Solid State Science and Technology, Vol. 16, No 1 (2008) 107-113
ISSN 0128-7389

PREPARATION OF SYNTHETIC ZEOLITES FROM COAL FLY ASH

Shamsul Kamal Sulaiman

Mineral Research Centre, Minerals and Geoscience Department,
Jalan Sultan Azlan Shah 31400, Ipoh, Perak, Malaysia

ABSTRACT

Coal Fly ash from Sultan Abdul Aziz Power Station in Kapar, Malaysia was characterized and used for the synthesis of zeolites. Coal Fly ash was pretreated with Wet High Intensity Separation (WHIMS) to remove undesirable iron components prior to the formation of synthetic zeolites. The synthesis method used was a hydrothermal treatment with NaOH activation at low temperature. The hydrothermal reaction produced stable zeolite P which increased in crystallinity as temperature and reaction time increased. Mineral transformation during hydrothermal treatment involved the dissolution of aluminosilicate glass and formation of synthetic zeolite P with a high Cation Exchange Capacity (CEC).

INTRODUCTION

At present, power stations are facing a serious problem associated with the use of coal for generating electricity. The high temperature burning of coal produces gases such as SOX, NOX and COX together with solid wastes, fly ash being the primary constituent. Due to nature of coal use, which is low in sulphur, and the advanced combustion technology used, the flue gas emmisions can be kept at a level below the maximum limit for air pollution legislation. However, the waste fly ash needs more careful handling due to its solid and lightweight nature. At present, most of the fly ash is dumped in disposal sites. Such sites require a large area and special construction and maintenance, which are quite expensive. Therefore, applications for the utilisation of the waste fly ash are desirable, to reduce the environmental and disposal cost. Hence, the synthesis of zeolites represents a possible use of this material.

EXPERIMENTAL METHODS

Raw Material
The sample of coal fly ash used in this study was obtained from Sultan Abdul Aziz Power Station in Kapar, Selangor.

After drying, a representative head sample was prepared by riffling for subsequent chemical, mineralogical and particle size characterisation. Chemical analysis was undertaken by atomic absorption and UV spectrometry; major mineral phases were determined by X-ray diffraction (XRD). All results are listed in Table 1.

Magnetic Pre-Treatment of Raw Material
Before the hydrothermal process could be used to synthesize zeolite, fly ash samples had to go through a magnetic pre-treatment. Many researchers[1-2] stated that the removal of undesireable iron components prior to the formation of synthetic zeolites improves zeolite crystallization and cation exchange capacity (CEC) values of zeolite. The process involved a series of tests using Eriez Wet High Intensity Magnetic Separation (WHIMS).

Corresponding Author: shamsul@jmgipoh.gov.my

Solid State Science and Technology, Vol. 16, No 1 (2008) 107-113
ISSN 0128-7389

Table 1: Characterisation of Kapar Coal Fly Ash

	Raw Fly Ash	+ 53µm Size Fraction	- 53µm Size Fraction
%SiO_2	52.11	50.11	53.10
%Al_2O_3	23.59	21.86	20.00
%Fe_2O_3	7.39	8.81	6.98
%TiO_2	0.88	0.72	0.92
%CaO	2.61	1.68	2.40
%MgO	0.78	1.32	1.08
%Na_2O	0.42	0.41	0.41
%K_2O	0.80	0.49	0.78
%P_2O_5	1.31	0.60	1.77
%SO_3	0.49	0.95	0.29
%MnO	0.03	0.03	0.02
%Loss on Ignition	5.59	11.28	4.85
Mineral Phases (by XRD)	Quartz Mullite Magnetite Spinel Ferrian	Quartz Mullite Magnetite Spinel Ferrian	Quartz Mullite Magnetite Spinel Ferrian

Zeolite Synthesis
In each hydrothermal test, a known weight 10g pre-treated raw material was reacted with a solution of sodium hydroxide (NaOH) using various solid-liquid ratios and alkali concentrations. The reaction mixture was heated at various temperatures and reaction times for the formation of zeolite

RESULT AND DISCUSSION

Magnetic Pre-Treatment

Effects of Feed Pulp Density
The results of effects of pulp density on Kapar fly ash iron removal tests are shown in Figure 1. As seen from the figure, WHIMS was able to remove maximum of 61.6% of the iron content when the pulp density of the feed was around 20%. The experiments indicated that using Eriez WHIMS with 20% pulp density and 8,000 Gauss (0.8 Tesla) magnetic field intensity, the iron content in Kapar fly ash was reduced from 7.39% to 3.12%.

Effects of Magnetic Field Intensity
The next series of experiments determined the optimum conditions for magnetic field intensity. In these experiments, the magnetic field intensity was varied from 2,000 to 11,000 Gauss (0.2 to 1.1 Tesla) and 20% feed pulp density was used throughout. The results of these tests are shown in Figure 2. As seen from the figure, the WHIMS was able to remove more than 60% of the iron content when the magnetic field intensity reached more than 8,000 Gauss (0.8 Tesla). The efficiency of iron removal decreased as the field intensity reached about 9,000 Gauss (0.9 Tesla). The highest iron separation was achieved at a field intensity of 8,700 Gauss (0.87 Tesla), whereby 61.69% of the iron component was removed. The remaining iron was probably distributed in the glassy constituent in low concentrations and was difficult to remove by magnetic separation [3]. These results suggest that it is adequate for the fly ash samples to be

Corresponding Author: shamsul@jmgipoh.gov.my

pre-treated with WHIMS using conditions of 20% feed pulp density and 8,700 Gauss (0.87 Tesla) magnetic field intensity.

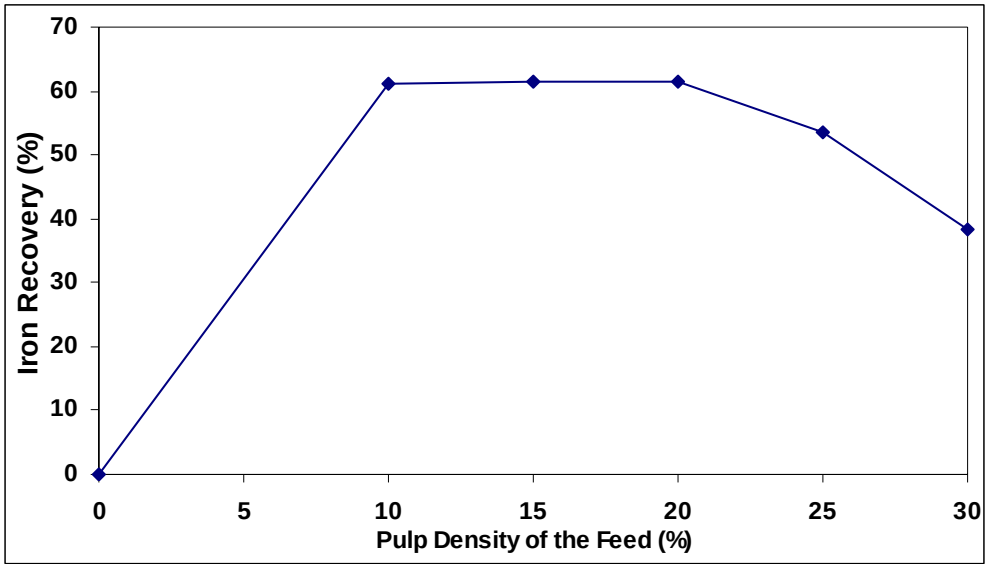

Figure 1 : Graph of Iron Recovery against Pulp Density of the Feed of Kapar Fly Ash Using WHIMS with Magnetic Field Intensity Constant at 8,000 Gauss

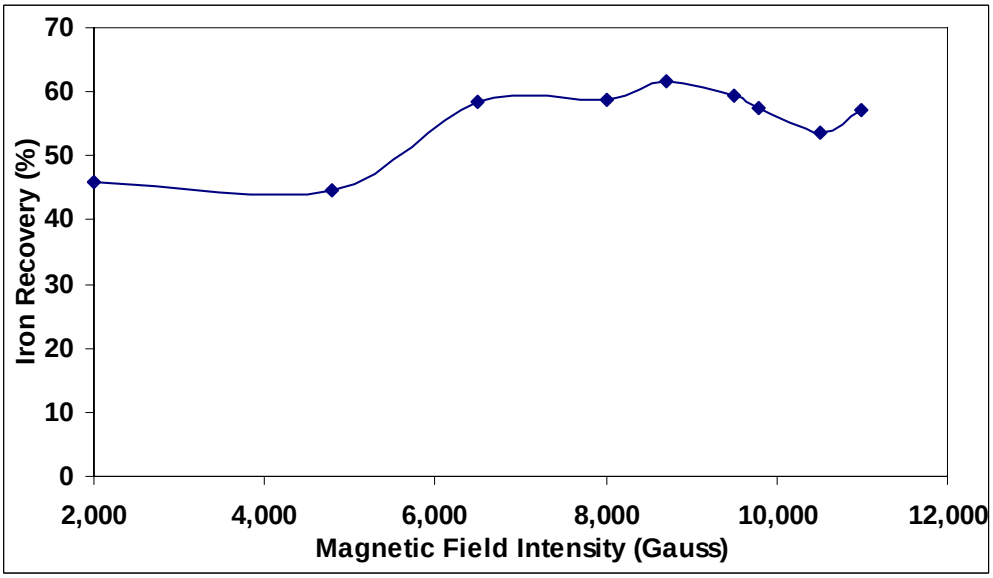

Figure 2 : Graph of Iron Recovery of Kapar Fly Ash Samples as a Function of Magnetic Field Intensity Using WHIMS with Pulp Density Constant at 20%

Mineral Transformation During Hydrothermal Treatment

Mineral transformation during hydrothermal treatment was studied by means of the XRD diffraction patterns. The relative intensities of the diffraction patterns of the two major fly ash crystalline phases, quartz and mullite, and synthetic zeolite formed (zeolite P), were measured at various reaction temperatures and reaction times. The results are presented in Figures 3 to 7.

Corresponding Author: shamsul@jmgipoh.gov.my

Solid State Science and Technology, Vol. 16, No 1 (2008) 107-113
ISSN 0128-7389

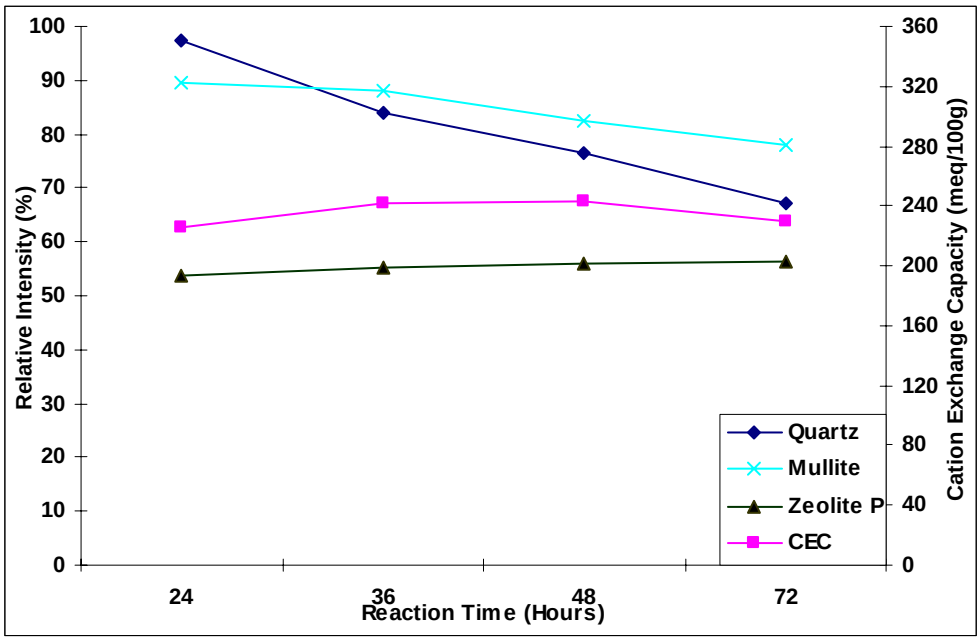

Figure 3 : Relative Intensities of XRD Reflections of Major Crystalline Phases and CEC Values against Reaction Time for Hydrothermal Treatment at 70°C

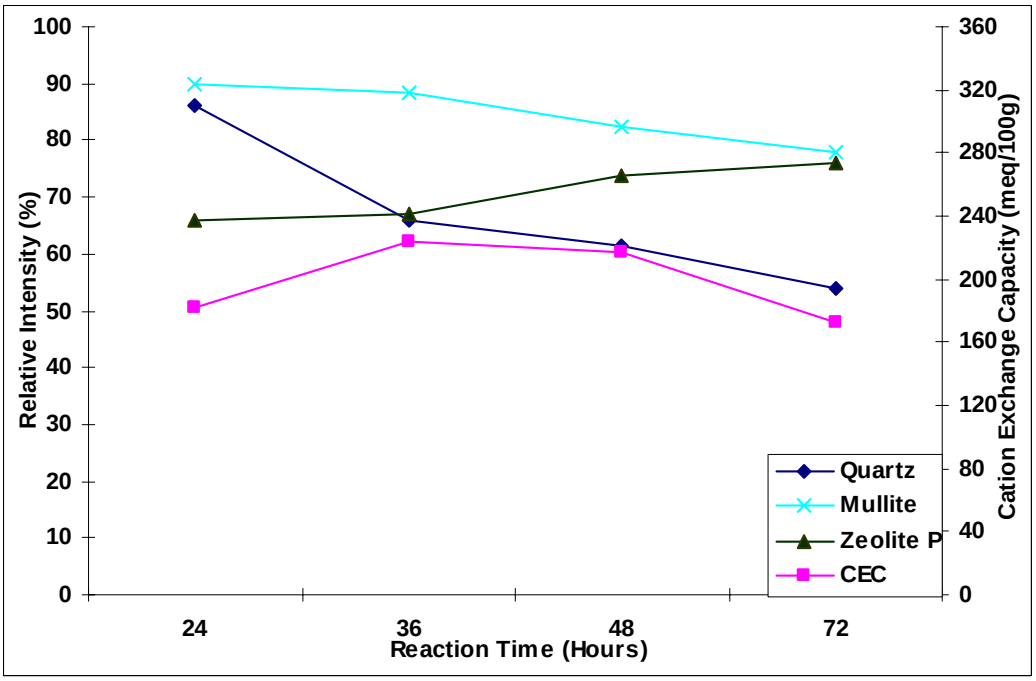

Figure 4 : Relative Intensities of XRD Reflections of Major Crystalline Phases and CEC Values against Reaction Time for Hydrothermal Treatment at 80C

Corresponding Author: shamsul@jmgipoh.gov.my

Solid State Science and Technology, Vol. 16, No 1 (2008) 107-113
ISSN 0128-7389

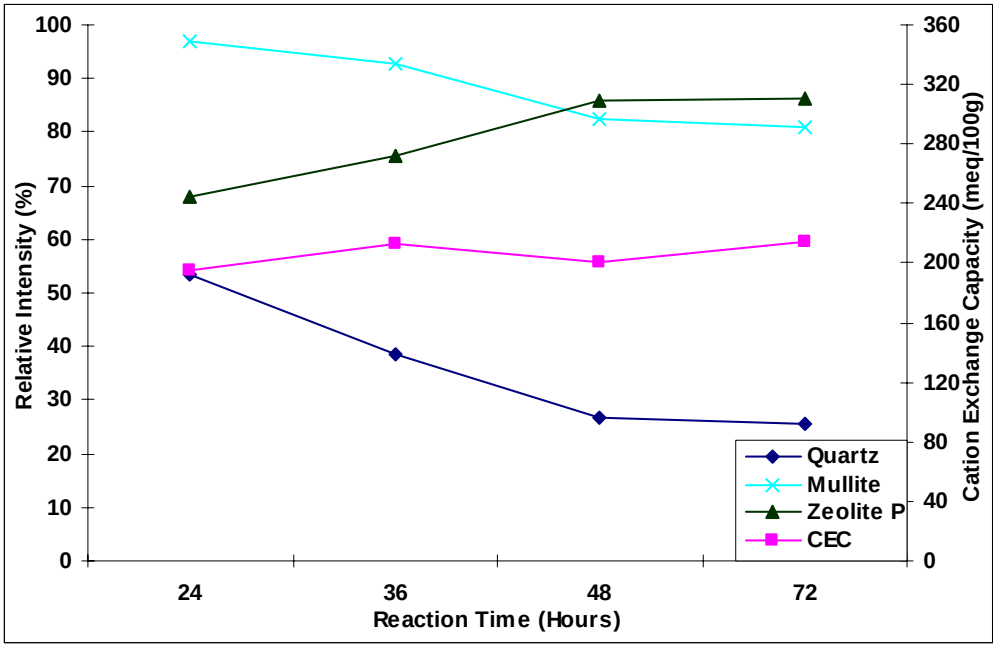

Figure 5 : Relative Intensities of XRD Reflections of Major Crystalline Phases and CEC Values against Reaction Time for Hydrothermal Treatment at 90C

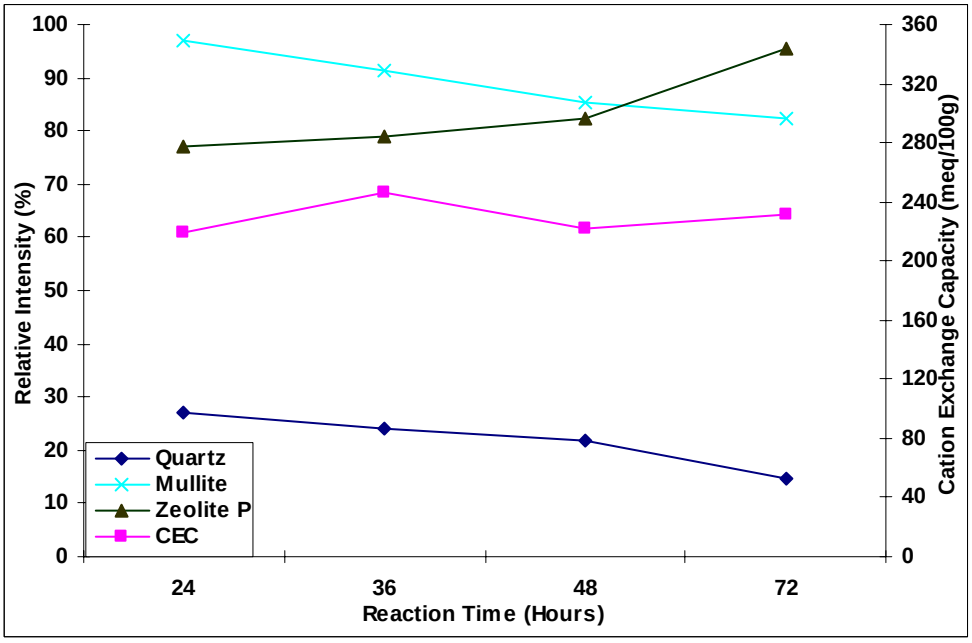

Figure 6 : Relative Intensities of XRD Reflections of Major Crystalline Phases and CEC Values against Reaction Time for Hydrothermal Treatment at 100C

Corresponding Author: shamsul@jmgipoh.gov.my

The mineral transformation phenomena observed in this study were consistent with the result of previous studies [4-5]. Alkali medium was always found to dissolve the aluminosilicate glass and the dissolution rate of silica was accelerated more than that of alumina by increasing temperature and reaction time. This is because mullite was more stable and more difficult to dissolve in comparison to quartz. The subsequent formation of synthetic zeolites rapidly consumed the dissolved species to feed the crystal growth crystallization of zeolite P which produce the highest CEC value, as when Kapar fly ash was treated with NaOH at 70˚C at a reaction time of 48 hours. In this stage, almost all the zeolite P produced is from the dissolution of aluminosilicate glass. The dissolution of impurities from fly ash is also a minimum in this stage and, therefore, the zeolite produced is almost purely from aluminosilicate material.

The prolonged reaction time of 48 hours at 70˚C and increasing hydrothermal reaction temperature to more than 70˚C produced synthetic zeolite P from the dissolution of aluminosilicate glass, quartz, mullite and impurities in Kapar fly ash. The lower CEC value in this stage was probably due to a desilication process, in which the silica and alumina dissolved by the alkali reaction were reprecipitated and formed a sodium-aluminum silicate “desilication” product [6].

In this stage also, a lot of impurities from fly ash dissolved in the solution because of increase of reaction time and temperature. The results agree with findings by many researchers [7-8] which show that prolonged reaction time and increasing temperature frequently result in contamination of zeolite product with undesirable elements such as Fe, Ti and Mn. These elements were thought to be present as soluble oxides in the coal fly ash and were expected to form oxy-anions upon dissolution under alkaline conditions. Jansen [9] has shown that the presence of impurities may affect the crystal form and chemical properties of the zeolite formed. While Inglezakis et al. [10] showed that the decreased of CEC in zeolite was due to surface dust such as precipitated salts and other impurities clogging part of the pore openings in the zeolite structure. Therefore, it is probably that incorporation of these impurities during crystallization of zeolite may in some way affect the CEC values of zeolite P.

Chang and Shih [11] also explain that with increasing temperature and reaction time, there is a possibility of ion exchange of impurities occurring in the samples with Na+ ions in the zeolites.

CONCLUSION

The following main conclusions are obtained from the results of this study:

- Magnetic separation was successful in removing iron from Kapar fly ash, considered to be deleterious to the zeolite formation process. Optimum separation conditions were achieved with 20% pulp density and 8,700 Gauss (0.87 Tesla) magnetic field intensity, with the removal efficiency of iron around 62%.
- Mineral transformation during hydrothermal treatment was studied by means of the XRD diffraction patterns with CEC values. The initial mineral

Corresponding Author: shamsul@jmgipoh.gov.my

transformation phenomenon was the dissolution of aluminosilicate glass in the sample and subsequent formation of synthetic zeolite P. Prolonged reaction time greater than 48 hours at 70˚C and hydrothermal temperature greater than 70˚C dissolved aluminosilicate glass, quartz, mullite and impurities from Kapar fly ash. The dissolution of these minerals consequently produced contamination in the synthetic zeolite P product with undesirable elements such as Fe, Ti and Mn. The presence of these impurities resulted in lowering the CEC value of synthetic zeolite P.

REFERENCES

[1]. M. Murat, (1992); *Clays Minerals*, **27**, 119-130.
[2]. W. J. Ball, (1986); *Proceeding of Seventh International Zeolite Conference*, Tokyo, Japan, 137-144.
[3]. R. T. Hemmings, E. E. Berry, B. J. Cornelius and B. E. Scheetz, (1986); *Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal III*, Material Research Society, Boston, USA.
[4]. A. Singer and V. Bergaut, (1995); *Journal of Environmental Science and Technology*, **29**, 1748-1753.
[5]. X. Querol, N. Moreno, J. C. Umana, A. Alastuey and E. Hernandez,(2002); *International Journal of Coal Geology*, **50**, 413-423.
[6]. N. M. Rice and J. M. Noone, (1984); *Proceeding of ASHTEC 84 – Second International Conference on Ash Technology and Market*, London, UK, 253-261
[7]. M. Tassopoulos and R. W. Thompson, (1987); *Zeolites*, **7**,243-248.
[8]. K. S. Hui and C. Y. H. Chao. (2005); *Microporous Mesoporous Materials*, **88**, 145-151.
[9]. J. C. Jansen, (2001); *Introduction to Zeolite Science and Practice*, Elsevier, Amsterdam, Netherlands
[10]. V. J. Inglezakis, K. J. Hadjiandreou, M. D. Loizidou and H. P. Grigoropoulou, (2001); *Water Research*, **35**, 2161-2166.
[11]. H. L. Chang and W. H. Shih, (1995); *Ceramic Translation*, **61**, 81-88,

Corresponding Author: shamsul@jmgipoh.gov.my