



## CHARACTERISTICS OF PORTLAND CEMENT PASTES WITH HIGH REPLACEMENT OF SLAG

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### ABSTRACT

The influence of substitution of Ordinary Portland cement by ground granulated blast-furnace slag up to 70% on the properties of silica fume-Portland cement composite pastes up to 12 months was studied. After one year, the composite cements pastes containing 50-70% slag exhibit suitable strength values compared to without slag sample. Also, XRD results show that the C-S-H are intensified with available increase indicating more dense structures and large amount of additional C-S-H in the presence slag content.

**Keywords:** composite cement, granulated slag, silica fume, physical properties.

### 1. INTRODUCTION

Mineral admixtures such as ground granulated blast-furnace slag (GGBS), fly ash and silica fume are commonly used in concrete because they improve durability and reduce porosity as well as improve the interface with the aggregate [1]. Economies (lower cement requirement), energy and environmental considerations have had a role in the mineral admixture usage and better engineering with performance properties. The lower cement requirement leads to a reduction for CO<sub>2</sub> generated by the production of Portland cement [2-5]. The engineering benefits from the mineral admixtures in cement result partly from their particle size distribution characteristics and partly from the pozzolanic and cementitious reactivity [6].

A laboratory investigation on optimum level of ground granulated blast-furnace slag (GGBS) on the compressive strength of concrete was studied [7]. GGBS was added according to the partial replacement method in all mixtures. A total of 32 mixtures were prepared in four groups according to their binder content. Eight mixes were prepared as control mixtures with 175, 210, 245, and 280 kg/m<sup>3</sup> cement content in order to calculate the Bolomey and Feret coefficient (KB, KF). For each group 175, 210, 245, and 280 kg/m<sup>3</sup> dosages were determined as initial dosages, which were obtained by removing 30 percent of the cement content of control concretes with 250, 300, 350, and 400 kg/m<sup>3</sup> dosages. Test concretes were obtained by adding GGBS to concretes in an amount equivalent to approximately 0, 15, 30, 50, 70, 90, and 110% of cement contents of control concretes with 250, 300, 350, and 400 kg/m<sup>3</sup> dosages. All specimens were moist cured for 7, 14, 28, 63, 119, 180, and 360 days before compressive strength testing. The test results proved that the compressive strength of concrete mixtures containing GGBS increases as the amount of GGBS enhances. After an optimum point, at around 55% of the total binder content, the addition of GGBS does not improve the compressive strength.

Blended cements containing large replacements of ordinary Portland cement (OPC) with blast-furnace slag (BFS) are currently used for encapsulation of nuclear

waste in the UK [8]. Up to 90% BFS is employed in encapsulation pastes, amounts which are much higher than those used in the construction industry. These percentages were defined to help reduce the heat evolution of the mixes and avoid problems associated with thermal cracking and loss of durability, and to ensure the pastes is sufficiently fluid for mixing and pouring into the encapsulation drums.

Hydration of blast-furnace slag produces a higher amount of calcium silicate hydrate (CSH) gel and a lower amount of calcium hydroxide (CH) than normal Portland cement at any given hydration age [9]. New hydration products of slag are formed during the hydration of BFS/Portland cement. This hydration of slag is accompanied by morphological changes and a decrease of capillary porosity of CSH products.

The objective of the present work is to study the influence of slag as constituent in composite cement on the physico-mechanical properties as well as kinetics of hydration of composite cement pastes. The water of consistency, as well as initial and final setting times of the cement pastes was determined. The kinetics of hydration in tap water as free lime and combined water contents of the hardened cement pastes up to one year were studied. The mechanical properties of the composite cement pastes such as total porosity and compressive strength must be determined. Some of the hydrated cement paste samples investigated by using XRD techniques.

### 2. MATERIALS AND METHODS

#### 2.1 Materials

##### 2.1.1 Ordinary Portland cement

The Portland cement provided was obtained from National Cement Company, Helwan. The physical properties of Portland cement which was determined by using the standard normal methods are presented in Table-1. The chemical analysis of starting materials (was carried out using the XRF technique) aided with normal wet chemical analysis technique are given in Table-2 (ASTM C114-1988) [10].

**Table-1.** Physical properties of Portland cement.

Properties	Results
Setting time (min)	
▪ Initial	108
▪ Final	165
Water of normal consistency (%)	27
Blaine surface area (m <sup>2</sup> /kg)	3.15

**Table-2.** Chemical analysis of the starting materials, (wt, %).

Materials	Oxides							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O
Portland cement	21.3	5.41	3.77	63.14	1.21	2.35	0.09	0.4
Silica fume	96.89	2.03	0.56	0.21	0.15	0.16	0.62	0.17
Granulated slag	39.89	13.72	2.56	26.38	3.47	1.22	1.06	1.0

### 2.1.2 Granulated blast-furnace slag

It was obtained from the Egyptian Iron and Steel Company, Helwan. It is usually obtained by water quenching of the molten slag. It was ground in a steel ball mill to obtain a Blaine surface area (4.56m<sup>2</sup>/kg). The results of chemical analysis of granulated slag were given in Table-2.

### 2.1.3 Silica fume

It is a by-product of the manufacture of ferro-silicon metals. It was obtained from ferrosilicon company, Edfo, Upper Egypt. The chemical analysis of the silica fumes (SF) after drying at 105°C for two hours is given in Table-2. Its surface area as measured by the BET methods is 20 m<sup>2</sup>/g.

## 2.2 Preparation of slag-OPC-silica fume composite cement

The dry constituents of OPC, silica fume and slag were mechanically mixed for 30 minutes in a porcelain ball mill to attain complete homogeneity. The samples were kept in airtight containers until the time of paste preparation. The mix compositions of different prepared composite cement are shown in Table-3.

**Table-3.** Mix composition of different composite cements, wt %.

Mix No.	Granulated slag	Silica fume	OPC
Mo	0	6	94
M <sub>1</sub>	40	6	54
M <sub>2</sub>	50	6	44
M <sub>3</sub>	60	6	34
M <sub>4</sub>	70	6	24

The water of consistency (ASTM C187) [11] and setting time (ASTM C191) [12] were determined. The

pastes were mixed with water of consistency, molded in one inch cubic molds for 24 hours, de-molded then immersed in tap-water up to one year. The kinetic of hydration were followed by the determination of free lime (ASTM 114) [10] and combined water contents after firing at 950°C for 30 minutes minus the weight of water in Ca (OH)<sub>2</sub>. The total porosity (ASTM C373) [13] and compressive strength were also measured up to one year. The mixing, molding and stopping of hydration were described elsewhere [14].

The compressive strength test was carried using a machine of the Seidener model having a maximum load of 600 KN. For each group, at least three specimens were tested and the average of the results was considered.

X-ray diffraction (XRD) analyses were performed using BRUKER D<sub>8</sub> ADVANCE, Target: Cu K<sub>α</sub>. The phases were identified with the help of the Appendix 1, on Tabulated Crystallographic Data[15].

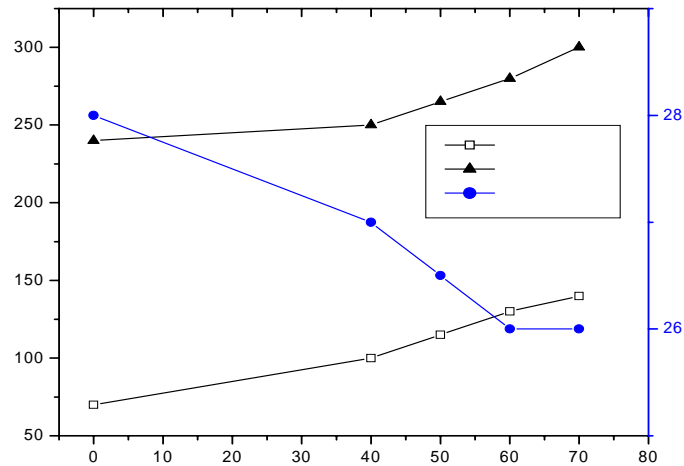
## 3. RESULTS AND DISCUSSIONS

### 3.1 Initial and final setting times

Initial and final setting times as well as water of consistency for prepared different mixes of composite cement are graphically represented in Figure-1. In general, the water consistency of composite cement pastes containing GGBS require less water compared to the cement paste without slag. Also, the initial and final setting time of the cement pastes increases with increasing slag content. The addition of silica fume accelerates the early stage of hydration of Portland cement and its individual compounds. The increased rate of hydration may be due to enhanced precipitation of hydration products on the surface of pozzolana which possibly serves as a nucleation site during the early hours when it exists as chemically inert filler. On the other hand, the setting process is associated with the formation of calcium sulphoaluminate hydrate. The formation of these hydrates depends on the reaction velocity of the aluminate compounds, amount of the phases, calcium sulfate and



calcium hydroxide. The Portland cement clinker acts as a source of calcium hydroxide that gives the correct alkalinity to form ettringite.

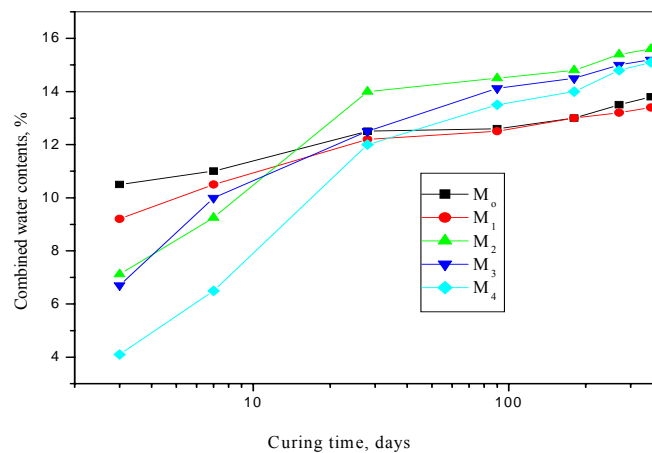


**Figure-1.** Water of consistency as well as initial and final setting time of different composite cement pastes.

### 3.2 Combined water content of composite cement

The values of combined water contents of composite cement pastes cured up to one year are graphically represented as a function of curing time in Figure-2. The combined water content increases with curing time for all the composite cement. This is due to continuous and progress of hydration products with time for one year. Also, the data show that the combined water contents of the cement pastes decreases with increasing of the slag content at early ages of hydration (3-28) days. This is may be due to the lack of clinker content as well as the weakness of the interaction of granulated slag at early

ages. On the other side, as the slag content increases in the cement paste the combined water enhances at later ages (90-360) days. In addition, cement pastes with 50% slag give a higher amount of combined water at 90-360 days than the other cement pastes. This indicates that the slag plays an important role in the hydration of the cement paste at later ages of curing time. Therefore, the cement paste without slag gives a higher amount of combined water at 3-28 days and a lower amount at 90-360 days. This shows the role of silica fume in activation of  $C_3S$  and may be  $\beta-C_2S$  at early ages of hydration.



**Figure-2.** Chemical combined water contents of different composite cement pastes as function of curing time.



### 3.3 Free lime of composite cement

The free lime contents of the composite cement pastes cured for (3, 7, 28, 90, 180, 270 and 360 days) are shown in Figure-3. The results show that the cement pastes without slag addition gives a higher amount of free  $\text{Ca}(\text{OH})_2$  than the other samples at all ages, while as the slag proportion increases the free lime decreases with curing time. This is due to that the increasing of slag till 70% is accompanied by a decrease in the clinker content. Therefore, the cement pastes containing 60 and 70% slag give a lower amount of free lime at all ages. On the other side, the free lime of cement paste without slag sharply enhances at (3-7) days. This is attributed to the activated silicate phases especially  $\text{C}_3\text{S}$  liberates more  $\text{Ca}(\text{OH})_2$

during the hydration. Also, the existence of  $\text{Ca}(\text{OH})_2$  accelerated the hydration of slag and the decreased content of  $\text{Ca}(\text{OH})_2$  enhanced the hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  promoting the more rapid and complete hydration of both clinker and slag in cement. The cement pastes with 50, 60 and 70% slag show increase of free lime up to 90 days and then decrease up to 360 days. This is mainly due to the fact that the clinker content decreases and consequently the free lime diminishes. Also, the rate of liberation of free lime is lower than its consumption with cement composite pastes containing silica fume and GGBS. Therefore, the residual free lime in cement pastes with higher values of slag (60 and 70%) decreases after 28 and 90 days up to 360 days.

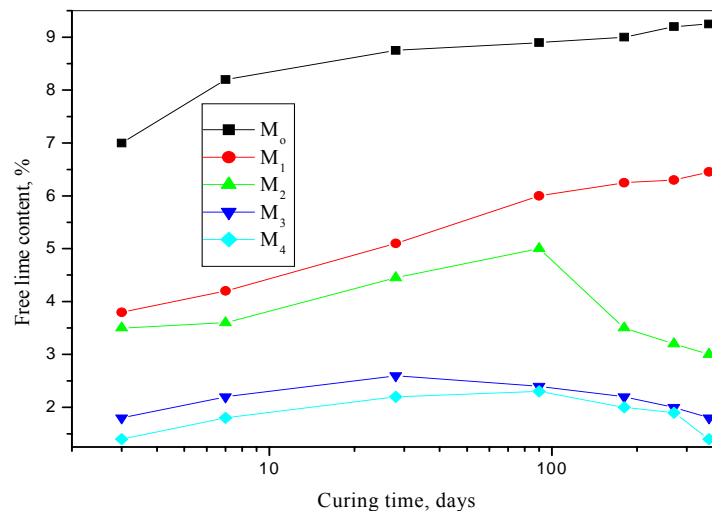


Figure-3. Free lime contents of different composite cement pastes as function of curing time.

### 3.4 Total porosity of composite cement

The total porosity of the hydrated pastes as a function of curing time is plotted in Figure-4. The total porosity of hardened cement pastes decreases with curing time for all cement pastes. This is due to the filling up of the available pores with the hydration products. It is evident that the sample containing silica fume only less porosity at 3 and 7 days while samples containing slag have less porosity at later ages (28-360) days. The presence of silica fume increases the rate of hydration during the first few hours of hydration, indicating that silica fume affects hydration by the nucleating affects of its surface when it still exists as inert filler. On the other side, increasing the slag content in the cement paste, the total porosity decreases at later hydration time (28-360 days). Hydration of blast-furnace slag produces a higher amount of C-S-H gel and a lower amount of C-H than normal cement at any given hydration age and accompanied by morphological changes as well as a decrease of the capillary porosity of C-S-H products (1).

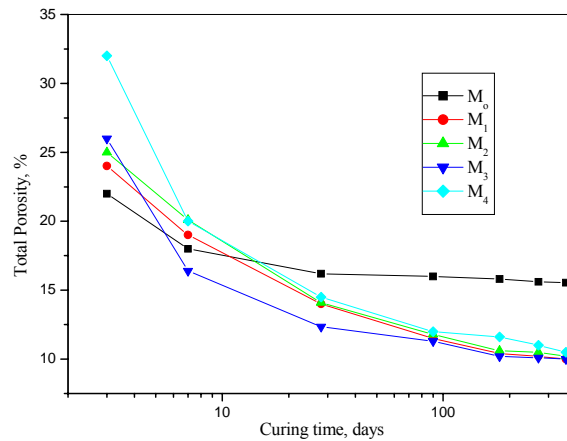
### 3.5 Compressive strength of composite cement

The compressive strength of the composite cement pastes is graphically represented as function of curing time for one year in Figure-5. The compressive strength increases with curing time for all cement pastes. This is attributed to the increase of the amount of hydrated products especially tobermorite gel (the main source of compressive strength). So, this leads to a corresponding increase in the compressive strength of the hardened cement pastes. It is observed that the early strength values of GGBS cement pastes are lower than that without slag. As the curing period is extended, the strength values of GGBS cement pastes increase more than the control sample. After one year, the GGBS pastes (40-50%) exhibit higher strength values compared to composite cement pastes without slag. Since the reactivity of the slag is slow and depends on the calcium hydroxide availability, the strength gain takes longer time with slag content. On the other hand, it can be seen that, the cement paste with the highest GGBS addition presents the highest compressive strength increase from seventh day up to one year. This shows that as the GGBS content is increased, the strength gain

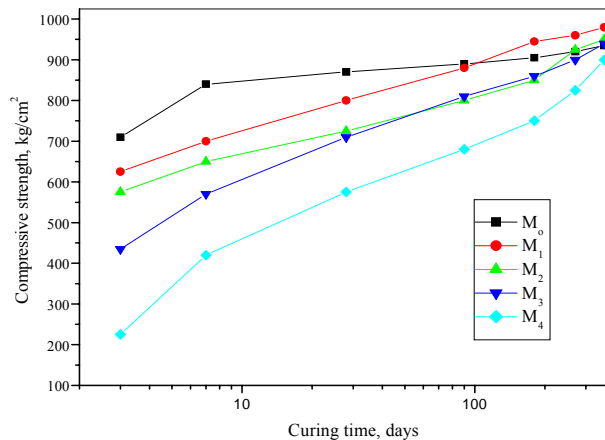


increases in time. Increasing the rate of hydration, and hence the early strength development, is done at the expense of the ultimate strength. One reason for this is that the microstructure formed during the accelerated hydration is usually coarser and less favourable for strength development. Contrary to this, slow hydration allows the formation of a microcrystalline or rather gel-like structure

of large surface area, which results in good strength. Another reason is that at high rate of hydration at early ages, large quantities of hydration products are formed around the un-hydrated particles, which impeded and slow down the later hydration, and therefore the rate of hydration decreases.



**Figure -4.** Total porosity of the hardened different composite cement pastes as function of curing time.

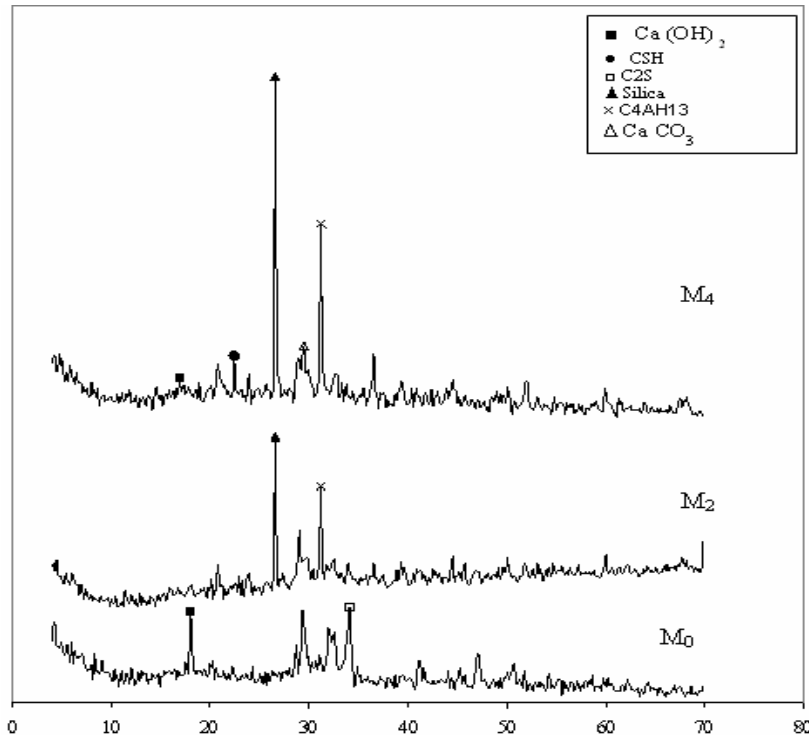


**Figure -5.** Compressive strength of the hardened different composite cement pastes as function of curing time.

### 3.6 XRD of composite cement

The XRD patterns of the hydrated cement composite pastes (0, 50 and 70% slag content) hydrated for 360 days in tap water are shown in Figure-6. The main phases detected in the patterns are calcium silicate hydrate ( $d = 3.07633$ ), calcium hydroxide ( $d = 4.9082$ ,  $d = 2.6263$ ) and  $\text{CaCO}_3$  ( $d = 3.0343$ ),  $\text{B-C}_2\text{S}$  ( $d = 2.7745$ ,  $d = 2.7465$ ) as well as  $\text{C}_4\text{AH}_3$  ( $d = 2.8568$ ). It is clear that, the peak of calcium hydroxide shows higher intensity in cement without slag (contain only 6% silica fume) and completely disappear in other samples. The intensity of  $\text{CaCO}_3$  peaks

decrease with increasing GGBS contents in the composite cement pastes. The C-S-H peaks are intensified with the slag increase indicating more dense structure and large amounts of additional C-S-H in the presence of 50 and 70% slag addition.  $\text{C}_4\text{AH}_3$  was also detected in GGBS containing sample. In addition, quartz peaks were also detected as a main constituent of slag. Also, residual un-hydrated peaks of  $\beta\text{-C}_2\text{S}$  phase were detected even after 360 days of hydration with the control paste while completely disappearance with slag samples.



**Figure-6.** XRD patterns of different cement composite pastes cured in tap water up to one year.

#### 4. ENERGY REQUIREMENT

Energy requirement in the production of different composite cement types, where secondary components are

added in the proportion usually employed in the industry is reported in Table-4.

**Table-4.** Energy required for the production of composite cement in comparison to Portland cement.

OPC	Different types of composite cement					
	OPC	M <sub>0</sub>	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>4</sub>
	Clinker 95% Gypsum 5%	OPC 94% Slag 0% SF 6%	OPC 54% Slag 40% SF 6%	OPC 44% Slag 50% SF 6%	OPC 34% Slag 60% SF 6%	OPC 24% Slag 70% SF 6%
OPC, MJ/ton	3230	3146	1836	1446	1156	816
Cost, \$/tone	10.0	9.5	5.6	4.5	3.5	2.4

The values are based on the total energy required of 3400 MJ/ton of clinker produced. Also, it can be supposed that grinding, handling and packing need 40 kwh (364MJ) and 45 kwh (409MJ) of Portland cements and Portland pozzolanic or Portland filler cement, respectively, and 55 kWh (500 MJ) per tone of Portland slag [16]. The energy employed for the transportation of secondary constituents and raw materials necessary for the manufacture of the substituted clinker has been considered in this computation. This energy varies from 6 to 60 MJ/tonne of cement, depending on the distance and the kind of transportation.

The difference between the energy required by the different composite cements and Portland cement was between 2330-1310 MJ/tonne. It was concluded that the

difference of cost saving between the production of Portland cement and composite cement was 10\$ to 2.4\$, respectively.

#### 5. CONCLUSIONS

It can be concluded that:

- Ground granulated blast-furnace slag could be used as a partial replacement of Portland cement up to 70% in composite cement, without decreasing the compressive strength;
- After one year, the composite cement pastes containing 40-70% slag exhibit suitable strength values compared to without slag sample; and
- The XRD results indicate that the C-S-H peaks are intensified with available increase indicating more



dense structure and large amounts of additional C-S-H in the presence of 50 and 70% slag addition.

## REFERENCES

- [1] Tufekci M., Demirbas A., Genc H. 1997. Evaluation of steel furnace slags as cement additives, *Cem. Concr. Res.* 27(11): 1713-1717.
- [2] Badogainnis E., Papadakis V.G., Chaniotakis E. and Tsvivilis S. 2004. Exploitation of poor Greek kaolins: strength development of metakaolin concrete and evaluation by means of k-value. *Cem. Concr. Research.* 34: 1035-1041.
- [3] Roy D.M, Arjunan P. and Silbee M. R. 2001. Effect of silica fume, metakaolin, and low-calcium fly ash on chemical resistance of concrete. *Cement Concrete Research.* 31: 1809-1813.
- [4] Ferraris C.H., Obla K.H. and Hill R. 2001. The influence of mineral admixtures on the rheology of cement paste and concrete. *Cement Concrete Res.* 31: 245-255.
- [5] Chan WWJ, CML Wu. 2000. Durability of concrete with high cement replacement. *Cement Concrete Research.* 30(6): 865-879.
- [6] Mehta PK. 1983. Pozzolanic and cementitious by-products as mineral admixtures for concrete - a critical review, Sp-79. *ACI.* pp. 1-48.
- [7] Oner A. and Akyuz S. 2007. An experimental study on optimum usage of GGBS for the compressive strength of concrete, *Cem. Concr. Compos.* 29: 505-514.
- [8] Borges P.H.R., Costa J.O., Milestone N.B., Lynsdale C.J. and Streatfield R.E. 2010. Carbonation of CH and CSH in composite cement pastes containing high amounts of BFS, *Cem. Concr. Res.* 40: 284-292.
- [9] Bohac M. and Gregerova M. 2009. The influence of blast-furnace slag hydration products on micro-cracking of concrete, *Mat. Charact.* 60: 729-734.
- [10] 1999. ASTM C114, Standard test methods for chemical analysis of hydraulic cement.
- [11] 2007. ASTM C187, Test method for normal consistency of hydraulic cement.
- [12] 2007. ASTM C191, Test method for time of hydraulic cement by Vicat method.
- [13] ASTM C373, Test method for determination of the porosity cement.
- [14] Didamony H., Haggag M.Y and Abu-El-Enein S.A. 1979. *Cement Concrete Res.* 8: 321.
- [15] Taylor H.F.W. 1997. *Cement chemistry.* 2<sup>nd</sup> Ed. Thomas Telford Publishing, London, U.K.
- [16] Ghosh S. N. and Yadav S. N. 1996. *Energy conservation and environmental control in cement industry.* Akademia books international, New Delhi, India.