

Geochemistry of Coal Ash in the Equatorial Wet Disposal System Environment

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Abstract—The coal utilization in thermal power plants in Malaysia has increased significantly which produces an enormous amount of coal combustion by-product (CCBP) or coal ash and poses severe disposal problem. As each coal ash is distinct, this study presents the geochemistry of the coal ash, in particular fly ash, produced from the combustion of local coal from Kuching Sarawak, Malaysia. The geochemical composition of the ash showed a high amount of silica, alumina, iron oxides and alkalies which was found to be a convenient starting material for the hydrothermal synthesis of zeolites with the higher Na₂O percentage being a positive factor for its alkaline activation; while the mineral phases are mainly quartz, mullite, calcium oxide, silica, and iron oxide hydrate. The geochemical changes upon alkali activation that can be predicted in a similar type of ash have been described in this paper. The result shows that this particular ash has a good potential for a high value industrial product like zeolites upon alkali activation.

Keywords—Coal ash, chemical composition, mineralogical composition, alkali activation, SEM.

I. INTRODUCTION

EACH coal ash or coal combustion by-product (CCBP) is distinct as it depends on the type of coal used, degree of pulverization, boiler system used, the method of ash collection system etc. [3], [4]. The enormous amount of coal ash poses a severe disposal problem which leads to a potential environmental problem. The coal ash also undergoes changes in disposal systems especially in wet disposal systems e.g., subsequent impoundment in ash ponds or lagoons [5]. The determination of the geochemistry of coal ash is essential in view of its distinctness and in its environmental management and utilization.

The adoption of a four-fuel (i.e., petroleum, hydropower, natural gas, and coal) mix energy policy to reduce single fuel dependency for power generation in Malaysia results a significant increase in coal utilization, mainly in coal-fired thermal power plants, which has resulted in increasing production of coal ash [1]. Coal utilization, mainly as fuel for power plants, has been increased significantly from about 4.2 million tons to about 13 million tons from 2000 to 2005, respectively [2]. The use of coal results in the generation of enormous amount of coal ash, as a by-product, due to combustion of the pulverized coal and limited studies are available on the geochemistry of the coal ash in particular fly

ashes produced from the combustion of this local coal from Sarawak, Malaysia. This is also essential for its potential behavior in wet disposal systems.

In this case i.e., the use of wet disposal systems, the exposure of these coal ashes to the high rainfall of this equatorial region also ensures a constant availability of water. Reactions like zeolitization occurs due to the ash water interaction between alkalis (Na₂O and K₂O in water) and major constituents (SiO₂ and Al₂O₃) of the ash [6], [7]. The formation of zeolites from coal fly ash has been demonstrated by Amrhein et al. [8] and amongst others. The zeolites have potential environmental applications such as the capacity for the removal of heavy metals from industrial sludge [9]-[11], flue gas and ammonia removal [12], [13], replacement of the phosphate in detergents [14] and the removal of radioactive waste [15], [16].

The geochemistry of a particular fly ash assist in gauging its reaction potentials and use as starting material for the synthesis of a high value industrial product like zeolite. This study presents the geochemistry of the fly ash produced from the combustion of local coal from a thermal power plant in Kuching, Sarawak, Malaysia, as well as, the prospects of its geochemical changes in wet disposal systems and its use as a raw material for the production of zeolites upon alkali activation.

II. EXPERIMENTAL INVESTIGATION

The fly ash samples were collected from the Sejingkat Thermal Power Plant, Sarawak, Malaysia. The three fly ash samples were collected from the Electro-Static Precipitator (ESP) and are designated as FA-01, FA-02 and FA-03.

The major chemical composition, calculated as major oxides, was obtained by using XRF (X-Ray Fluorescence Spectroscopy) model Shimadzu 1700, Japan. The mineralogical composition was determined with an X-Ray diffraction (XRD) spectrometer (Rigaku, Japan) using a graphite monochromator and Cu-K α radiation. The fly ash samples were scanned on a 2 θ ranging from 5 to 80° and the Joint Committee on Powder Diffraction Standards (JCPDS) were used to identify the phases. The Scanning Electron Microscope (SEM) was used to study the morphology of the fly ash samples. The particle size distribution (PSD) or gradation of the fly ash samples was determined by using laser particle size analyzer (Coulter LS100Q). The specific surface area of the fly ash samples was determined by using the Brunauer, Emmett, and Teller (BET) technique with a Micromeritics ASAP 2010 Surface Analyzer. The specific

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gravity (G_s) was determined as per the guidelines provided by ASTM [17].

III. RESULTS AND DISCUSSION

A. Chemical Composition

The chemical compositions of fly ash samples (i.e., FA-01, FA-02 and FA-03) investigated in this study are shown in Table I. All the fly ash samples tested in the present study falls in the Class F category as per ASTM C 618-94 [18]. The typical values are also presented in Table I [19]. It can be noticed that the chemical composition of the samples tested are quite similar except slightly different for a few elements like CaO, SO_3 , and Fe_2O_3 . In addition they are within the general limits in which major elements are present in fly ashes.

TABLE I
CONCENTRATION OF MAJOR OXIDES (%) IN FLY ASH SAMPLES

Oxide (%)	Typical range [19]	FA-01	FA-02	FA-03	Reference [20]
SiO ₂	30-60	60.9	59.1	59.4	59.9
Al ₂ O ₃	10-40	24.5	24.1	24.4	27.2
Fe ₂ O ₃	5-30	7.53	9.07	7.6	4.3
MgO	0.5-4	1.53	1.36	1.71	0.03
CaO	2-20	1.59	1.84	2.22	1.01
Na ₂ O	-	0.2	0.32	0.23	0.06
K ₂ O	-	3.31	3.53	3.91	0.9
P ₂ O ₅	-	0.26	0.24	0.23	0.23
SO ₃	-	0.08	0.35	0.17	0.15
TiO ₂	-	0.13	0.16	0.15	2.30
Alkalies (Na ₂ O+ K ₂ O)	1-4	3.15	3.85	4.14	0.96

B. Mineral Phases

A typical XRD pattern for the sample FA-01 is shown in Fig 1. The mineralogical composition of the fly ash samples was mainly quartz, mullite, hematite and calcite. Mullite ($Al_6Si_2O_{13}$) is the primary product of the breakdown of clay, ferric oxide of pyrite and calcium oxide of calcite while quartz has remained unchanged.

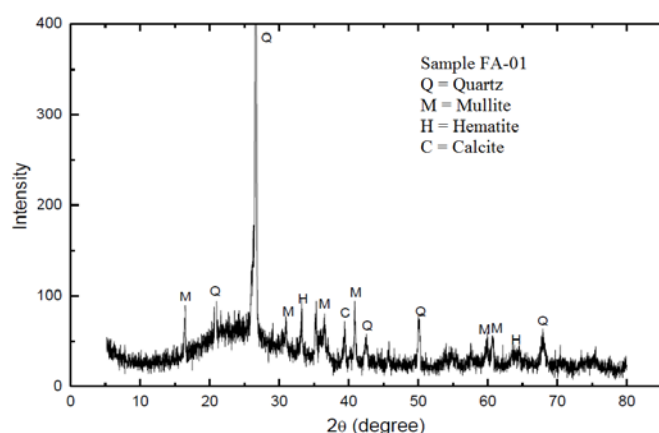
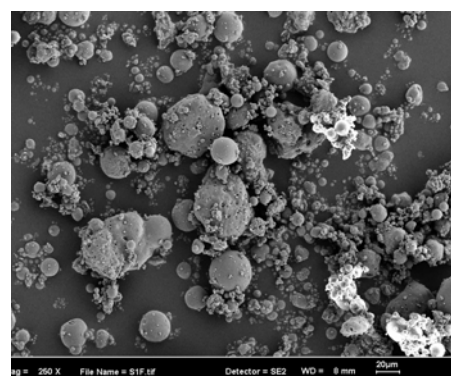


Fig. 1 X-Ray diffractograph for sample FA-01

IV. ALKALI ACTIVATION SIMULATION PROSPECTS

A. Suitability of Morphological Features

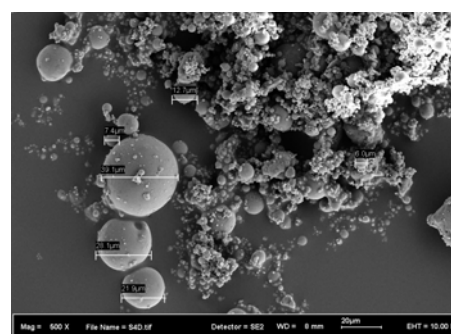
The SEM images of the three fly ash samples are presented in Figs. 2 (a) to (c). From the figure it can be noticed that the fly ash particles are predominantly spherical shape, although some irregular shape particles are also present. Some porous particle have been observed in samples FA-01 and FA-02 and this accounts for the higher BET surface area in samples FA-01 and FA-02, when compared with sample FA-03.



(a)



(b)



(c)

Fig. 2 Scanning Electron Microscope of the fly ash samples: (a) Sample FA-01; (b) Sample FA-02; and (c) Sample FA-03

B. Suitability of Physical Parameters

The results of the particle size distribution, specific gravity (G_s) and specific surface area are shown in Table II, while the particle size distribution graph is plotted in Fig. 3. For the sake

of accuracy, the average specific gravity was taken from the mean of five tests. From the gradational curves in Fig. 3 it can be observed that the sample FA-03 is finer than FA-01 & FA-02 and the sample FA-02 is the coarsest. The specific gravity of the sample FA-03 is also higher which may be due to the higher amount of silt sized particles. The BET surface areas presented in Table II also shows that the first two samples (i.e., FA-01 & FA-02) have a higher surface area than the third sample (FA-03). This is due to the fact that the first two samples are more porous than the third sample and SEM results, mentioned above also show the same trend.

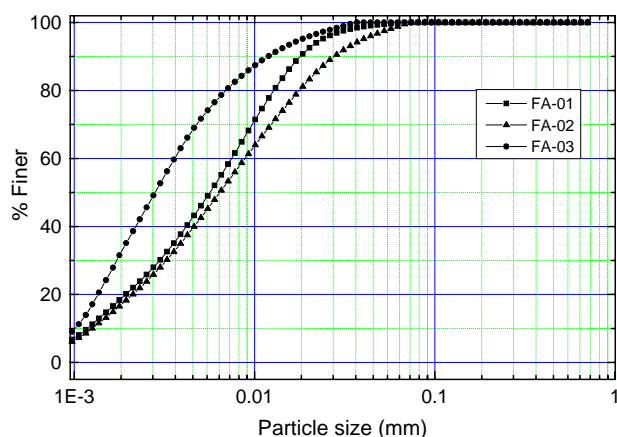


Fig. 3 Particle size distribution of the fly ash samples

TABLE II
PHYSICAL PROPERTIES OF THE FLY ASH SAMPLES

Sample	Particle size distribution (%)			Specific gravity, G_s	BET surface area (m^2/g)
	Clay	Silt	Sand		
FA-01	20.80	79.20	0	2.08	1.797
FA-02	19.15	80.29	0.56	2.07	1.605
FA-03	35.84	64.16	0.00	2.24	0.344

C. Characteristics and the Prospective Changes

The characteristics and the prospective changes due to ash-water interaction in wet disposal systems are discussed in this section. Earlier studies have shown that changes in coal ash properties through alkali activation under different conditions. One study has demonstrated this changes with ash interaction in water using 160ml of 3.5N NaOH (analytical reagent grade) with solid-liquid ratio equal to 0.125g/l [21] at 100°C maintained by using a water bath then filtered, washed repeatedly with distilled water and dried [20].

A comparison of the chemical composition of the untreated fly ash used in their study with the present study is presented in Table I. Upon comparison the amounts of the major constituents (SiO_2 and Al_2O_3) do not differ much but the samples of this study have significantly higher alkali values. The higher amount of Na_2O is desirable for the alkali activation and the synthesis of zeolites in the $Na_2O-Al_2O_3-SiO_2-H_2O$ reaction system. It has been found that NaP1 zeolite is formed when the Na_2O/SiO_2 mole ratio was 0.7 [21]. The fly ash treated with a higher Na_2O concentration solution ($Na_2O/SiO_2 = 1.3$) formed hydroxysodalite as the dominant

zeolite phase. Therefore, as the major composition of coal ash i.e., SiO_2 and Al_2O_3 of the fly ashes in this study are similar with the above study, so the alkali activation simulation in the later may serve as an analogue for deducing the prospects for property changes in the ash under similar conditions in ash pond or lagoons.

As alkali activation proceeds, it is noticed that the dissolution of silica is increased, leaving the other major oxides Al_2O_3 and Fe_2O_3 which, therefore, increases proportionately. The changes in the chemical phases can be expected due to the results of alkali activation and the two major crystalline phases i.e., quartz and mullite losing their predominance due to the production of NaP1 zeolite. Also the particle size distribution showed vast changes with a reduction in particle size as silica dissolution caused by etching and the specific surface area decreases. The sizes also found in this study will decrease in size resulting in a change in the silt-size to clay-size ratio and BET surface areas. As a corollary specific gravity increase can be expected as perforations due to silica dissolution may allow entrapped air to escape [22].

D. Starting Material for Conversion to Zeolites

The hydrothermal alkaline method has been used for the conversion of fly ash to zeolite. The major coal ash constituents involved in alkali activation are SiO_2 and Al_2O_3 , and the amount of Na_2O found in the ash supplements is required to be added externally. In this study each of the fly ash samples constitutes 60% of SiO_2 and 25% of Al_2O_3 which brings their total to 75%. In comparison with typical values given in Table I, the values of SiO_2 are at the highest end of the typical range provided, while the percentage of Al_2O_3 values are an approximately average value. This high silica ash represents a good starting material for the synthesis of zeolites. However, the Si/Al mole ratio in fly ash is also an important criterion as it determines the type of zeolite synthesized. The low Si/Al mole ratio in fly ash allows the synthesis of low-Si zeolites with high cation exchange capacities for transition metals and ammonium ions, selectivity for polar molecules and with large pore volumes [23]. The mole ratio of $SiO_2:Al_2O_3 = 3.75:1$ compares very favorably with that of 3.97 as a low ratio for the synthesis of low-Si zeolites [24].

V. CONCLUSION

The chemical composition of the fly ash in this study shows a high amount of SiO_2 , Al_2O_3 and alkalis; while the mineral phases present are mainly quartz, mullite, hematite and calcite. The particles were found to be predominantly silt-sized particle. According to the ASTM D 618-94, all the fly ash samples tested fall in the category of Class F ash. It is inferred that the alkali activation will also cause changes in these properties as found in the similarly compared ash. The chemical composition makes it a convenient starting material for the hydrothermal synthesis of zeolites with the higher Na_2O composition as a positive factor for its alkaline activation.

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