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MINERAL COMPOSITION AND PROPERTIES OF MODIFIED FLYASH

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ABSTRACT

Fly ash is one of the surplus products created in the combustion process. In industry, fly ash usually refers to ash produced during combustion of coal and is usually taken from the chimneys of thermal power plants. Currently, in Vietnam burning coal to generate electric energy are necessary. Fly ash discharged occupied huge area and polluting the environment. Thus the study of fly ash recycling reasonable to reuse waste enormous resources will have economic and environmental significance. Fly ash of Pha Lai Thermal Power Plant (FA-PL) was modified in strong alkaline conditions (NaOH 3N), stirred at a temperature of 100^0C for 1h obtained with a mixture of minerals including: quartz accounts for 24 - 26%, accounting for 22-24% mullite, zeolite Na-P2 accounted for 24-26%, other types of small mineral occupies 10-16%, the rest is amorphous accounted for 8-20%. This modified product has cation exchange capacity (CEC) of 170 cmol/kg, it is 5.6 times larger than the original fly ash (30 cmol/kg). With high CEC values open up new vistas in using modified fly ash material to handle with polluted soil and water environment.

Keywords: fly ash, zeolite, CEC, heavy metals.

INTRODUCTION

The thermal power plant in Vietnam (Pha Lai, Ninh Binh) annually emit millions of tons of fly ash. In addition to applications in the industrial sector (eg cement additive), construction sector (e.g. production of lightweight concrete, road construction materials blending)... there is now some study in Vietnam to explore the possibility of using fly ash in the environmental field (Thu N.T *et al*., 2001; Chuy N.D *et al*., 2002).

Normally fly ash is gray color and includes round, smooth, can be solid or hollow particles with equivalent particle size limon (< 75μm), the density is ranged from 2.1 to 3.0 and the area surface from 170 - 1000 m^2 kg^{-1} (Roy *et al*., 1981; Tolle *et al*., 1982; Mattigod *et al*., 1990). Components of fly ash depend on the origin of coal, coal-fired facilities and the time of burning coal. The four main groups of fly ash are: anthracite, bituminous, sub-bituminous and lignite. Bituminous contain mainly silica oxide, aluminum oxide, iron oxide and calcium. Lignite and sub-bituminous contains less silicate and iron oxides, while the calcium and magnesium content higher than bituminous. Anthracite is usually only a small amount of fly ash and less common than the above groups (Ahmaruzzaman, 2010). Fly ash can find minerals like quartz, kaolinite, illite, and a number of other minerals such as calcite, pyrite or hematite. Mineralogical composition more or less affects some physic-chemical properties of fly ash (Ahmaruzzaman, 2010).

Adsorption capacity of fly ash is due to the presence of the oxide Si, Fe, Al in the composition. In addition, a factor such as porosity, surface area is large relative increases adsorption capacity of fly ash (Bayat, 2002). It has long been studied fly ash was used as a cheap adsorbent to remove heavy metals from water (Gangoli *et al*., 1975; Yadava *et al*, 1987; Feng *et al*., 2004; Alinnor, 2007), and fly ash can also be applied to the soil to limit the mobility of pollutants, especially heavy metals (Rautaray *et al*., 2003; Mittra *et al*., 2005; Kumpiene, 2007; Lee *et al*., 2008).

Mutual adsorption phenomena on the surface of fly ash between metal cations and organic matter can occur. The organic material adsorbed on the surface of fly ash particles due to the adsorption surface and create expanded with more adsorption sites for metal cations (Wang *et al*., 2008). Adsorption affinity of fly ash for metal cations is very different and depends on the characteristics of each metal (valence, ion size), concentration and exposure time. In general affinity adsorbent of fly ash is greater for Pb than Cd (Mathur *et al*., 1989; Ricou *et al*., 2001, Rio *et al*., 2002). Fly ash can be activated to increase the absorption capacity (Wang *et al*., 2005) or can be modified to create materials with high adsorption capacity (eg, zeolites) (Querol *et al*., 2002).

MATERIALS AND METHODS

Materials

The fly ash used in the study was obtained from the Pha Lai Thermal Power Plant (Vietnam) have CEC of 30 cmol/Kg (denoted as FA-PL). Basic properties of the FA-PL are presented in Table-1.

Result in Table-1 shows that the chemical composition of the FA-PL consists of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, Li_2O, P_2O_5 and residual coal, water, but mainly SiO_2 (42%), Al_2O_3 (accounting for 19.38%), Fe_2O_3 (4.6%) and the rest small proportion (<2.8%) and residual coal.

Research methods

Modified fly ash

Weight 10g FA-PL, poured into flasks of 250 ml. Adding 100 ml of NaOH 3N, cover glass funnel to the condenser and magnetic stirrer, heating at a temperature of 100°C for 1 hour.

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Then the sample was centrifuged to remove impurities and NaOH. After centrifugation solids extracted and put into autoclave maintained at a temperature of 90^0C for 24 hours. Solids after drying is grinded through 0.25 mm sieve. Products modified (denoted MFA-PL) were analyzed to determine pH, CEC and mineral composition.

X-ray diffraction (XRD)

X-ray diffraction method is applied to the study, the structure of FA-PL and MFA-PL. The samples were recorded on X-ray diffraction, Advanced D8 Brucker (Germany), CuKα ray tube with a 0.01-intensity discharge tube; scanning angle from 0.5 to 200, the gap is essentially determined by XRD is top 001.

Table-1. Basic properties of the FA-PL.

Properties	Units	Values
Loss on ignition	%	27.77
SiO_2	%	42.00
Fe_2O_3	%	4.60
Al_2O_3	%	19.38
CaO	%	1.58
MgO	%	0.60
SO_3	%	0.00
K_2O	%	2.80
Na_2O	%	0.77
P_2O_5	%	0.01
Pb	%	0.01
Cu	%	0.01
pH_{KCl}	-	8.31
CEC	Cmol/kg	30.00
Density	g/cm^3	2.19

Source: Hai N.X *et al*, 2007

RESULTS AND DISCUSSIONS

Morphology and properties of MFA-PL

Morphology of MFA-PL

SEM picture of MFA-PL compare with FA-PL:

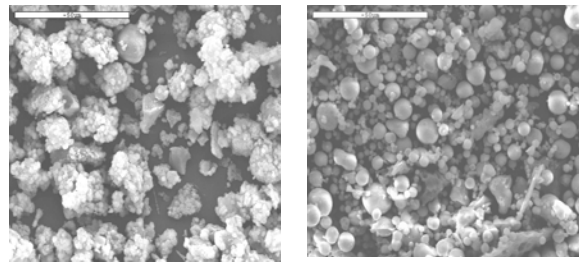

Figure-1. Morphology of MFA-PL (left) compare with FA-PL (right).

Photo taken with a scanning electron microscope (SEM) showed that the crystals are formed fairly uniform in size and linked together to form blocks scales. Morphology of the product after modified (MAF-PL) completely different than the original fly ash (FA-PL) showed hydrothermal reaction has completely destroyed the original structure of fly ash to create a new crystalline form (Figure-1).

Properties of MFA-PL

Modified fly ash (MFA-PL) analyzed the basic criteria related to adsorption capacity is pH_{KCl}, CEC (Table-2).

Table-2. Properties of MFA-PL.

Properties	Values	Unit
pH_{KCl}	9,04	-
Cation-exchange capacity (CEC)	170	cmol/kg

The change in material properties are as follows:

- **PH_{KCl}:** original fly ash (FA-PL) has pH_{KCl} = 8.31 and modified materials MFA-PL has pH_{KCl} = 9.03. After modified process, the material is alkaline.
- **CEC:** Materials after modified MFA-PL has CEC = 170 cmol/kg, it's about 5.6 times higher than the original fly ash (CEC = 30 cmol/kg).

Mineral composition of MFA-PL compare with FA-PL

X-ray diffraction (XRD) of MFA-PL compare to FA-PL is shown in Figure-2:

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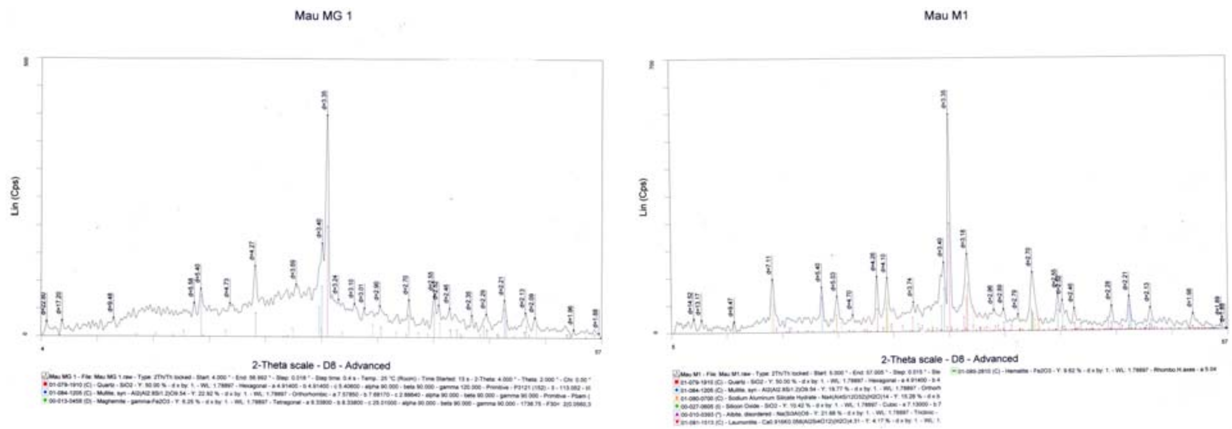

Figure-2. X-ray diffraction (XRD) of MFA-PL (right) compare to FA-PL (left).

Modified fly ash (MFA-PL) have X-ray diffraction with the appearance of sodium aluminum silicate ($Na_4(Al_4Si_{12}O_{32})(H_2O)_{14}$) this is a form of zeolite was named as Na-P2 (S. Hansen, U. H˚ akansson and L. F¨alth, 1989) (Figure-2). In addition to quartz components also appear characteristic peaks of mullite ($Al_6Si_2O_{13}$). X-ray diffraction has a flat baseline than the original FA-PL. This can be explained by the amorphous phase in original fly ash was dissolved by NaOH 3N.

Table-3. Mineral composition of FA-PL and MFA-PL.

STT	FA-PL		MFA-PL	
	Mineral composition	**Content** (%)	**Mineral composition**	**Content** (%)
1	Quartz - SiO_2	21-23	Quartz - SiO_2	24-26
2	Mullite - $Al[AlSi_2O_5]$	24-26	Mullite - $Al[AlSi_2O_5]$	22-24
3		-	Sodium aluminum silicate - $Na_4(Al_4Si_{12}O_{32})(H_2O)_{14}$	24-26
4		-	Oxyt Silica - SiO_2	4-6
5		-	Albite - $NaAlSi_3O_8$	3-5
6	Hematite + Magnetite (γF_2O_3)	4-6	Hematite - F_2O_3	3-5
7	Amorphous	45-51	Amorphous	8-20

The results in Table-3 show that the product was created consisting of sodium aluminum silicate-$Na_4(Al_4Si_{12}O_{32})(H_2O)_{14}$ is zeolite Na-P2 with 24-26%. This is the main reason for the increased cation exchange capacity (CEC) of modified fly ash. In addition, new silicate oxide and albite with small content (3-6%) creates. Amorphous reduced to 8-20%.

CONCLUSIONS

Fly ash of Pha Lai Thermal Power Plant (FA-PL) was modified in strong alkaline conditions (NaOH 3N), stirred at a temperature of 100^0C for 1h obtained with a mixture of minerals including: quartz accounts for 24 - 26%, accounting for 22-24% mullite, zeolite Na-P2 accounted for 24-26%, other types of small mineral occupies 10-16%, the rest is amorphous accounted for 8-20%.

The formation of materials with zeolite structure (Na-P2) is the major cause of increased cation exchange capacity (CEC) of the modified fly ash (MFA-PL).

This modified product has cation exchange capacity (CEC) of 170 cmol/kg, it is 5.6 times higher than the original fly ash (30 cmol/kg). With high CEC values open up new vistas in using modified fly ash material to handle with polluted soil and water environment.

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