International Journal of GEOMATE, Jan., 2017, Vol. 12, Issue 29, pp. 38-45
Geotec., Const. Mat. & Env., ISSN:2186-2990, Japan, DOI: http://dx.doi.org/10.21660/2017.29.45158

PERFORMANCE OF MULTI BLEND CEMENT CONTAINING FLY ASH, GRANULATED BLAST FURNACE SLAG AND LIMESTONE

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ABSTRACT: Investigations carried out revealed that multi blend cements containing fly ash, granulated blast furnace slag (GBFS), and low- and cement-grade limestone have performance (particularly strength development characteristics) comparable in their respective mortar samples. This paper highlights the impact of the addition of low-grade limestone on the performance of mortar samples prepared using multi blend cements and on the hydration mechanism of neat pastes of multi blend cement. The results indicate that in a multi blend cement of fly ash, GBFS, low-grade limestone and clinker, up to 70 % of clinker can be replaced gainfully and the performance of resultant mortar samples prepared using multi blend cement containing cement-grade and low-grade limestone were comparable. Investigations on the hydration mechanism indicated that hydrated multi blend cements containing low- and cement-grade limestone contained the additional phase of calcium carbo aluminate. Further, the rate of formation of calcium carbo aluminate is comparable in hydrated systems containing both low- and cement-grade limestone. The investigations revealed that the quality of limestone, particularly its calcium carbonate content, did not affect the hydration mechanism in multi blend cement. Therefore, low-grade limestone can be gainfully utilised in the manufacture of multi blend cement.

Keywords: Multi blend cement, Low grade limestone, Fly ash, Granulated blast furnace slag

1. INTRODUCTION

Various types of hydraulic cements specified by the Bureau of Indian Standards (BIS) include Ordinary Portland Cement (OPC), Portland Pozzolana Cement (PPC), Portland Slag Cement (PSC), recently specified composite cements and various other special purpose cements. Fly ash conforming to IS 3812 (Part 1): 2013 and GBFS conforming to IS 12089: 1987 are used in the manufacture of PPC and PSC respectively. Composite cements use a blend of additives, including fly ash and GBFS. The present Indian composite cements standard does not permit the use of limestone either alone or in combination with other additives. However, the Indian standard for OPC permits use of up to 5 % by weight addition of limestone as a performance improver with $CaCO_3$ not less than 75 %. European standard EN-197 similarly permits the use of limestone, with $CaCO_3$ not less than 75 %, in Portland Limestone Cement (PLC) as well as in composite cements.

In India, a large quantity of low grade limestone is available, including overburden and mine rejects, which is currently unutilised in cement manufacture. Therefore, in order to establish the technical suitability of using low grade limestone in the manufacture of cement, investigations were taken up for simultaneous use of fly ash not conforming to Indian standard specification, IS:3812, which is also not presently used in cement manufacture, GBFS and low-grade limestone in multi blend cements.

Observations of the hydration mechanism of multi blend cements were carried out by X-Ray Diffraction (XRD) evaluation. The results indicated that during hydration, with water as a curing medium at ambient conditions, hydration products such as ettringite and portlandite were formed as well as an additional phase, calcium carbo aluminate. To compare the impact of quality of limestone addition on hydration mechanism, multi blend cements containing cement-grade limestone were also investigated. The investigation further revealed that the quality of limestone did not impact the hydration mechanism, both in terms of rate as well as hydration products, as observed using instrumental techniques such as XRD and Scanning Electron Microscopy (SEM). Low grade limestone therefore can be utilised gainfully in the manufacture of cement without affecting the hydration process.

2. LITERATURE REVIEW

Antoni et al. reported that a 5 % addition of limestone in the system enhanced the properties of cement and 45 % substitution (30 % metakaolin and 15 % limestone) gave better mechanical properties at 7 and 28 days than the 100 % control OPC [1]. Steenberg et al. reported a synergetic effect with mixtures of limestone and calcined clays at the same clinker content as in composite Portland cements. Samples of CEM-I Portland cement with either 30 % limestone or 30 % calcined clay resulted in 28 days standard mortar strength, compared to the control sample CEM-I, of 78 % and 60-84 % respectively. The variation for the samples with calcined clay was due to differing reactivity of the calcined clay. A third sample type, with a mixture of the same calcined clays and limestone at the same replacement level (total 30 %) invariably resulted in higher strengths than would be predicted by the results of binary systems; relative 28 days strengths were as high as 109 % of CEM-I strength. The underlying mechanism for this effect was the formation of carboaluminate hydrates as detected by XRD and NMR [2]. Carrasco et al. studied the interaction between limestone filler and blast-furnace slag and analysed mortars in which Portland cement (PC) was replaced by up to 22 % LF and BFS. Results showed that compressive and flexural strength evaluated at 2, 7, 14, 28, 90 and 360 days were affected in different ways by the presence of mineral additions [3]. Müller found that Portland composite cements (CEM II-M, EN-197-1) are most effective with combinations of limestone and GBFS by demonstrating their carbonation, resistance to chloride penetration and resistance of concrete to freeze-thaw with de-icing salt [4]. Piechówka-Mielnik and Giergiczny investigated the physical and mechanical properties of Portland composite cements (CEM-II/A,B-M), with additions of limestone, GBFS, silica fly ash and calcium fly ash. They reported that a 10 % addition of ground limestone to Portland composite cement changed its strength properties by a small amount. However, larger additions of limestone in Portland composite cement resulted in significant strength decrease, for all ages investigated [5]. Scrivener reported that based on a series of experimental and thermodynamic studies it was observed that limestone in fact reacted with alumina from the clinker phases to form mono and/or hemi carboaluminate [6]. Sun et al. studied the use of a jet mill to grind the cement blends of OPC with 15 % limestone and OPC with 40 % fly ash. It was observed that when jet mill grinding was used, the average particle size of the powders decreased to approximately 4 μm or less with a narrower particle size distribution than that achieved using ball milling [7]. Ipavec et al. studied the formation of the carboaluminate phase during the hydration of calcite-containing PC. In the early stage of hydration of calcite-containing PC, hemicarboaluminate formed, which converted into monocarboaluminate with increased hydration time. Hemicarboaluminate was formed within the first day and the content of hemicarboaluminate increased up to the third day of hydration. After 3 days of hydration, a conversion into monocarboaluminate began and the intensities of hemicarboaluminate reflections diminished gradually. Though these were still present in a 28-day hydrated sample, none could be detected in a 100 days hydrated sample [8]. Chaturvedi et al. reviewed the hydration mechanism of cement systems containing fly ash, GBFS, limestone, etc. and found that the simultaneous additions of these materials have a synergetic effect on the hydration and performance of the resultant cement systems [9],[10].

3. MATERIALS AND EXPERIMENTATION

3.1 Raw Materials and Properties

Fly ash, GBFS, low- and cement-grade limestone, clinker and gypsum samples were collected from various sources and characterised for their chemical and mineralogical compositions. The chemical analysis indicated that the CaO content of low- and cement-grade limestone was 33.40 % and 44.50 % respectively. The detailed chemical analysis of the limestone samples are given in Table 1. Physical performance evaluation of the fly ash indicated that the fineness level was 270 m^2/kg and did not conform to Indian standard specification, IS:3812. The glass content in the fly ash and GBFS, as estimated by optical microscopy, was found to be 43 % and 94 % respectively. Chemical analysis of the gypsum sample found the purity of the gypsum to be 86.4 %. XRD studies of fly ash samples indicated the presence of quartz, mullite, and hematite phases along with amorphous content. Scanning electron microscope (SEM), in the secondary electron mode, was used to carry out morphological studies of fly ash at an accelerating voltage of 15 kV. SEM studies indicated that most of the fly ash particles were in the spherical shape and agglomerated beside angular to irregular shaped quartz and hematite particles.

Table 1 Chemical analysis of low- and cement-grade limestone

Oxides (*% by mass*)	Cement grade Limestone	Low grade Limestone
LOI	35.67	27.23
SiO_2	11.85	23.91
Fe_2O_3	1.94	3.82
Al_2O_3	2.95	7.15
CaO	44.50	33.40
MgO	1.06	2.25
Na_2O	1.32	1.58
K_2O	0.40	0.38

3.2 Preparation of Multi Blend Cements Containing Fly Ash, GBFS and Limestone

Samples of multi blend cements were prepared in a laboratory scale ball mill by inter-grinding fly ash, GBFS, low- and cement-grade limestone, clinker and gypsum. For comparative evaluation of the hydration mechanism, multi blend cement samples were prepared both with and without additions of limestone. The multi blend cement without limestone was designated as COM-2. The weight proportions of multi blend cements containing limestone are provided in Table 2. All these multi blend cement samples were ground to Blaine fineness in the range of 340$\pm$10 m^2/kg in the laboratory scale ball mill of 10 kgs capacity, 30.5 cm long and 30.5cm in diameter. The rotational speed of the ball mill was kept between 40-45 rotations per minute.

To investigate the hydration mechanism, samples were prepared by halting the hydration at fixed intervals using acetone. 100 g multi blend cement samples were weighed in plastic bottles, and 40 ml of distilled water added. The mix was stirred for 5 minutes with a glass rod and the cement paste thus obtained was sealed with two layers of lids. These plastic bottles were placed in a sealed container for 1, 3, 7 and 28 days. At the desired age, the samples were crushed and the hydration was halted by immersion of the crushed sample in acetone for 39 minutes and then filtered. This process was repeated 7-8 times. The samples were then sealed and placed in desiccators for XRD and SEM investigations.

Table 2 Weight proportions of multi blend cements containing limestone

Cement Sample	Wt. proportions (%)				
	Fly ash	GBFS	Low-grade Limestone	Cement-grade Limestone	Mix of clinker +gypsum
COM-2-CLS-5	15.0	40.0	-	5.0	40.0
COM-2-CLS-10	15.0	40.0	-	10.0	35.0
COM-2-CLS-15	15.0	40.0	-	15.0	30.0
COM-2-LLS-5	15.0	40.0	5.0	-	40.0
COM-2-LLS-10	15.0	40.0	10.0	-	35.0
COM-2-LLS-15	15.0	40.0	15.0	-	30.0

3.3 Physical Performance Evaluation

Physical performance evaluation of multi blend cements containing 40 % GBFS, 15 % fly ash and varying dosages of low- and cement-grade limestone was carried out up to 28 days as per the relevant Indian Standard. Results are given in Table 3. The interpretation of results indicates that multi blend cement samples show variation in setting time values, particularly in the initial setting time. The normal consistency was found to increase with increasing content of both types of limestone. The increase in normal consistency was attributed to the presence of a finer fraction in fly ash as well as limestone. Interpretation of the compressive strength values indicated that the performance of multi blend cement containing varying dosages of low- and cement-grade limestone were comparable at all levels of addition of limestone.However,the addition level of 10 % was considered optimum based on the results of the physical performance evaluation and the compressive strengths as mentioned in Indian standard specification, IS:16415 for composite cements [11] and was selected for the investigation into the hydration mechanism.

Table 3 Physical performance of multi blend cements containing limestone

Cement Sample	Fineness (m^2/kg)	Normal Consistency (%)	Setting Time (Min.)		Comp. Strength (MPa)		
			IST	FST	3 d	7 d	28 d
COM-2-CLS-5	341	28.5	215	265	20.0	30.5	40.0
COM-2-CLS-10	353	27.5	220	305	17.0	26.0	36.0
COM-2-CLS-15	349	27.5	220	310	18.0	25.0	30.0
COM-2-LLS-5	346	27.5	210	285	22.0	32.0	42.0
COM-2-LLS-10	343	28.5	230	300	20.0	26.0	38.0
COM-2-LLS-15	334	28.8	250	310	17.0	24.0	28.0

Note: IST and FST are the initial and final setting time.

4. RESULTS AND DISCUSSION

In the case of multi blend cements, the results obtained clearly indicated that limestone could be added up to 10 %, with performance comparable to that of control cement containing 15 % fly ash and 40 % GBFS. The investigation further revealed that the quality of limestone did not play a significant role; low-grade limestone can be utilised gainfully up to 10 %. The properties of multi blend cements were found to depend on the quality of clinker and mineral additions, as well as fineness and particle size distribution. Interpretation of the compressive strength values indicated that the performance of multi cement blend containing 10 % limestone of both types was comparable, and meets the compressive strength requirement as laid down in the Indian standard for composite cement [11].

Hydrated samples at 1, 3, 7 and 28 days were studied using XRD and SEM for phase formation and morphological characteristics. The XRD results indicated that at 1 day of hydration, there was increased ettringite formation in the samples with limestone additions. This increase in ettringite formation was due to the increased hydration, due to the addition of limestone. The results of 3, 7 and 28 days hydration confirmed the observations of 1 day hydration with a further increase in the formation of ettringite and the formation of an additional hydrated phase of calcium and aluminium termed as calcium carbo aluminate hydrate (CCA).

To study the effects of the addition of low- and cement-grade limestone, both in terms of quality and quantity of the hydration mechanism of multi blend cements, the peak intensities (estimated as counts per second) of the mineral phase CCA was calculated using XRD (though semi quantitative). The results are provided in Table 4. The additionally formed CCA phase was observed only in the case of limestone added cement blends. This phase was not observed in the control cement blends containing fly ash and GBFS only. The addition of limestone resulted in the formation of CCA hydrated mineral phase, which started after 1 day and reached its maximum within 3 days. 93.5 % formation took place in cement blends containing low-grade limestone, with slightly higher formation of 98 % for the blends with cement-grade limestone. Further formation of CCA took place at a relatively slower rate as observed in Fig. 1. At the age of 28 days, formation of hydrated CCA phase was ~ 94 % of that of cement blends containing cement-grade limestone as provided in Fig. 2. These results indicate that the content of calcium carbonate in limestone did not have a significant effect on the formation of the hydrated CCA phase. SEM images of multi blend cement containing low- and cement-grade limestone hydrated at 28 days show the denser hydrated matrix; a result of the formation of CCA. This can be clearly observed in Fig. 3. The formation of the hydrated CCA phase had resulted in densification of the cement matrix and the filling of pores with additional calcium silicate hydrate [CSH] contributing to pore size refinement in the hydrating matrix.

Table 4 Peak intensities of hydrated complex mineral phase CCA

Cement Samples	Peak intensity of complex mineral phase (counts/s) at X days after hydration			
	1 Day	3 Days	7 Days	28 Days
COM-2	None observed	None observed	None observed	None observed
COM-2-LLS-10	None observed	215	225	230
COM-2-CLS-10	None observed	240	245	245

5. CONCLUSION

The results obtained clearly indicate that multi blend cements with additions of limestone up to 10 % give performance comparable to that of control cement containing 15 % fly ash and 40 % GBFS. The investigation further revealed that the quality of limestone does not play a significant role; low-grade limestone can be utilised gainfully up to 10 % with overall clinker replacement up to 70 % by weight. The properties of multi blend cements were found to depend on the quality of clinker and mineral additions, besides fineness and particle size distribution.

XRD and SEM studies of hydrated samples of multi blend cement indicated that low-grade limestone could be added up to 10 % and the hydration mechanism including its rate and hydration products were comparable to that of cement blends containing 15 % fly ash and 40 % GBFS alone as well as cement-grade limestone. The investigation further revealed that the effect of quality of limestone did not have a significant effect and low-grade limestone can be utilised gainfully up to 10 %. XRD studies of hydrated samples of multi blend cement indicated increased formation of ettringite and CCA hydrate at 3, 7 and 28 days, further contributing to improving

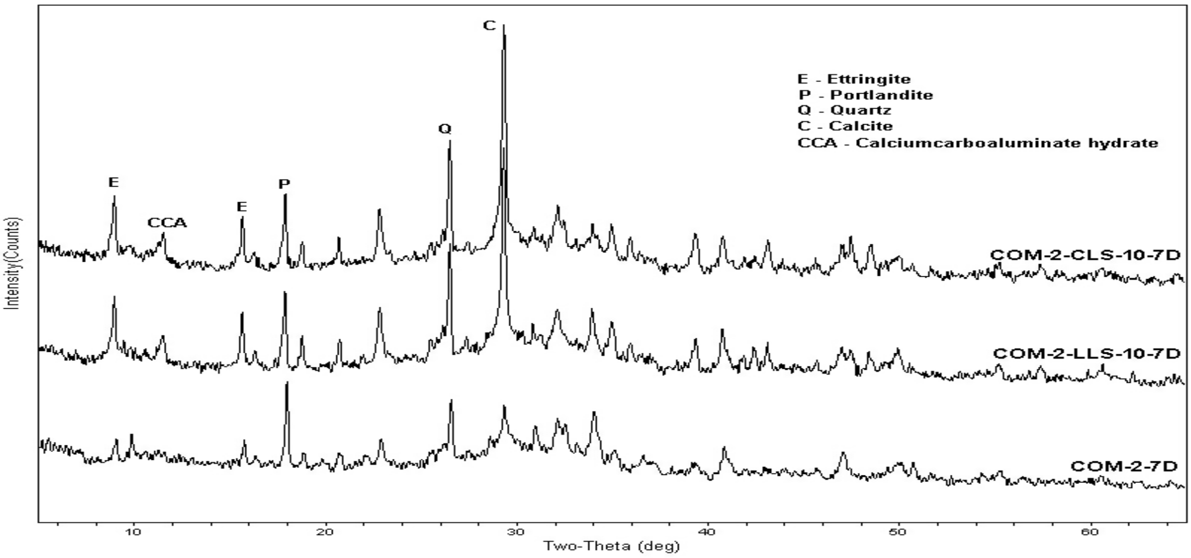


Fig.1 XRD of hydrated pastes of control cement COM-2 and multi blend cement samples containing low and cement grade limestone at 7 days

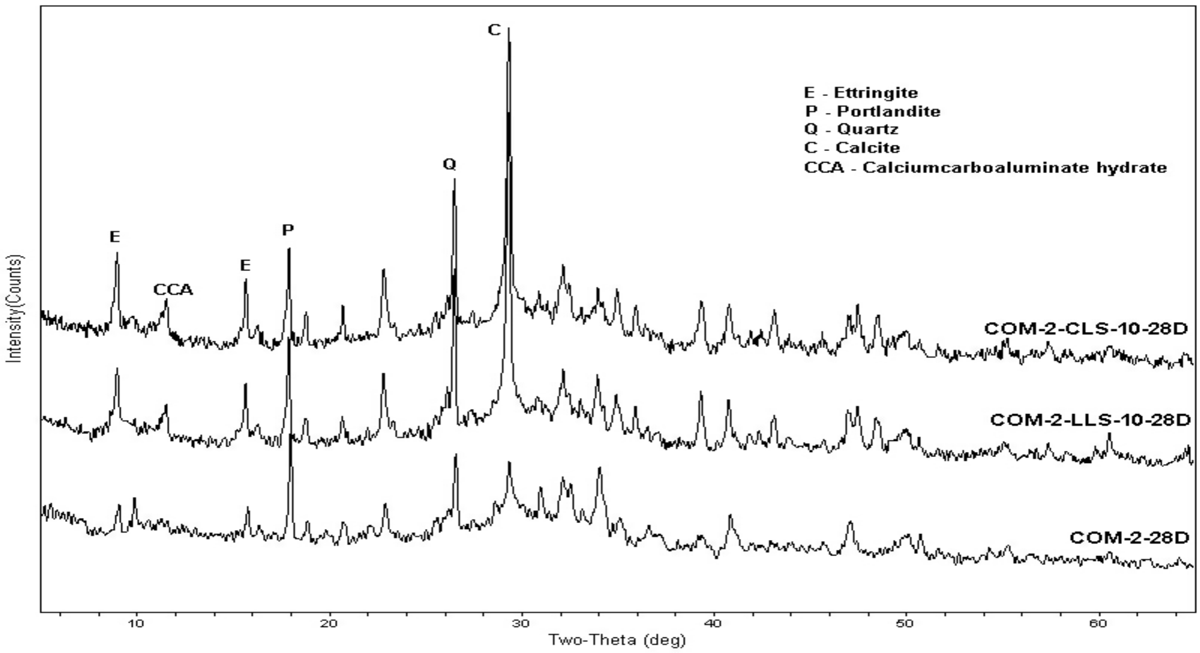
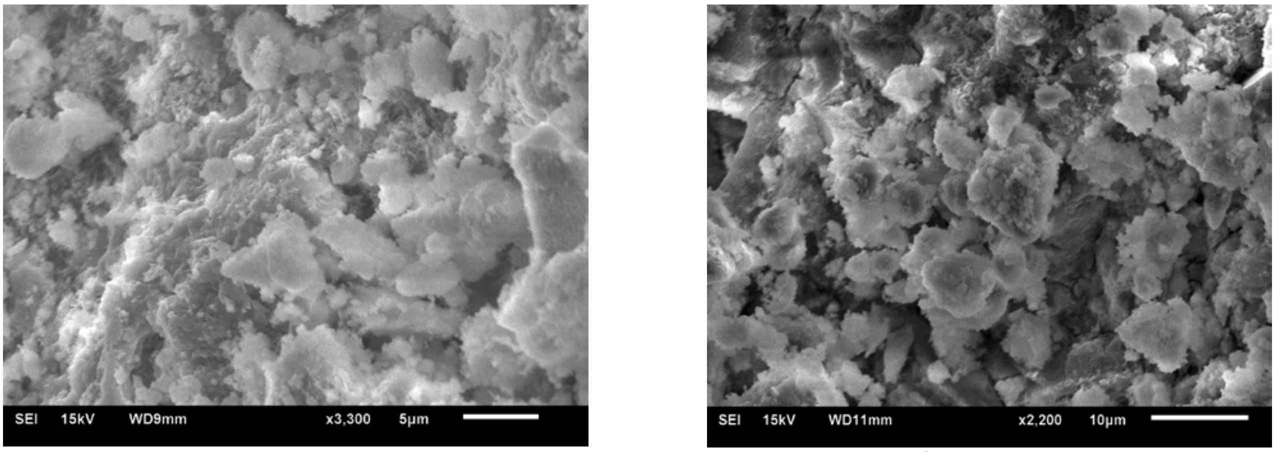


Fig.2 XRD of hydrated pastes of control cement COM-2 and multi blend cement samples containing low and cement grade limestone at 28 days

the morphology of hydrating multi blend cement paste. This phenomenon has a positive impact on compressive strength development in the system thus countering the dilution effects due to increased mineral addition. The rate of formation of CCA hydrate was comparable in multi blend cement containing low-grade limestone as well as cement-grade limestone at the addition level of 10 % of limestone.



(a) (b)

Fig.3 SEM images of 28 day hydrated multi blend cement containing (a) low-grade limestone and (b) cement-grade limestone

6. ACKNOWLEDGEMENTS

The authors have used the results of the experiments carried out at National Council for Cement and Building Materials under the guidance provided by Prof A K Sahu of Department of Civil Eng., Delhi Technological University, Delhi as PhD supervisor.

7. AUTHORS CONTRIBUTIONS

The design and experimentation, interpretation of data and drafting the manuscript was done by S K Chaturvedi as part of his PhD under the guidance of Prof A K Sahu who critically reviewed and revised the manuscript.

8. ETHICS

This manuscript is original and contains unpublished material. The corresponding author confirms that all of the authors have read and approved the manuscript and no ethical issues involved.

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International Journal of GEOMATE, Jan., 2017, Vol. 12, Issue 29, pp. 38-45.
MS No. 45158 received on March 13, 2016 and reviewed under GEOMATE publication policies.

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