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EFFECT OF LIMESTONE ON THE HYDRATION CHARACTERISTICS OF PORTLAND-POZZOLANA CEMENT MORTARS

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Abstract

The aim of this work is to utilize some Egyptian by-products such as granulated blast-furnace slag (GBFS) and fired clay or waste clay bricks known as Homra to produce economic blended cement. The effect of addition of limestone as a filler on the hydration characteristics of such blended cements was investigated.

The effect of artificial pozzolana (waste clay bricks) and GBFS in the absence and presence of limestone on the physico-chemical and mechanical properties of the hardened cement pastes was studied.

A various dry cement blends were prepared by mixing of ordinary Portland cement (OPC) with waste clay bricks (WCB) or GBFS as partial replacement of OPC (0, 10, 20 and 30%) and the optimum constitution was established as 10%. Other cement blends were also prepared by partial replacement of OPC by limestone (LS) (0, 2.5, 5.0 and 7.5 %) and the optimum composition was found to be 5%. This was followed by mixing of the optimum constitution of 85 % OPC: 10 % GBFS: 5 % LS and 85 % OPC: 10 % WCB: 5 % LS blends. Each of cement blend was mixed with water using the standard water of consistency and the setting time was determined.

The physico-chemical properties of the hardened mortars, made of each cement blend with a ratio of 1:3 of cement blend:sand a water/solid ratio of 0.50, were tested for compressive strength, chemically combined water content and free water content at different ages of hydration of 1, 3, 28 and 90 days. In addition, thermal analysis and X-ray diffraction analysis were carried out on some selected samples.

Keywords:

Limestone, Waste clay bricks, Granulated blast-furnace slag, Ordinary Portland cement and Physico-chemical properties.

Introduction

The research of the economic binder by using the industrial by products (blast furnace slag, silica fume, Waste bricks) and the natural resources (natural pozzolana, limestone) is a major concern to reduce the deficit recorded during the manufacture

of Portland cement **[1].** In last years, a large effort of research was provided on the use of the supplementary cementitious materials as a partial replacement to Portland cement **[2]**. A partial replacement of cement by mineral admixture such as, waste bricks, silica fume or blast furnace slag in cementing materials mixes would help to overcome these problems and lead to improvement in the workability, strength and durability of cementing materials **[3]**.

Addition of limestone powder to cements and concretes in the U.S. have developed along a much different path than that taken in Europe, where limestone/cement blends have been employed for many years. After years of discussion, it was only in 2004 that the ASTM International C150 standard specification for Portland cement was modified to allow the incorporation of up to a 5% mass fraction of limestone in ordinary Portland cements **[4]**. An extensive survey of the literature available at that time conducted by the Portland Cement Association **[5]** concluded that "in general, the use of up to 5% limestone does not affect the performance of Portland cement." Higher addition rates of 10 to 15% are currently being discussed, particularly in Canada where the Canadian Standards Association (CSA) may supersede its American (International) counterpart in moving to higher levels **[6]**.

The effect of artificial pozzolana (waste brick) on the physico-chemical properties of cement manufactured was investigated. The waste brick is generated by the manufacture of clay bricks. It was used in the proportions of 0, 10, 20 and 30% by mass of cement to study its effect on the physico-chemical properties of cement incorporating artificial pozzolana **[7]**.

The physical-mechanical properties and durability in micro-concretes, by employing calcinated and grinded clays as replacement material, by 30% of ordinary Portland cement (OPC) were studied. Therefore, clay soil was employed, which is mainly composed by low-purity-kaolin mineral, so as to obtain calcined clays to be used as supplementary cementious minerals **[8].**

Blended cements based on the partial replacement of Portland cement clinker (PC) by solid wastes have been the subject of many investigations in recent years. The use of the replacement materials offer cost reduction, energy savings, arguably superior products, and fewer hazards in the environment. These materials participate in the hydraulic reactions, contributing significantly to the composition and microstructure of hydrated products **[9, 10]**.

The aim of this work is to utilize some Egyptian by-products such as granulated blast-furnace slag (GBFS) and fired clay or waste clay bricks known as Homra to

produce economic blended cement. The effect of addition of limestone as a filler on the hydration characteristics of such blended cements was investigated.

Materials and Experimental

Materials

The starting materials used in this investigation are ordinary Portland cement (OPC) from Helwan cement company, Egypt Limestone powder from Helwan quarries, fired or waste clay bricks from clay bricks industries, and ground blast-furnace slag (GBFS) from the steel factory in Tebbin, Helwan, Egypt. The tap water was used in mixing and curing process.

Table (1) Chemical composition and Blaine area of the starting Materials, wt%.

Oxides (%)	Portland Cement	Limestone	Waste(Fired) Bricks	GBFS
SiO_2	20.67	2.49	59.78	33.93
Al_2O_3	5.52	0.05	18.71	8.91
Fe_2O_3	3.42	0.11	9.87	2.61
CaO	63.19	53.23	2.84	39.89
MgO	2.28	0.81	1.57	5.56
SO_3	2.41	0.07	1.19	1.24
Cl	0.02	0.03	0.42	0.37
K_2O	0.13	0.13	0.87	1.82
Na_2O	0.08	0.13	0.03	0.38
L.O.I	2.2	42.7	3.6	4.3
Total (sum)	99.90	99.75	98.88	99.01
Blaine cm^2/g	3124	4102	3250	3404
Sieve/90 µm	3.1	7.2	12	9

Experimental

Preparation of dry mixes

Various dry mixtures are prepared. The blank mixture is composed of ordinary Portland cement (OPC). Partial replacements of OPC by limestone (L), granulated blast-furnace slag (GBFS) and fired bricks (F) were carried out. Each dry mix was homogenized for few minutes in "Herzog Vibration Grinding Mill Hp-M 100p" to

obtain complete homogeneity then kept in airtight containers until the time of cement paste preparation was reached.

In this investigation, five types of blended cements are studied as shown in Table (2)

Table (2) Composition and designation of dry mixes.

System	Mix	Composition %			
		OPC	Limestone	Slag	Fired Bricks
OPC	M_0 = Mopc	100	-	-	-
OPC-L	Portland limestone cement				
OPC-L	$M_{L2.5}$	97.5	2.5	-	-
	M_{L5}	95	5	-	-
	$M_{L7.5}$	92.5	7.5	-	-
OPC-S	Portland slag cement				
OPC-S	M_{S10}	90	-	10	-
	M_{S20}	80	-	20	-
	M_{S30}	70	-	30	-
OPC-F	Portland fired clay bricks cement				
OPC-F	M_{F10}	90	-	-	10
	M_{F20}	80	-	-	20
	M_{F30}	70	-	-	30
OPC-SL	Portland slag-limestone cement				
OPC-SL	M_{S10-L}	85	5	10	-
OPC-FL	Portland fired clay bricks-limestone cement				
OPC-FL	M_{F10-L}	85	5	-	10

Preparation of cement pastes and mortars

a) Preparation of cement pastes

Each dry cement blend is mixed with the required amount of water using standard water of consistency. The dry mixture is placed on a smooth non-absorbent surface and a crater is formed in the center by the aid of a trowel and the required amount of water is poured into the crater. The dry mixture around the outside of the crater is slightly troweled over the remaining mixture to absorb water for about one minute. The mixing operation is then completed by vigorous mixing by trowel for about three minutes. At the end of mixing, the paste is directly pored into the moulds, and the initial and final setting times are determined by using Vicat needle apparatus.

b) Preparation of mortars

Mortar pastes are prepared using cement: sand dry mixture ratio of 1:3 by mass and mixed with 50% water/cement ratio using automatic mixer. The freshly prepared mortar paste was placed in stainless steel (40×40×160 mm) moulds in two approximately equal layers. Each layer is compacted and pressed until homogeneous specimen is obtained. The moulds were then vigorously vibrated, by a Jolting apparatus, for a few minutes to remove air bubbles and to give a better compaction of the mortar. The surface of the mortar was smoothed by the aid of thin edged trowel.

c) Curing

Immediately after moulding, the moulds will kept inside humidity cabinet TPS (Thermal Product Solutions-Lunaire) for 24 hours at 100% RH and a constant temperature of 23 ±1º C. In the following day, the specimens are demoulded and cured in tap water till the time of testing for compressive strength test at 1, 3, 7, 28 and 90 days is reached **[11].** The curing water was renewed every week.

Water of consistency and setting time measurements

The water requirement of cement is a very important factor affecting the quality of concrete. The Standard consistency test is primarily made to adjust the consistency of cement paste suitable for the setting test, not to analyze the water requirement of cement. The amount of mixing water required to give standard consistency as well as the setting time are measured by using Vicat needle apparatus.

Compressive strength test

The compressive strength test is carried out using a hydraulic test machine of type universal flexure/compression equipment ToniNORM (Toni technik Gmbh, Germany) with integrated data processing program "ToniTrol Expert" **[12]**.

Stopping of hydration

Stopping of hydration of hardened mortar paste is carried out by removing free water at a specified testing time to stop the hydration reaction and render the material less susceptible to carbonation. The crushed specimens from compressive strength tests were placed in a solution mixture of 1:1 (v:v) methanol:acetone to stop the hydration as described elsewhere **[13]**. To stop the hydration reaction at any age of hydration, a representative sample of about 10 g of freshly crushed sample after the determination of compressive strength was taken, grinded and placed in glass beaker containing 100 mL of 1:1 (methanol: acetone) solution mixture, stirred by

magnetic stirrer for 30 minutes and the solid residue was filtrated through a sintered glass funnel. The solid sample, thus obtained, was dried at 70-80 ºC for one hour and then kept inside an airtight bottle.

Determination of combined water contents

The determination of combined water content (W_n) is carried out using three exactly weighed representativee samples of hydration stopped specimens, ignited in porcelain crucibles at 1000º C for 45 minutes in a muffle furance and cooled in a desiccatore. The combined water content is the percentage of the weight loss with respect to weight after ignition.

$$W_n\ \% = \frac{\text{Weight before ignition} - \text{Weight after ignition}}{\text{Weight after ignition}} \times 100 - L$$

Where L is the ignition loss of anhydrous cement

Differential thermal analysis (DTA)

The DTA technique is applied using differential thermal analyzer of the type Setaram instrumentation and regulation (Labsys ™ TG-DSC1600, French). A sample of 20 mg is placed in alumina crucible with a heating rate of 10 ºC/min using Alumina as a reference material. All measurements are done in Nitrogen-atmosphere.

Results and Discussion

The effect of limestone on the hydration characteristics of Portland cement, fired bricks-Portland cement and granulated blast furnace slag-Portland cement blends is investigated. This study includes the investigation of water of consistency, setting time, combined water contents and compressive strength. In addition, phase composition of the hydrated phases is examined by using different ional thermal analysis technique (DTA).

Setting time test

The partial substitution of OPC by 2.5% limestone is accompanied by elongation of setting times; since the limestone with lower contents acts as a retarder with gypsum. Higher limestone contents lead to a marked decrease in setting time due to the lower water demand of the fresh cement pastes (water of consistency). The mixes containing granulated blast furnace slag and those containing fired bricks wastes showed a marked increase in the setting times. It can be noticed that as the ratio of such supplementary materials increases the setting times increase. This

observation can be explained as a result of the less hydraulic properties of these supplementary materials compared to ordinary Portland cement.

Table (3) Results of setting time

Mix	Initial setting time (min)	Final setting time (h & min)	Water consistency (w/c, %)
M_0	18 min	1 h 45 min	30.75
$M_{L(2.5)}$	30 min	1 h 39 min	32.00
$M_{L(5)}$	25 min	1 h 22 min	31.00
$M_{L(7.5)}$	20 min	0 h 57 min	30.25
$M_{S(10)}$	50 min	2 h 15 min	29.50
$M_{S(20)}$	95 min	3 h 19 min	28.75
$M_{S(30)}$	113 min	4 h 15 min	27.50
$M_{F(10)}$	105 min	3 h 50 min	29.25
$M_{F(20)}$	115 min	4 h 05 min	30.50
$M_{F(30)}$	122 min	4 h 29 min	31.00
$M_{SL(10+5)}$	90 min	2 h 80 min	27.00
$M_{FL(10+5)}$	75 min	2 h 50 min	28.75

Compressive Strength

The results of compressive strength of the investigated mixes are given in Table (4). The values of compressive strength of the hardened Portland cement pastes in absence and presence of limestone (mixes M_0, $M_{L2.5}$, M_{L5} and $M_{L7.5}$) increase with hydration age up to 90 days. This is due to the progress of the hydration reaction leading to the formation of more hydration products precipitate in the pore system. The presence of 2.5% limestone increases the values of compressive strength especially at later ages (7 up to 90 days). Such observation can be attributed to the pore filling effect of this ratio of limestone. Addition of more limestone (5 or 7.5%) leads to a slight decrease in the values of compressive strength at later ages of hydration. The decrease in the values of compressive strength by adding more limestone can be explained to the dilution of Portland cement.

The mixes containing blast furnace slag show less values of compressive strength compared to the blank mix (M_0) nearly at all hydration ages. This can be explained to the replacement of part of Portland cement which is more hydraulic by less reactive one. As the ratio of slag added increases the values of compressive strength decrease, see Table (4).

Table (4) Results of compressive strength

Mixes	Compressive strength kg/cm^2				
	1 day	**3 days**	**7 days**	**28 days**	**90 days**
M_0	32	181	245	433	476
$M_{L(2.5)}$	32	177	264	436	481
$M_{L(5)}$	33	173	255	405	459
$M_{L(7.5)}$	31	169	249	399	423
$M_{S(10)}$	43	146	205	367	409
$M_{S(20)}$	37	130	183	330	374
$M_{S(30)}$	30	90	120	237	268
$M_{F(10)}$	39	159	221	407	451
$M_{F(20)}$	28	128	181	352	411
$M_{F(30)}$	21	96	146	293	349
$M_{SL(10+5)}$	34	163	274	385	478
$M_{FL(10+5)}$	47	183	282	380	442

The mixes containing fired bricks (M_F) show less values of compressive strength compared to the blank mix (M_0) at all hydration ages. As the ratio of the added fired bricks increases the values of compressive strength decrease. Again, this can be attributed to the less reactivity of fired bricks compared with Portland cement. It can be noticed that the result of compressive strength of these mixes are higher than those containing blast furnace slag at all hydration ages. This can indicate that the fired bricks have more pozzolanic reactivity than blat furnace slag.

The presence of 5% by mass limestone in the mixes containing 10% by mass blast furnace slag ($M_{SL(10+5)}$) improved significantly the values of compressive strength compared those of mix M_{S10} without limestone at all hydration ages up to 90 days. This can be attributed to two factors; the first one is the filling effect of limestone to the pore system. The second factor may be the acceleration effect of limestone to the pozzolanic reaction between slag and the liberated calcium hydroxide from hydration of Portland cement. Such reaction produces more calcium silicate hydrates (CSH) which consider the main binding agent. Therefore, the values of compressive strength improved.

The presence of 5% limestone in the mix blended with 10% fired bricks (M_{F10}) improved the values of compressive strength compared with those of the mix without limestone at early ages up to 7 days. This can be explained as a result of the filling effect of the added limestone to the pore system. From the results of compressive strength, shown in Table (4), it can be consider the mixes $M_{L2.5}$, M_{L5}, $M_{SL(10+5)}$ and $M_{FL(10+5)}$ optimum mixes for producing economic blended Portland cement with good quality.

Chemically combined water content (W_n, %)

The results of chemically combined water contents (W_n, %) of the various hardened mortar pastes cured under tap water as a function of hydration age up to 90 days are given in Table (5). In general, all the investigated mortar mixes showed a continuous increase of combined water content with hydration ages up to 90 days. This is due to the progress of the hydration of the hydraulic components.

Mortar mixes containing limestone showed higher values of chemically combined water contents than the blank mortar mix (without limestone) at early ages of hydration, up to 3 days, while as, at later ages, from 7-90 days the values of combined water of the mortar mixes are lower than those of blank mortar mix.

The higher values of chemically combined water contents of the mixes blended with limestone at early ages of hydration may be related to the formation of carboaluminate phase. While as, the less values of combined water contents at the later ages of hydration could be attributed to the dilution of the active component of the mix with Portland cement. As the ratio of limestone increases the combined water contents decreases at later ages of hydration.

Table (5) Results of Combined water contents (W_n)

Mixes	Combined Water (W_n %)				
	1 day	3 days	7 days	28 days	90 days
M_0	2.06	2.33	3.86	4.07	4.44
$M_{L(2.5)}$	2.31	2.66	3.25	3.70	4.70
$M_{L(5)}$	2.46	3.29	3.55	3.90	4.21
$M_{L(7.5)}$	2.77	3.15	3.71	4.24	4.35
$M_{S(10)}$	2.67	2.99	3.57	4.32	4.69
$M_{S(20)}$	2.45	2.68	2.92	3.67	4.06
$M_{S(30)}$	2.28	2.49	2.56	3.30	3.77
$M_{F(10)}$	2.55	3.13	4.19	4.88	5.96
$M_{F(20)}$	3.23	3.32	4.38	5.12	5.73
$M_{F(30)}$	2.32	2.91	3.00	4.69	4.94
$M_{SL(10+5)}$	4.26	4.49	4.79	5.71	6.96
$M_{FL(10+5)}$	4.68	4.87	5.08	5.45	6.63

The mortar mixes containing 10% blast furnace slag showed slightly higher values of chemically water contents compared to the blank mix at most of the hydration ages. While the mixes containing higher ratios of blast furnace slag than 10% showed slightly lower values of combined water contents than the blank mix at later ages of hydration. As the ratio of the slag increase from 20 to 30 more decrease in combined occurred at later ages of hydration is observed ,this may be attributed to the dilution effect caused by the presence of the less active slag compared to Portland cement.

The hardened mortar mixes containing fired bricks showed higher values of combined water contents at all the hydration ages compared to the blank mortar mix. This can be attributed to the formation of more calcium silicate hydrate with high water content.

In addition, the mixes containing 10% slag or fired bricks in presence of limestone showed higher values of combined water contents than all the investigated mixes. This can be explained to the formation of calcium carboaluminate phase which contains high water contents as well as the formation of calcium silicate hydrate with high water content.

Differential thermal analysis (DTA)

The DTA thermograms obtained for the hardened mortar paste made of OPC are shown in Fig. (1) After 1, 3 and 28 days of hydration. The thermograms of the hardened OPC mortar paste after 1 day of hydration indicate the appearance of four main endotherms located at 66, 470, 570 and 680-750 ºC (Fig. 1a). The endotherm appeared at 66 ºC is due to the removal of free moisture, while the endotherm located at 470 ºC is attributed to the dehydration of free calcium hydroxide (CH). The endotherm appeared at 570 ºC is mainly due to the α-β quartz transformation. A double endotherm could also be distinguished at the temperature range of 680-750 ºC which represents the decomposition of calcium carbonate (CC) with different degrees of crystallinity. After 3 days of hydration of OPC mortar, five endothermic peaks are observed at 67, 146, 470, 570 and 750 ºC (Fig. 1b).

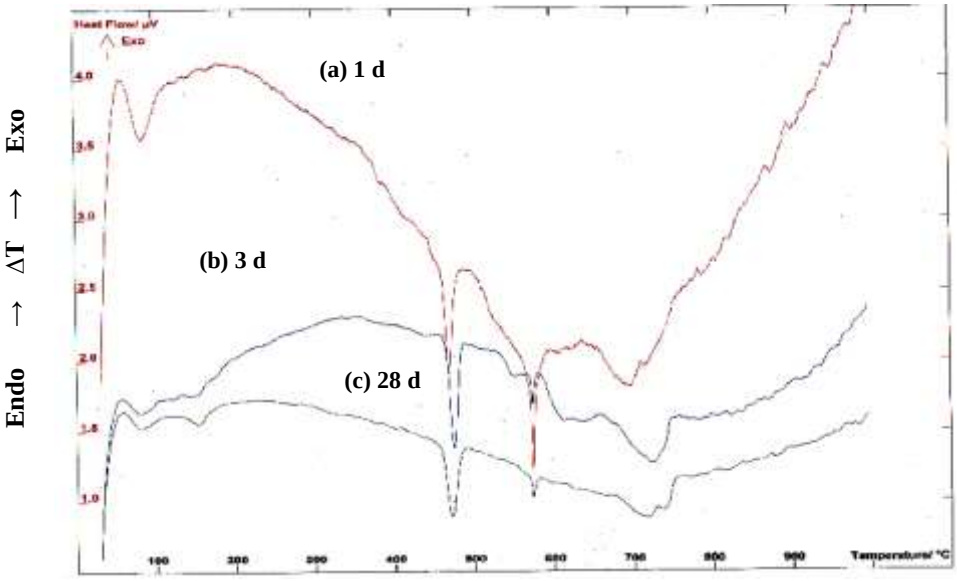

Fig. (1) DTA thermograms of hardened OPC mortars paste after 1, 3 and 28 days of hydration.

The endotherms located at 67,146 and 470 ºC are due to the removal of free water, dehydration of calcium silicate hydrates (CSH) and calcium hydroxide (CH), respectively. In addition, the endotherm appeared at 570 ºC is due to α -β quartz transformation; while, the broad endotherm located at 750 ºC is due to the decomposition of calcium carbonate. After longer ages of hydration of OPC mortar paste, the DTA thermograms obtained after 28 days demonstrated the existence of six endothermic peaks located at 65, 140, 470, 571, 680 and 750 ºC (Fig. 1c).

The endotherms located at 65, 140, 470 and 570 ºC are mainly due to the same phase identified after 3 days of hydration, while the two endotherms located at 680 and 750 ºC are mainly due to the decomposition of the nearly amorphous and crystalline calcium carbonate, respectively (Fig.1c). The results of Fig.(1) indicated the formation and later accumulation of CSH phases with increasing age of hydration from 3 to 28 days of the hardened OPC mortar pastes as shown from the intensity of the endotherm located at 140 ºC.

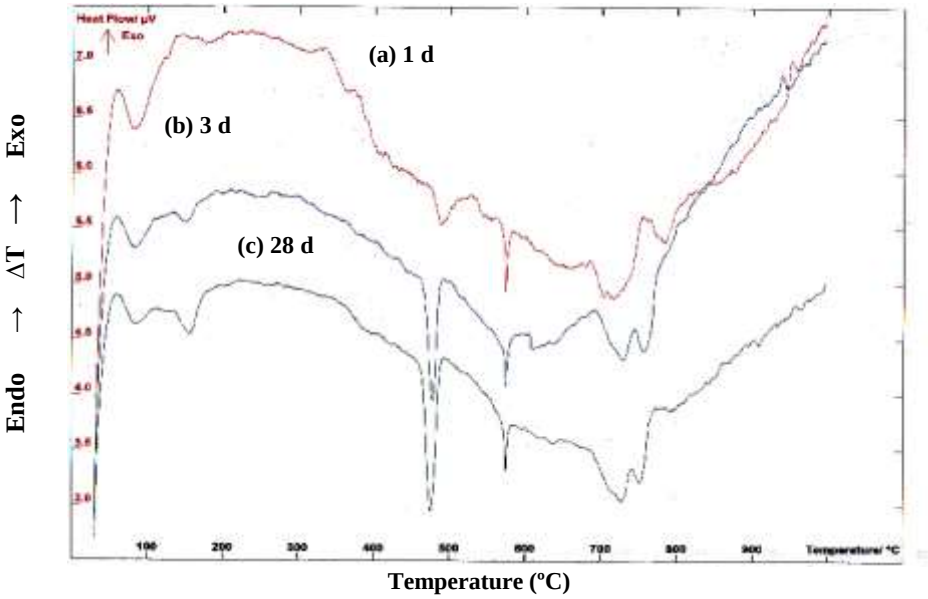

Fig.(2) DTA thermograms of hardened limestone cement mortars paste made from 95 wt % OPC and 5 wt % limestone after 1, 3 and 28 days of hydration.

The DTA thermograms obtained for the hydrated M_{SL}-blend made of OPC (95%), limestone (5%), mortar paste for 1, 3 and 28 days are shown in Fig. (2). Evidently, the endotherms appeared in Fig. (2) indicate the same endothermic peaks observed for OPC mortar paste with one main basic difference; namely, the

endotherms characteristic for the decomposition of calcium carbonate appeared with higher intensities and shifted to higher temperatures of 720 and 770 ºC. This is mainly due to the limestone present in the dry OPC-limestone blend.

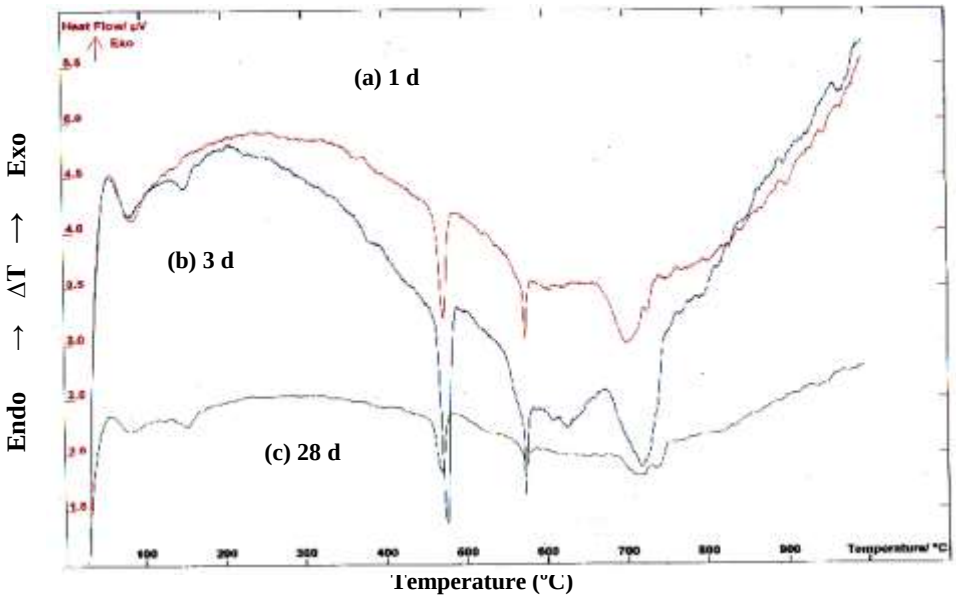

Fig. (3) DTA thermograms of hardened slag cement mortar paste made of M_{S20} blend (80 wt % OPC and 20 wt % slag) after 1, 3 and 28 days of hydration.

The DTA thermograms obtained for the hardened M_{S20}-blend, made of OPC (80%) and (20%) granulated slag, mortar paste after 1, 3 and 28 days of hydration are shown in Fig. (3). After 1 day of hydration; four endotherms could be clearly distinguished at 88, 463-473, 570-574 and 680-720 ºC; these endotherms are attributed to the removal of free water and the dehydration of CH, α-β quartz transformation and decomposition of calcium carbonate, respectively.

In addition, one exothermic peak is observed at 896-903 ºC; this exotherm is due to re-crystallization of pseudo-wollastonite (CS) which is due to the CSH formed as a result of the pozzolanic interaction between granulated slag and the free lime liberated from OPC hydration. After 3 days of hydration of M_{S20} mortar , five endotherms are observed at 63,140-153 , 464-476 ,570 and 680-720 ºC; these are characteristic for free water , CSH , CH, α -β quartz and $CaCO_3$, respectively.

Evidently, the endotherm characterizing CH phase located at 464-476 ºC, appeared with higher intensity after 3 days of hydration; this indicates that the amount of free CH released from OPC hydration exceeds the amount of free CH consumed by the pozzolanic reaction with granulated slag. In addition, the

exothermic appeared at 887-953 ºC is due to the re-crystallization of pseudo-wollastonite (CS) phase; this is attributed to the CSH phase formed by the pozzolanic interaction of slag with free CH. The thermogram obtained for the hardened M_{S20} blended cement mortar after 28 days of hydration displayed the appearance of the same endothermic peaks obtained after 3 days of hydration with two main basic differences; namely the relatively low intensity of the endotherm characteristic for the dehydration of CH with a relatively high intensity of the endotherm characterizing the CSH.

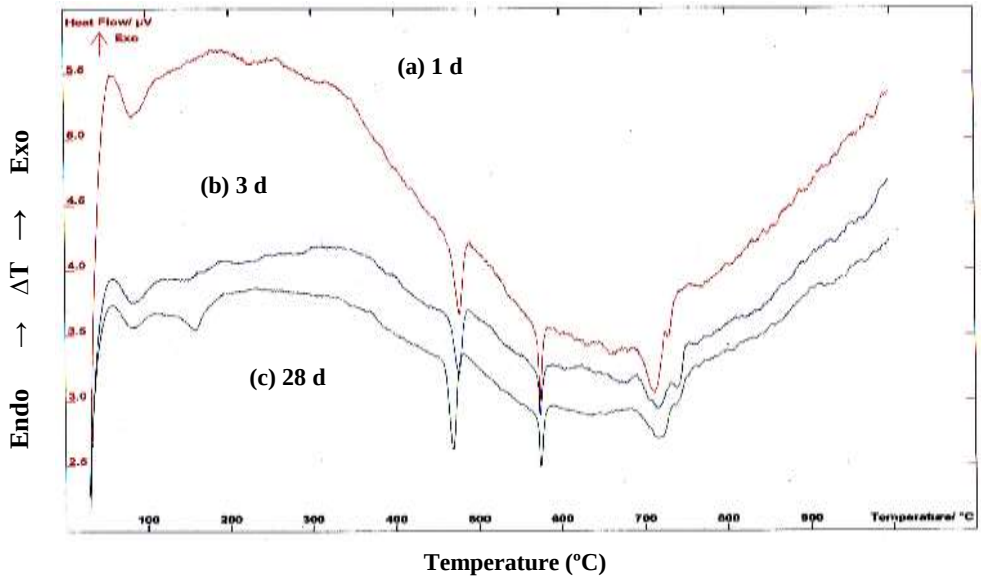

Fig. (4) DTA thermograms of hardened pozzolanic cement mortars made of M_{F20} blend (80 wt % OPC and 20 wt % fired bricks) after 1, 3 and 28 days of hydration.

This is attributed to the pozzolanic activation of granulated slag which resulted in the consumption of larger amounts of CH indicating that the free CH consumed by slag hydration exceeded the free CH liberated from OPC hydration; therefore, a net decrease in the CH content is observed. The exotherm appeared at 955 ºC characterizing pseudo-wollastonite phase could also be distinguished.

Fig. (4) shows the DTA thermograms of the hardened M_{F20} blended content (80% OPC + 20% fired clay bricks) mortar paste after 1, 3 and 28 days of hydration. Evidently, the results of Fig. (4) demonstrate mostly the same endotherms observed in Fig. (3) M_{S20}-blended cement mortars. Only, one basic difference exists in case of

M_{F20} mortar paste; namely, continuous increase in the intensity of the endotherm characterizing the CH phase with increasing the age of hydration up to 28 days.

This indicates that the amount of CH liberated from OPC hydration is always greater than the amount of CH consumed by the pozzolanic reaction with fired bricks which reflects on the relatively low pozzolanic activity of fired bricks as compared to granulated slag. The exothermic peak characteristic for pseudo-wollastonite phase could also be distinguished at 906 ºC.

Conclusion

The main conclusions could be derived from the investigation are summarized as follow:

1- Incorporation 2.5% by mass limestone to Portland cement improves the compressive strength of the hardened mortar.
2- Blending Portland cement with 5% by mass limestone causes a reduction in compressive strength of the hardened mortar by an average value of 2.5 % during investigated period.
3- The mixes blended with 10% blast furnace slag and 5% limestone or 10% fired bricks and 5% limestone showed resemble values of compressive strength compared with blank.
4- Therefore; there are four optimum mixes can be used to produce economic blended Portland cement, these mixes are $M_{L2.5}$, M_{L5}, $M_{SL(10+5)}$ and $M_{FL(10+5)}$.

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