Properties of Ternary Blended Cement Containing Metakaolin and Fly Ash

Mohd Fadzil Arshad[1,5], Megat Azmi Megat Johari[2], Muhd Nurhasri Mohd Sidek[3] & Mazlee Mohd Noor[4]

Institute for Infrastructure Engineering and Sustainable Management (IIESM)
[1]Faculty of Civil Engineering
Universiti Teknologi MARA (UiTM), Malaysia
[2]School of Civil Engineering, Engineering Campus
Universiti Sains Malaysia
[3]Faculty of Civil Engineering
Universiti Teknologi MARA (UiTM), Malaysia
[4]Schools of Materials
Universiti Malaysia Perlis, Malaysia
[5]Email: Fadiil2003@yahoo.co.uk

ABSTRACT

This paper presents the results of a laboratory study on the properties of Ternary Blended Cement (TBC) containing blends of ordinary Portland cement (OPC), Metakaolin (MK) and Fly Ash (FA). Analyses on the cementitious properties and engineering concrete properties containing TBC produced have been performed. The resulted was than compared with those of OPC and binary blended cementitious (BBC) systems containing OPC:MK and OPC:FA. In general, the results show that the inclusion of MK and FA in TBC alter the properties and performance of the cement paste and concrete to a certain degree as well as the resulting the TBC could potentially be used in the concrete construction industry.

***Keywords**: Ternary blended cement, binary blended cement, metakaolin, fly ash*

ISSN 1675-7009

Introduction

The utilization of pozzolanic materials as mineral additives or as cement replacement materials was accepted by the concrete industries. The inclusion of these materials reported to improve the concrete properties and increased the durability of concrete matrix. Since most of the pozzolanic materials are considered as waste materials, therefore the utilization of pozzolanic materials was also believed to reduce the production cost of cementing materials and at the same time reducing the waste management problems.

Pozzolanic materials are known as siliceous or siliceous and aluminous materials that react chemically with calcium hydroxide to form compounds with cementitious properties in the presence of water [1]. The utilization of pozzolans resulted reduce the temperature rise during the hydration process of concrete, improvement in durability and enhancement in strength, although in some cases strength develops more slowly [1]. Pozzolans added to the concrete produced pozzolanic reaction where in the presence of moisture the pozzolan produced additional calcium silicate hydrate and in the same time reducing the amount of $Ca(OH)_2$ [2].The utilization of pozzolan was become establish especially in achieving a high strength and high performance of concrete. For the time being the pozzolans only used in binary blended system and the optimum replacement of the pozzolan to OPC was reported to be not more than 20 %.

To optimise the utilization of pozzolan in the concrete industries the idea of producing TBC was proposed. TBC is generally terms a combination of three cementitious components in a mix which allows higher total Portland replacement. The utilization of TBC allows the designer to best optimized mix properties for the project which may result in higher replacement/lower cement factor that is directly impact on improving mix economics and sustainability implications [3]. Pozzolans that recommended to be used in preparing TBC are Fly Ash (FA), Ground Granulated Blast Slag (GGBS) and Silica Fume (SF).

Metakaolin (MK) is a by product of kaolin clay. The kaolin clay was calcined in an electrical furnace at a specific temperature (600-800 °C) and specific time (2 to 4 hours) to produce MK. Ambroised *et al*. [4] stated that the optimum temperature in calcining kaolin clay to form optimum MK is 700 °C. The silica and alumino contained in kaolin clay were transformed to active pozzolanic materials due to the calcinations process and it become suitable materials to be used as cement replacement materials. In term of performance of MK as mineral admixture of concrete, MK is found to have superior strength development and similar chloride resistance to SF concrete, besides improved porosity and fining the pore sizes of MK concrete than the control (plain) concrete [5]. The filler effect resulting from the fine powder of MK is the reason of MK concrete to ameliorate substantially the resistance to chemical attacks in comparison with ordinary concrete [6]. Even the used of MK is reported to give a positive effect on the mechanical properties of concrete, but in terms of workability effect, it was reported that the MK reduces the workability of concrete [7].

The use of fly ash (FA) in combination with Portland cement (PC) to produce structural concrete has found to increase application in the construction industry over the last 20 years. This is due to the potential environmental, technical and economic benefits to be obtained from the use of FA. High FA levels can be used in combination with PC to produce concrete covering the range of design strengths typically required in practice. However, this may lead to problems with early strength, which may be of significance for some aspects of construction [8]. The used of FA has been reported to result in either similar or enhanced engineering performance in comparison to PC concrete, but when it comes to the durability aspect, high content of FA may slightly lead to poorer performance. It was suggested that the high content of FA used in concrete, should be combined with appropriate minerals such as pozzolanic materials with specific properties to produce better properties of concrete. Even some of the minerals are costly (e.g. SF), but the lower cost of fly ash could offset the increased cost of the minerals.

This study focus on utilisation of waste pozzolans products such as FA and by product of kaolin known as Metakaolin (MK) added together with OPC to produce ternary blended cement (TBC) with an objective to increase up the optimum percentage replacement of pozzolan to OPC without affecting the concrete properties.

Methodology

Materials

Materials used to produce TBC were OPC, MK and FA. MK used is a product of kaolin clay calcined in an electrical furnace at 700 °C for 3 hours. The calcination temperature and time were selected based on previous work done by Fadzil *et al*. [8], while FA was a waste product of coal power plant supplied by YTL Cement (Malaysia) Bhd. The chemical composition of OPC and pozzolanic materials used was identified by XRF analysis. Chemical composition, density and specific surface area were identified and presented in Table 1. A materials used for concrete mixes are OPC, prepared binders, river sand, granite coarse aggregates with maximum size of 10 mm, water and Glenium C380 superplasticizing admixture.

Table 1: Chemical Composition, Density and Specific Surface Area (SSA) of Binder Materials

Composition	OPC (%)	MK (%)	FA (%)
SiO_2	20.0	55	48
Al_2O_3	5.70	38	17
Fe_2O_3	2.90	0.65	2.7
CaO	63.0	0.07	2
MgO	0.99	0.9	0.29
K_2O	1.2	2.5	0.64
SO_3	3.50	0.04	0.3
LOI	2.8	2.1	8.3
Density (g/cm^3)	3.018	2.63	2.17
SSA (m^2/g)	0.38	8.61	0.402

Preparation of TBC and BBC

TBC was prepared by blending OPC, FA and MK powder in dry condition in a blender machine at specified mix proportion until homogenous mixed obtained. The mix proportions were obtained based on the optimum compressive strength of concrete cubes at 28 days of curing period using binary blended cementitious system containing OPC:FA and OPC:MK. To identify the performance of TBC, three types of cementitious systems, namely; OPC, OPC+ FA and OPC+ MK were prepared and used in the investigation. The mix proportions of prepared binders are as stated in Table 2.

Table 2: Binders Mix Proportions

	OPC	OPC+FA	OPC+MK	OPC+FA+MK
OPC (%)	100	70	90	60
FA (%)	-	30	-	30
MK (%)	-	-	10	10

Testing

The investigation on the properties and performance of TBC was determined based on two major properties named as cementitious properties and concrete properties. The TBC identified properties were then compared with the properties of OPC, OPC+FA and OPC+MK. The cementitious properties are refered to properties stated in BS12 [7]. The stated properties are chemical composition, water requirement, setting time and soundness. The chemical composition was identified using XRF apparatus, water requirement and setting time was determined using Vicat apparatus, while the soundness of the binders paste determined by using Le-Chatalier apparatus.

The concrete properties identified are concrete workability, strength, porosity and permeability value. Four concrete mixes were prepared to assess the effects of the different binder combinations on the engineering properties of concrete. Details of the mix proportions are given in Table 3. The control mix was prepared using OPC, while the other mixes were prepared by replacing part of the OPC with the respective pozzolans on mass-for-mass basis. A total binder content of 500 kg/m^3 and a constant water/binder ratio 0.33 were used. The superplasticiser was used at a dosage rate of 20 l/m^3 to maintain slump values in the range of 60 to 180 mm. The materials were proportioned so that the concrete mixes achieved minimum 28 day strength of 60 MPa. All concrete materials were mixed in a pan type concrete mixer for 3 minutes and cast into the relevant moulds. The properties and workability of concrete were determined through slump and flow table test. The compressive strength of the concrete was identified by casting the concrete into steel moulds (100 × 100 × 100 mm) in three layers and each layer was compacted using a vibrating table for 15 second. A total of 84 concrete cubes were prepared and all samples were cured in water at a temperature (27 $\pm$ 5 °C) for 1, 3, 7, 28, 84, 168 and 336 days. At all testing ages, three cubes were

Table 3: Concrete Mix Proportions

Mix Designation	OPC (kg/m^3)	MK (kg/m^3)	FA (kg/m^3)	Coarse Agg. (kg/m^3)	Fine Agg. (kg/m^3)	Water (kg/m^3)	SP (l/m^3)
OPC	500	-	-	1200	565	165	20
OPC:SF	450	50	-	1200	565	165	20
OPC:FA	350	-	150	1200	565	165	20
OPC:FA:SF	300	50	150	1200	565	165	20

tested for its compressive strength using concrete compression machine. All testing was conducted in accordance with BS 1881 [6].

Test for porosity and permeability were carried out using cylindrical concrete samples of 50 mm Ø × 40 mm thickness. The cylindrical samples were extracted by coring a concrete prism with a coring machine with diamond core bit. The concrete prism was made by casting fresh concrete into prism steel moulds (100 × 100 × 500 mm) in three layers and each layer was compacted using a vibrating table for 15 seconds. The prism samples were then cored to obtain the cylindrical samples and cured in the same condition as stated before. At all testing ages, 2 samples were tested for porosity and another 2 samples were tested for permeability.

The test for porosity is based on the method developed by Cabrera and Lynsdale [9]. The cylindrical samples were placed in a vacuum dessicator with a vacuum pressure of 1 bar for 3 hours. Then, de-aired water was introduced into the dessicator until the specimens are fully submerged and vacuum pressure of 1 bar was applied to the specimens for another 3 hours. After this period, the pressure was increased to atmospheric pressure with specimens remaining submerged and left another 1 hour. Then the specimens are taken out from the dessicator and weighed in water (W_3) and in air (W_2), after which they are placed in an oven at 105 °C for 24 hours. The dry weight (W_1) of the specimens is then obtained. The total porosity (P) of the concrete is calculated using the following equation:

$$P(\%) = [(W_2 - W_1)/ (W_2 - W_3)] \times 100 \quad (1)$$

In identifying the permeability of concrete, the cylindrical samples are dried in an oven at 105 °C for 24 hours. The samples were then removed and silicon rubber is applied onto the curved side of the samples and kept to dry in desiccators for another 1 day, the samples are then placed into the airtight permeability cell and a gas pressure of two bars is applied. The time of gas flow is recorded using bubble meter. The flow time is repeatedly measured and recorded for 5 minutes. To obtain the gas permeability the following relation is used:

$$K = 2P_2(VL \times 1.76 \times 10^{-16})/ A(P_1^2 - P_2^2) \quad (2)$$

All tests were carried out based on standard specification stated in selected British Standard and accepted selected journal papers.

Result and Discussion

Cementitious Properties

Table 4 shows the chemical composition of prepared binders. From the table, it shows that the CaO composition of TBC binders found to be lowest compared to OPC, OPC+MK and OPC+FA. The reduction of CaO content may give an effect to the hydration of cement paste known as dilution effect. Beside that TBC also found to have highest SiO_2 and Al_2O_3 content as compared to other types of prepared binders. The increased value of SiO_2 and Al_2O_3 may increased the production of C-S-H and C-A-H values in the harden cement paste and responsible in altering the cementitious properties of TBC.

Table 5 present the cementitious properties of a binders tested. The results portray that the cementitious properties of TBC been altered due to the inclusion of pozzolanic materials at 40 % as a mineral replacement materials to OPC. TBC (referred to water/binder ratio values) needs

Table 4: Chemical composition of prepared binders

	OPC	OPC: MK	OPC: FA	TBC
CaO	63	34	49	31
SiO_2	20	41	26	40
Al_2O_3	5.7	13	13	17
Fe_2O_3	2.9	3	2.3	2.6
MgO	0.99	0.63	0.97	0.77
SO_3	3.5	2.1	2.7	1.8
K_2O	1.2	1	1.3	1.2
Na_2O_3	0.058	0.13	0.049	0.1
LSF	0.935	0.524	0.246	0.222
IR	0.9	0.95	1.4	1.2
LOI	2.8	3.9	4.2	3.6

Table 5: Cementitious Properties of Prepared Binders

Binder properties	OPC	OPC+MK	OPC+FA	TBC
W/B ratio	0.33	0.37	0.36	0.41
Initial Setting time (min)	120	150	145	165
Final Setting time (min)	240	320	295	315
Soundness (mm)	0.15	0.35	0.85	0.35

more water of 0.24 % than OPC in order to achieve the standard consistency requirements. The observed trend of increasing water demand with inclusion of FA and MK could be attributed to the much higher fineness of the FA and MK in comparison to OPC. Hence, for the binders containing FA and MK, especially the TBC, their water demand should be higher than OPC. The use of FA has normally been associated with the reduction in water requirement of concrete due to the spherical shape and smooth surface texture of FA particles. However, the results of the present study show the opposite trend. According to Popovics [10], the inclusion of FA in a TBC system may have water reducing effect, depending on the quality of the FA, it may compensate the increase water requirement caused by MK. In the present study, the much higher fineness of the FA in comparison to OPC and the higher loss on ignition of the FA could have contributed to the greater water demand.

Table 5 also presented the effect of binder types on the setting characteristics of the different binders measured using the Vicat apparatus. It is clear that the effect of BBC and TBC is to increase both the initial and final setting times of the binder pastes. The observed retardation in setting times could be mainly attributed to the combined effect of a lower cement content and higher water/binder ratio for the binder pastes containing BBC and TBC systems, since part of the cement were replaced by MK and FA. As demonstrated in Table 5, the binder pastes containing BBC and TBC require greater amount of water to achieve standard consistency compared to OPC. Hence, these binder pastes should have higher water/binder ratio than the OPC control paste. Water/binder ratio has been recognized as one of the important factors that could influence the setting characteristics of cement and concrete [5].

The soundness of the binder pastes were assessed using the Le Chatelier apparatus and the results are shown in Table 5. It generally shows that the use of FA and MK tend to increase the expansion of the binder pastes. The binder paste containing FA recorded the highest value of expansion. However, the use of TBC tends to reduce the expansion of the binder paste containing FA. Nevertheless, the expansion values exhibited by all binders are significantly lower than the maximum limit stipulated in the code of practice. BS 6610 [1996] put a limit on the potential expansion of neat cement paste where the expansion of cement should not be more than 10 mm. The unsoundness of cement will affect the concrete quality at later ages which could disrupt and damage the concrete.

Concrete Properties

Concrete properties identified in this study referred on 4 perimeters stated as concrete workability, concrete compressive strength, concrete porosity and concrete permeability values. Figure 1 presents the effect of binders to the workability of concrete. From the figure, it shows that the workability of concrete containing TBC was reduced about 23 % as compared to other types of binders. Even though the workability of TBC found to reduce but the concrete is still considered as workable concrete and can be improved by using superplasticiser. The low workability of TBC is due to high surface area provided by the inclusion of FA and MK.

Figure 2 presents the effect of the different binder types on the compressive strength of concrete. The concrete compressive strength containing TBC at early age strength is found lower than that of OPC, but higher than that of BBC concrete containing FA. In fact, the 28 days and long-term strength of the TBC concrete are comparable to that of OPC. Hence, the inclusion of MK has improved to a certain degree the rate of early strength development of BBC concrete containing FA. This could be attributed to the filler effect and acceleration in OPC hydration as a result of MK inclusion. However, in the case of long-term strength, no significant improvement could be seen from the TBC concrete when compared to OPC. This could be due to the much lower amount of cement for this concrete as 40 % of the OPC component was replaced with FA and MK. Consequently, the amount of $Ca(OH)_2$ produced by OPC hydration should be lower which could hamper pozzolanic reaction. The

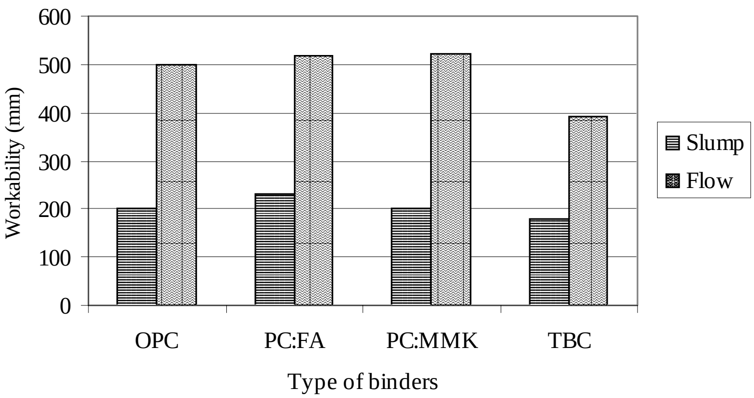

Figure 1: Effect of Binders to Workability of Concrete

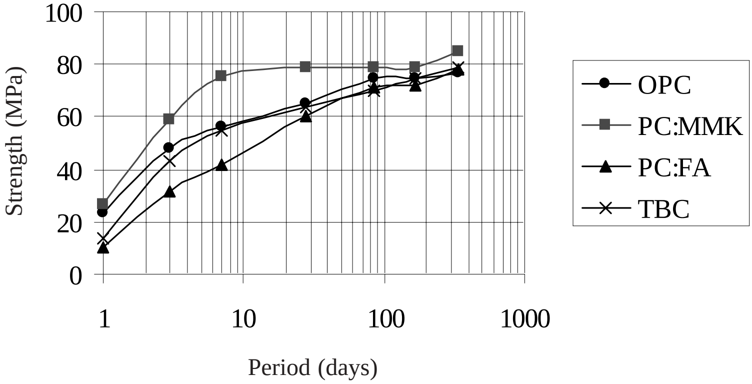

Figure 2: Compressive Strength of Concrete

same trend was observed by Zichao *et al*. [11], on TBC system containing OPC, FA and SF. According to Zichao *et al*. [11], the small contribution to long-term strength in such a system is due to the $Ca(OH)_2$ produced was preferentially consumed by the pozzolanic reaction of SF, thereby decreasing extensively the quantity of a $Ca(OH)_2$ available for reacting with FA.

The porosity of concrete containing prepared binders is presented in Figure 3, it is clear that the use of TBC reduces the porosity of concrete compared to OPC and improves the porosity of BBC concrete with FA. The BBC with MK was found to have the lowest porosity. The inclusion

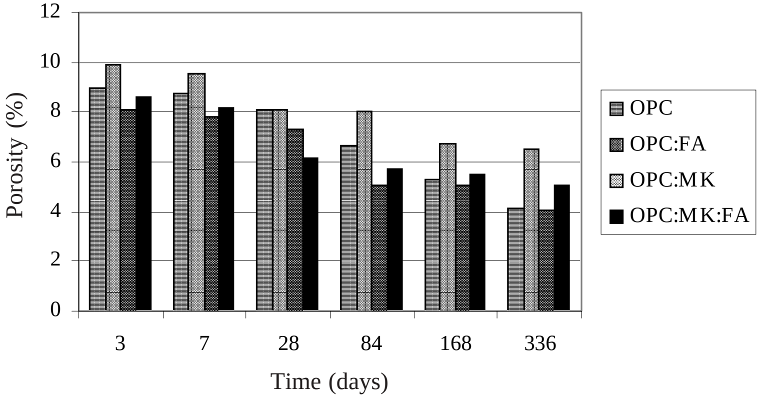

Figure 3: Concrete Porosity

of MK in TBC system has improved the porosity of the BBC concrete containing FA by about 10 %. Besides being highly reactive pozzolan, the finer particles of the MK could have contributed as filler, hence, reducing to a certain degree the porosity of the TBC concrete.

The test results for gas permeability are shown in Figure 4. At early ages, the gas permeability of the TBC concrete is higher than that of OPC and BBC systems containing MK. The TBC concrete only shows comparable permeability with OPC after the age of 168 days. This could be due to the lower amount of hydration products from the lower cement content and lower content of CaO in TBC system. The permeability of concrete is directly associated with the quantity of hydrated cementitious product at any given time [12]. In comparison to the BBC concrete containing FA and BBC concrete containing MK, the TBC has improved the permeability of HSC containing BBC with FA system by about 15 % but increased the permeability value of HSC containing BBC with MK by about 25 %. The inclusion of MK into the TBC cementitious systems had improved the permeability of HSC and the inclusion of FA was responsible for late permeability performance of TBC in the HSC produced. According to Thomas *et al.* [9], the combination of MK and FA in TBC systems improved the performance of cement through the effect of MK which compensates for low early strength of concrete with FA.

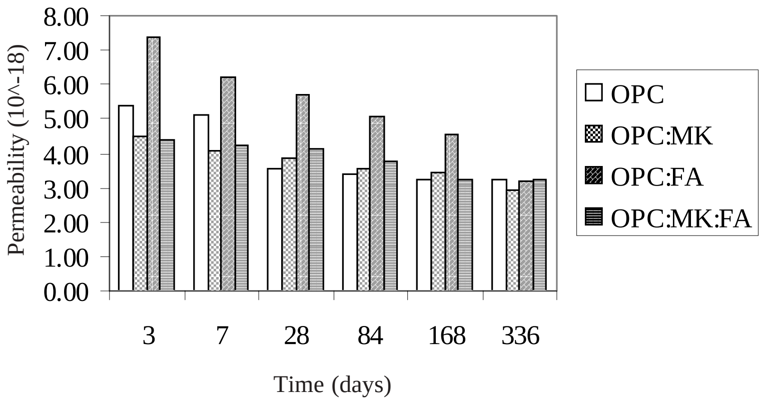

Figure 4: Concrete Permeability

Conclusions

From the results presented in this paper, the following conclusions are offered:

1. The CaO content of TBC found to reduce as the OPC replaced by FA and MK to about 40 % and the reduction is significantly alter the performance and properties of cement paste and concrete containing TBC.
2. The utilization of TBC found to increase the water demand and setting time of the cement paste but, the cementitious properties of TBC is still under acceptable limit.
3. The compressive strength of concrete using TBC achieved the same strength level with that of OPC at 28 days even though 40 % of the OPC content was replaced with the pozzolanic materials.
4. The used of TBC containing OPC:FA:MK improved the water absorption and porosity of concrete compared to OPC and OPC:FA concretes.
5. The used of TBC containing OPC:FA:MK improved the permeability of concrete as compared to OPC and OPC:FA concretes.

Acknowledgment

The authors would like to thank the Universiti Teknologi MARA (UiTM) and Universiti Sains Malaysia (USM) for providing grant and facilities, and to YTL Bhd. for providing the Fly Ash that enable the study to be conducted.

References

[1] Khatib, J. M. 2007. Metakaolin concrete at a low water to binder ratio. *Construction and Building Materials*.

[2] Hong-Sam Kim, Sang-Ho Lee, and Han-Young Moon. 2007. Strength propertiesand durability aspects of high strength concrete using Korean metakaolin. *Construction and Building Materials* 21. pp. 1229-1237.

[3] Cabrera, J. G. and Lynsdale, C. J. 1988. Measurement of chloride permeability in superplasticised ordinary cement mortars and pozzolanic cement mortars. *International conference on measurement and testing in civil engineering*, LyonVilleurbanne, pp. 279-291.

[4] Ambroised, J., Murat, M. and Pera, J. 1985. Hydration reaction and hardening of calcined clays and related minerals: extension of research and general conclusion. *Cement and Concrete research* 15. pp. 261-268.

[5] Neville, A. M. 2002. *Properties of concrete*, 4th edition, Prentice Hall, England.

[6] British Standard Institution, BS 1881, Part 116, 1983. *Method of determination of compressive strength of concrete cubes*, BSI, London.

[7] British Standard Institution, BS 6610, 1996. *Pozzolanic cement with pulverized-fuel ash as pozzolana*, BSI, London.

[8] Mohd Fadzil Arshad, Megat Azmi Megat Johari, Mazlee Mohd Noor, Mad Lias b Kamal. 2002. The Potential of Metakaolin produced from locally available kaolin as a mineral admixture for concrete," *Proceedings of Malaysian Science Technology Conference*, pp: 105-112.

[9] British Standard Institution, BS 12. 1996. *Specifications for Portland Cement*, BSI, London.

[10] Popovics, S. 1993. Portland cement-fly ash-silica fume system in *concrete, Advance Cement Based Materials* 1 (2) pp. 83-91.

[11] Zichao Wu and Tarun, R. N. 2002. Properties of concrete produced from multicomponent blended cements. *Cement and Concrete Research* 32, pp. 1937-1942.

[12] Thomas, M. D. A., Shehata, M. H., Shashiprakash, S. G., Hopkins, D. S. and Cail, K. 1999. Use of ternary cementitous systems

containing silica fume and fly ash in concrete. *Cement and Concrete Research*, pp. 1207-1214.

[13] Basu, A. and Aydin, A. 2004. A method for normalization of Schmidt hammer rebound values, *International Journal of rock mechanics and mining sciences* 41, pp. 1211-1214.

[14] British Standard Institution, BS 4550: Part 3. 1978. *Methods of testing cement,* Part 3. Physical tests, section 3.4 Strength tests.

[15] McCarthy, M. J. and Dhir, R. K. 2005. Development of high volume fly ash cements for use in concrete construction. *Fuel* 84, pp. 1423-1432.

[16] Poon, C. S., Kou, S. C. and Lam, L. 2006. Compressive strength, chloride diffusivity and pore structure of high performance metakaolin and silica fume concrete. *Construction and Building Materials* 20. pp. 858-865.

[17] Padney, S. P., Singh, A. K., Sharma, R. L. and Tiwari, A. K. 2003. Studies on high-performance blended/multiblended cements and their durability characteristics. *Cement and Concrete Research* 33, pp. 1433-1436.

[18] Sabir, B. B., Wild, S. and Bai, J. 2001. Metakaolin and calcined clays as pozzolans for concrete: a review. *Cement and Concrete Composite*, vol. 23, pp. 441-454.

[19] Malhotra, V. M. and Kumar, P. Mehta. 2004. *Pozzolanic and cementitious materials.* Advances in Concrete Technology, vol. 1, Taylor & Francis, London.