetic zeolite in pellet form by using simple ceramic technology and to investigate its applying for wastewater decontamination.

The present study was divided into two part. Former, to developing and modifying our synthetic zeolite into pellet form and later was its applying for metal removal in wastewater.

## **2. Material and method**

### **2.1 Coal Fly ash**

Coal fly ash, was supplied from Mae Moh Coal Fired Power Plant in Thailand, was used as the raw material of zeolite synthesis.

### **2.2 Zeolite Synthesis**

NaOH was used as alkali sources for zeolite synthesis. The coal fly ash was added to 1 M alkali solution to prepare fly ash slurry. Solid-liquid ratio was 140g/350ml. In the 500 ml Volumetric flask with reflux condenser, zeolite was synthesized from the slurry under the agitation and atmospheric pressure condition at reaction temperature of 383 K. The reaction time for zeolite synthesis was 96 h.

### **2.3 Physical and chemical properties of coal fly ash and synthetic zeolite**

The physical properties of coal fly ash and synthetic zeolite were measured as follows. The chemical composition was analyzed by using an X-ray fluorescence analysis equipment. Cation exchange capacity (CEC) of sample was observed. The surface structure was observed by a scanning electron microscope (JEOL , JSM-840 A). The surface area was analyzed by using BET nitrogen sorption equipment (BET Micromeritics , Gemini 2375). The identification of crystalline materials in coal fly ash and synthetic zeolite was carried out by an X-ray diffraction equipment (Philips , 1830). And The particle size and the specific gravity was analyzed by using Laser particle size analysis equipment (Malvern Instrument , Mastersizer S) and by using pycnometer bottle, respectively.

### **2.4 Synthetic zeolite pellet**

Each 200 g. of synthetic zeolite powder was used to prepare each batch of slurry. The pore forming agent and binder added to this slurry were poly(vinyl alcohol) (PVA , degree of hydrolysis = 88 mol.%) and bentonite, respectively. The aqueous

suspension containing 0, 5, 10, 15 wt.% PVA and 100, 95, 90, 85 wt.% synthetic zeolite powder, respectively on a dry weight basis of synthetic zeolite powder by adding 10 wt.% binder on dry weight basis of each batch, were mixed together within the planetary mixer (Hobart, Kitchen Aid K555) for 3-5 min. After that the mixtures were dried in the tray dryer at  $60^{\circ}\text{C}$  to obtain a residual moisture content of 20 wt.% with respect to the mixtures and then, ground by oscillating granulator (KSL , 9-73) until pass 8# mesh which were called granules. The granules were pressed uniaxially at room temperature under the force not less than 55 Kg to produce disk-shaped green pellet (70 mm. diameter, about 44 mm. thickness).

## 2.5 Effect of temperatures on the strength and apparent density of pellet

were carried out by heating samples of green pellets which containing 15 wt.%PVA in the presence of oxygen up to  $500 - 900^{\circ}\text{C}$  for 3 hrs at a constant rate ( $10^{\circ}\text{C} / \text{min}$ ). The pellets were then cooled rapidly down to room temperature in desiccator and used to measure apparent density and hardness (Monsanto hardness tester) for finding the relationship between these properties and various temperature. Moreover, the result as a appropriated temperature will used for heating each green pellet of different amount of PVA up in the next experiment.

## 2.6 Modified synthetic zeolite pellet

The evolution of the pores and strength of green pellets with temperature were conducted on each green pellet of different amount of PVA and heated in the presence of oxygen up to a temperature from topic 2.5 for 3 hr at a constant rate ( $10^{\circ}\text{C} / \text{min}$ ). The pellets were then cooled rapidly down to room temperature in desiccator and the resulting pellets were called pellet formula 0P, 5P,10P and 15P following amount of PVA 0, 5, 10 and 15 wt.%, respectively and used to measure hardness, abrasion, cation exchange capacity (CEC), specific surface area and apparent density.

## 3. Results and discussion

### 3.1 The Physical and chemical properties of coal fly ash and synthetic zeolite

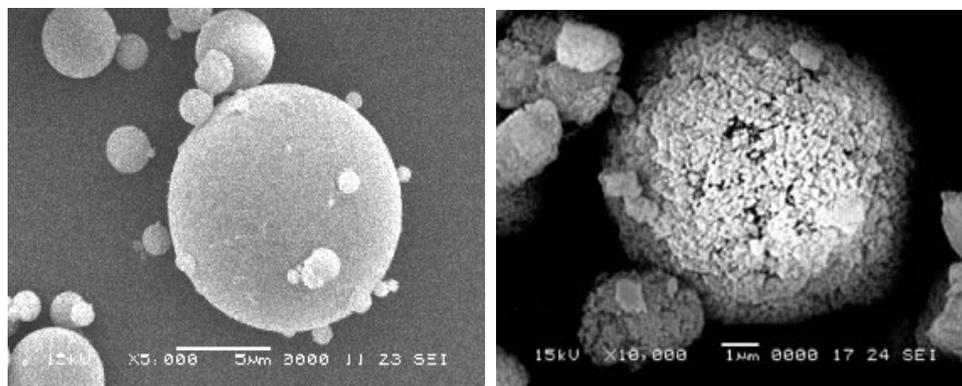


Fig.1 SEM photograph of fly ash particles x 5000 (left) and zeolite particles x 10000 (right)

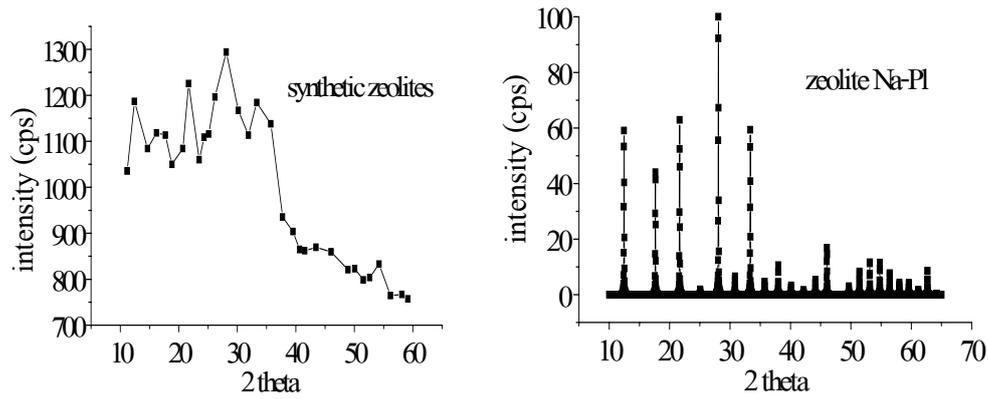


Fig. 2. XRD of synthetic zeolite (left) and zeolite Na-P1 (JCPDS 39-0219) (right) [8]

Table 1 Some properties of coal fly ash and synthetic zeolite

Properties (%wt)	Coal Fly Ash	Synthetic Zeolite
SiO <sub>2</sub>	42.38	36.10
Al <sub>2</sub> O <sub>3</sub>	23.67	19.67
CaO	13.90	12.15
Fe <sub>2</sub> O <sub>3</sub>	12.30	9.25
Na <sub>2</sub> O	1.83	5.44
MgO	2.50	2.13
K <sub>2</sub> O	2.48	1.80
TiO <sub>2</sub>	0.42	0.38
P <sub>2</sub> O <sub>5</sub>	0.18	0.16
LOI	0.64	12.83
BET (sq.m/g)	2.15	56.17
CEC (meq/g)	0.07	2.49
Avg. particle size (micron)	16.39±0.08	63.63±2.13
Specific Gravity	2.26	2.39
Zeolite	-	Na-P1 (JCPDS 39-0219)
Zeolite content (%)	-	54

Fig. 1 shows the SEM images of fly ash particles before and after alkaline treatment. The original fly ash particles had a smooth surface because the surface is covered by an aluminosilicate glass phase [9]. After the reaction, the surface became rough, indicating that zeolite deposited on the surface of fly ash particles.

Table 1 shows the physical properties and chemical composition of coal fly ash and synthetic zeolite. The amount of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> within zeolites was lower when compared to coal fly ash. This is may be due to the dissolution of aluminum-silicate in glass phase into alkaline solution during alkaline treatment and then aluminate

and silicate ions are condensed to form an aluminosilicate gel, which is a prematerial of zeolite crystal, covering the outer surface of fly ash and so, aluminate ions and silicate ions are not supplied from fly ash due to its coverage onto the particle surface. An increase in  $Na_2O$  contents of the products is caused by captured sodium ions, to neutralize the minus charge on aluminate in zeolite structure when zeolite crystal is formed [10]. The amount of Mg, Fe, K and Ca, which are impurities, were reduced. This indicated that these impurities were dissolved into alkaline solution during alkaline treatment. Moreover, the particle size of zeolite were increased compared to fly ash. This may be due to the change in the structure of fly ash in which more spaces occurred within the structure, and this resulted in the increases of specific surface area and cation exchange capacity [11].

Table 2 Summary of results for zeolite synthesized from coal fly ash by hydrothermal alkaline treatment

Si/Al	L/S (ml/g)	Synthesis Condition	Zeolite Product (%)	CEC (meq/g)	Ref.
1.27	8	NaOH 2 M 100 <sup>o</sup> C 24 hr.	Na-P1 (64)	3.0	[9]
2.20	12.5	NaOH 0.5 M 90 <sup>o</sup> C 95 hr.	Na-P1 (10-15)	0.7	[3]
1.47	2.5	NaOH 1 M 110 <sup>o</sup> C 96 hr.	Na-P1	12.7	[1]
1.52	2.5	NaOH 1 M 110 <sup>o</sup> C 96 hr.	Na-P1 (54)	2.5	Present study

After the contact between fly ash particles and 1 M of NaOH solution at 110<sup>o</sup> C under the atmospheric pressure for 96 hours, the outer part of fly ash particle, the glass phase, were dissolved into alkaline solution in the amount that higher than the Crystal phase due to its higher solubility into the alkaline solution [9]. Zeolite Na-P1 is the typical product by zeolitization of coal fly ash [7,10,12-15], is classified into the gismondine group and the pore size is 3.1 x 4.5 A<sup>o</sup> [8]. The formation of zeolite Na-P1 is preferable to achieve a high CEC values of the zeolitized fly ash [13]. The results of this experiment agree well with other studies which are summarized in table 2.

### 3.2 Effect of temperatures on the strength and apparent density of pellet

From fig. 3. showed that at 800<sup>o</sup> C, the apparent density was reduced, this is probably due to most of PVA which are organic materials and water being decomposed at high temperature. Burnout usually takes place in oxidizing atmosphere at moderately elevated temperatures and, in general, becomes complete by 600 to 700<sup>o</sup> C for pure polymers and sometimes at higher temperature in presence of ceramic powder Moreover, at this temperature it still can't be perfectly decomposed due to its 10-20 wt.% residual carbon. [16]

However, at temperatures more than  $800^{\circ}\text{C}$ , the apparent density was increased. This may be due to the pore structures of the pellets were melt down or initial sintering at higher temperatures around  $900^{\circ}\text{C}$  resulting in small pores within the pellet, thus increasing the apparent density. This explanation was supported by the hardness of the pellets in which the hardness was  $800^{\circ}\text{C}$  through  $900^{\circ}\text{C}$  due to its much shrinking. Consequently, the final temperature of  $800^{\circ}\text{C}$  was selected to be controlled for heating each green pellet of different amount of PVA up in the next experiment

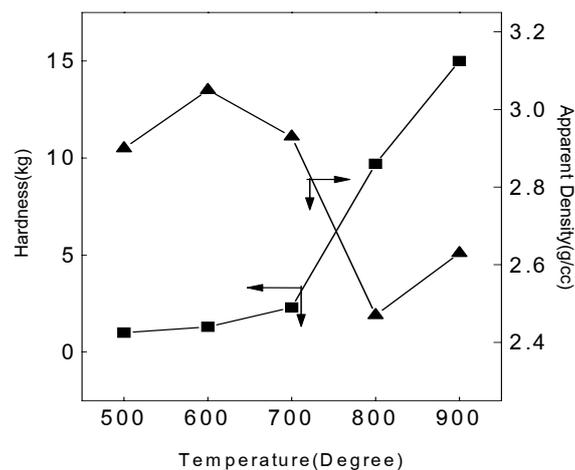


Fig. 3. Effect of heating temperature on the hardness and apparent density of synthetic zeolite pellet 15P

### 3.3 Modification of synthetic zeolite pellet

Table 3. Some properties of modified synthetic zeolite pellet in this study

Modified Zeolite Pellet	BET (m <sup>2</sup> ./g.)	App. Densiity (g/cm <sup>3</sup> )	Hardness (Kg.)	% Abrasion (%)	CEC (meq/g.)
0P	8.37	2.40	8	0.2	0.28
5P	11.88	2.48	9	0.2	0.25
10P	10.45	2.41	9	0.2	0.25
15P	28.68	2.46	10	0.1	0.55

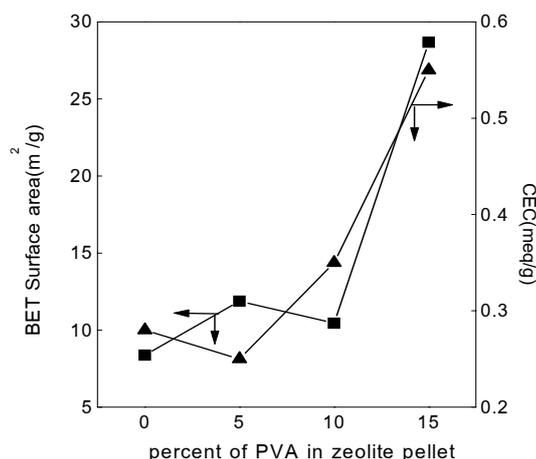


Fig. 4. Effect of the amount of pore forming agent into pellet on its specific surface area and CEC after burnout

Table 3 and fig. 4 showed the properties of modified synthetic zeolite pellet each formula after PVA burnout. As, expected, the pellet without PVA as OP formula had lowest specific surface area, moreover, it's much lower than 56.17 sq.m/g of synthetic zeolite powder. This is due to its losing external surface area for replaced to small void within the pellet after being compressed in die. In the contrast, the higher the amount of PVA added, the higher the specific area were within the pellets after burnout. An increasing in the specific surface area within pellets was probably due to PVA, which were first penetrated within the pellet, were burning out leaving large pores spreading all over the pellets [17]. In the same tendency, the higher the amount of PVA added, the higher the cation exchange capacity the pellets had. Despite the lack of the relationship between the apparent density and the cation exchange capacity which was quite complicate, an increasing in specific area may result in more surface of the pellet in which the surface have more exchange site for ion exchange process.

## 5. conclusions

For zeolite synthesis, it showed that our zeolite, which was hydrothermally synthesized (1 M of NaOH solution at 110 °C 1 atm 96 hr) from Mae Moh Coal Fired Power Plant in Thailand, were Na-P1 type (JCPDS 39-0219) which is the typical product by zeolitization of coal fly ash and preferable to achieve a high CEC values (2.49 meq/g).

Effect of heating temperatures on zeolite green pellet, the temperatures was optimized through some physical properties of synthetic zeolite pellet after PVA, which play in 'pore forming agent' role, was burning out. When the temperature was increased, a mechanical strength was gradually increased until 800 °C and had been rapidly increased after 800 °C. While its apparent density had been rapidly decreasing at 800 °C and then increased after that.

Otherwise, due to leaving large pores behind after burnout at selected temp as 800 °C, the specific surface area was increased with increasing PVA content

(maximum 28.68 sq.m/g at 15% PVA dry wt. content) for modifying pellet stage. Consequently, the cation exchange capacity was increasing in the same tendency (maximum 0.55 meq/g at 15% PVA dry wt. content). This may be implied that these artificial pore probably can be increasing ion accessibility.

For present study, however, the lack of the relationship among other properties of pellet which was quite important for this application. So, it still want to further study in more detail.

## References

- [1] Puliwekin P.(2002). "Cadmium removal from water by using zeollite synthesized from coal fly ash". M.Eng Thesis, Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, Thailand.
- [2] Thongkum M.(1999). "Zeolite synthesis form coal fly ash". M.Sci Thesis, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Thailand.
- [3] Mouhtaros T., Charistos D., Kantiranis N., Filippidis A., Kassoli-Fournaraki A., and Tsirambidis A. (2003). "GIS-type zeolite synthesis from Greek lignite sulphocalcic fly ashes promoted by NaOH solutions". *Microporous mesoporous mater.*, 61, 1-3, 57-67
- [4] Amrhein, Ch., Haghnia, G.H., Kim, T.S., Mosher, P.A., Gagajena, R.C., Amanios, T., De la Torre, L., 1996. Synthesis and properties of zeolite from coal fly ash. *Environ. Sci. Technol.* 30, 735-742.
- [5] Lin, C.F., His, H.C., 1995. Resource recovery of waste fly ash: synthesis of zeolite-like materials". *Environ. Sci. Technol.*, 29, 1109 -1117
- [6] Queral X.,Plana F.,Alastuey A., and Lopez-Soler A. (1997). "Synthesis of zeolite-like from fly ash". *Fuel*, 76(8), 793-799
- [7] Querol X.,Moreno N.,Umana J. C.,Alastuey A.,Hernandez E.,Lopez-Soler A., Medinaceli, A., Valero, A., Domingo, M.J., Garcia – Rojo, E., 2001a. Synthesis of Na zeolites from fly ash in a pilot plant scale. Examples of potential environmental application. *Fuel* 80, 857 – 865.
- [8] Treacy M. M. J., and Higgins J. B. (2001). *Collection of simulated XRD powder patterns for zeolites*. Amsterdam : Elsevier.
- [9] Inada M.,Eguchi Y.,Enomoto N., and Hojo J. (2005). "Synthesis of zeolite from coal fly ashes with different silica-alumina composition". *Fuel*, 84, 299-304
- [10] Murayama N.,Yamamoto N., and Shibata J. (2002). "Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction". *Int. J. Miner.Process.*, 64, 1-17
- [11] Breck, Donald W. (1974). *Zeolite molecular sieves: structure, chemistry, and use*. John Wiley & Sons, New York
- [12] Holler H, Wirsching U. Zeolite formation from fly ash. *Fortschr Mineral* 1985;63:21 – 43.
- [13] Querol X.,Moreno N.,Umana J. C.,Alastuey A.,Hernandez E.,Lopez-Soler A., and Plana F. (2002). "Synthesis of zeolites from coal fly ash: an overview". *Int.J.of Coal Geol.*, 50, 413-423
- [14] Steenbruggen G, Hollman GG. The synthesis of zeolite from fly ash and the properties of the zeolite products. *J Geochem Explor* 1998;62:305 – 9.

- [15] Hollman G. G., Steenbruggen G., and Janssen-Jurkovicova M. (1999). "A two – step process for the synthesise from coal fly ash". *Fuel*, 78, 1225 -1230
- [16] Barklouti S., Bouaziz J., Chartier T., and Baumard J.-F. (2001). "Binder burnout and evolution of the mechanical strength of dry-pressed ceramics containing poly(vinyl alcohol)". *J. of the Euro.Cer.Soc.*, 21, 1087-1092
- [17] Khadhraoui M., Watanabe T., and Kuroda M. (2002). "The effect of the physical structure of a porous Ca-based sorbent on its phosphorus removal capacity". *Wat.Res.*, 36, 3711-3718