Effect of Bogue Potential Phases of Clinker on the Mechanical Strength of Fly ash-Limestone Based Portland Composite Cement

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Keywords

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Abstract

Continuous rise in population coupled with infrastructural requirements leads to increasing demand of cement which is projected to be around 4.8 billion tons by 2030 and 6.0 billion tons annually by 2050 from current production level of more than 4.2 billion tons [1], and this further requires judicious use of natural resources, particularly limestone on one side and to mitigate carbon and energy footprints on other for sustainable development. Therefore, to bring down environmental impact during cement production, cement industries have been engaged over the years to substitute Portland cement with alternative cementitious materials; fly ash, granulated blast furnace slag, limestone etc individually or in combination of two-three mineral constituents in the manufacture of blended cements, which showed better durability characteristics in comparison to ordinary Portland cement. The formulation and commercialisation of these cements largely depends on the quality of Portland clinkers in terms of oxide constituents, potential as well as actual phase composition, morphology and granulometry of alite and belite grains, along with availability and quality of the cementing materials, prevalent standard norms and regulations.

In view of above, present paper highlights the effect of different clinkers in terms of potential minerals as per Bogue calculations (CL-1: C₃S-48.20%, C₃A-6.30%; CL-2: C₃S-54.20%, C₃A-9.30% and CL-3: C₃S-60.05%, C₃A-9.0%) on mechanical strength of fly ash-limestone based ternary cement blends, Portland composite cements, similar to CEM-II/A, B-M as per EN-197-1, prepared with 15, 20, 25, 30 and 35% by weight fly ash and 5 & 10% by weight limestone, by inter-grinding of all cement constituents process, maintaining Blaine's fineness at 370±10m²/kg, and the results of compressive strength at different curing ages showed optimum strength development in case of clinker CL-2 with potential phases, C₃S-54.20% and C₃A-9.30%, thus leading to better management of natural resources and extended mine life.

1. Introduction

Cement production is an energy intensive process and contributes to about 7% global carbon emission in the atmosphere, resulting in climate change [2]. Global cement industry has adopted various technologies to curtail down carbon and energy footprints from cement production to restrict global rise in temperature well below 2°C and towards 1.5°C to achieve net zero GHG emission by 2050 and carbon negative thereafter (according to Paris agreement CoP21/CMP11-2015 on climate change) [3], and replacement of Portland clinker with non-clinker constituents such as fly ash, granulated blast furnace slag, limestone, silica fume without increasing the production of basic Portland clinker (blended cements) is proved to be the most effective approach, and which has outpaced other low carbon technologies [4]. Blended cements in general imparts improved durability characteristics to concrete and provides higher resistance to chemical attack, lower permeability of concrete and improved resistance against alkali silica reaction due to the synergic reaction amongst various non-clinker constituents.

Fly ash and granulated blast furnace slag are widely used cementing materials in the manufacturing of blended cements, because they cover the broad spectrum of civil engineering applications. In India, about 217 million tonnes of fly ash is generated annually across the country [5], and out of which about 58.34 million tons (26.88%) fly ash, conforming to the requirements of Indian Standard IS:3812(I)-2013 [Pulverised Fuel Ash-Specification, Part-I: For Use as Pozzolana in Cement, Cement Mortar and Concrete] used in cement sector. Granulated blast furnace slag is generated to the tune of about 27 million tons and is almost utilized, although mostly available in the eastern part of the country.

Limestone, widely available natural material in comparison to other Supplementary Cementitious Materials (SCMs), can also be used as cementing material usually as clinker substitute, which can directly influence the cement properties. Cement grade limestone with CaCO₃≥75% is generally used in the manufacture Portland Limestone Cement (PLC), with feasibility of using low grade limestone/ dolomite limestone in the manufacture of Portland Dolomite Cement (PDC), due to the synergy between aluminates from Portland clinker and carbonates from limestone. Several studies showed that limestone has an influence on cement hydration by incorporating additional nucleation sites and space for hydration, and C₃A reaction with limestone has a direct influence on the properties of cementitious materials. C₃A reacts rapidly after mixing with water, influencing the rheology and setting of cement, which can be regulated with addition of gypsum, resulting in formation of ettringite [Ca₆Al₂(SO₄)₃(OH)₁₂.26H₂O] (AF_t) during early hydration, and then monosulfate [Ca₄Al₂O₆(SO₄)₁₄H₂O] (AF_m) after the first 16 hours of hydration, when the concentration of sulfate ions is not sufficient for the formation of ettringite [6]. In limestone induced cement system, C₃A reacts with carbonates to form hemi-carboaluminate [3CaO.Al₂O₃.0.5CaCO₃.11.5H₂O] (Hc) and mono-carboaluminate [3CaO.Al₂O₃.CaCO₃.11H₂O] (Mc) phases, and as a consequence more sulfate is available to form ettringite, resulting in reduced porosity [7] and permeability of cement paste [8]. Addition of limestone in cement is known to contribute in development of the microstructure of the hardened matrix [9]. The inter-grinding of Portland clinker with limestone results in improved particle size distribution and increased finer particle fraction [10] leading to wider size distribution and improved workability. The fine limestone particles act as nucleation sites [11] leading to increasing the rate of hydration of the clinker and hydration products development at early ages [12], resulting in faster setting [13].

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Ternary blended cements, like Type-II Portland Composite Cement, according to EN-197-1 using a combination of fly ash and limestone seems to be better than using only one of them. Mohapatra et al. (2019) [14] investigated the superiority of composite cement containing both fly ash and granulated blast furnace slag in comparison to fly ash/slag-based cement in terms of workability, slump retention, strength development, owing to the synergic reaction between fly ash and granulated blast furnace slag. Ternary and quaternary cement blends offer more flexibility and better properties depending upon the quality, fineness and proportioning of individual mineral constituents in comparison to binary blends [15] [16]. Use of fly ash as a cement replacement material increases the long-term strength and durability of the concrete, but at early ages the strength of fly ash concrete is low, so the other options to achieve early age strength under compression has to be explored and Portland cement-fly ash-limestone is a novel cement system owing to synergic reaction between fly ash and limestone. The changes in hydration products resulting from these small limestone powder contents coincides with an increase in compressive strength. The presence of small amount of limestone in cement stabilize ettringite, thus leading to increase in volume of hydrates [17]. This effect was amplified for the fly ash/limestone blended cements due to additional alumina provided by the fly ash reaction [18] [19] [20], resulting in enhancement in compressive strength. In another study, Mounanga et al. (2011) [21] analysed the effects of the addition of limestone on the mechanical properties of Ordinary Portland Cement (OPC), fly ash, GBF slag-based binary and ternary-binder mortars and found that 8-17% addition of limestone led to early age reactivity equal or higher than OPC and the accelerating effect of limestone was more sensitive in the case of mortars containing fly ash.

In view of scarcity of most proven materials like fly ash and granulated blast furnace slag in future, as it is estimated that the production of these materials is projected to be around 16% of cement production by 2050 [22], there is a need to explore alternative sources of cementing materials to avoid an increase in clinker to cement ratio (clinker factor, CF) and even to support its reduction. Normally, properties of Portland composite cements; CEM-II/A, B-M, as per Europe standard EN-197-1, are determined by the quantity and kind of mineral addition, but present paper highlights the influence of quality of Portland clinkers having different potential mineral composition in terms of C_3S and C_2S , determined as per Bogue calculation on the physical and mechanical characteristics of fly ash-limestone based Portland composite cement, identical to CEM-II/A, B-M as per EN-197-1 consisting of siliceous fly ash and limestone.

2. Testing process

In present investigation, three types of Portland clinkers (CL-1, CL-2 and CL-3), cement grade limestone (LST), fly ash (FA) and gypsum (GYP) were taken up and analyzed for constituents' oxides as per Indian standards IS:4032-1985 [Methods of Chemical Analysis of Hydraulic Binders], IS:1760 (I)-1991 [Methods of Chemical Analysis of Limestone, Dolomite and Allied Materials], IS:1727-1967 [Methods of Tests for Pozzolanic Materials (Fly ash)], IS:1288-1982 [Methods of Test for Mineral Gypsum] respectively. Based on the oxide constituents of clinkers, potential phases; C_3S , C_2S , C_3A and C_4AF were determined by Bogue calculations as per the equations i-iv, without carrying out free CaO corrections.

Different ordinary Portland cements; OPC-1, OPC-2 and OPC-3 were designed and prepared as base samples corresponding to clinkers CL-1, CL-2 and CL-3 by inter-grinding of both cement constituents; clinker and gypsum simultaneously (Table 1), maintaining clinker factor 0.95 [defined as a ratio of weight percentage of clinker to cement in cement mix; for example 95% by weight clinker in 100% by

weight cement shows clinker factor 0.95], in laboratory ball mill in the batch of 6.0 kg with charging ratio (weight of material : weight of balls) of 1:5 for about 50-minutes, to achieve Blaine's fineness of $310 \pm 10 \text{ m}^2/\text{kg}$ [measured according to test method IS:4031(2)-1999, Determination of Fineness by Air Permeability Method] and 3.5% SO_3 content (Table 1).

Table 1: Mix design of ordinary Portland cement

Cement code	Constituents (weight percentage)				Clinker factor (CF)
	Portland clinkers			Gypsum	
	CL-1	CL-2	CL-3	GYP	
OPC-1	95.0	-	-	5.0	0.95
OPC-2	-	95.0	-	5.0	0.95
OPC-3	-	-	0.95	5.0	0.95

Portland Pozzolana Cement (PPC) blends were prepared using all above different types of Portland clinkers with varying doses of 20, 25, 30 and 35% by weight fly ash (FA) by inter-grinding technique, to achieve Blaine's fineness at $370 \pm 10 \text{ m}^2/\text{kg}$ and 3.5% SO_3 content, with corresponding clinker to cement ratios (clinker factor) of 0.75, 0.70, 0.65 and 0.60 (Table 2). These PPC samples were prepared initially by inter-grinding of clinker and gypsum in ball mill for 10-minutes and then ground with addition of fly ash for 52-55 minutes, maintaining same charging ratio, as discussed above. PPC blends prepared using clinker CL-1 and 20, 25, 30 and 35% by weight fly ash, were coded as PPC-1-20, PPC-1-25, PPC-1-30 and PPC-1-35. PPC blends prepared with clinkers CL-2 and CL-3 were coded accordingly (Table 2).

Table 2: Mix design of PPC blends prepared using different clinkers with varying doses of fly ash

Cement code	Constituents (weight percentage)					CF
	CL-1	CL-2	CL-3	GYP	FA	
PPC-1-20	75.0	-	-	5.0	20.0	0.75
PPC-1-25	70.0	-	-	5.0	25.0	0.70
PPC-1-30	65.0	-	-	5.0	30.0	0.65
PPC-1-35	60.0	-	-	5.0	35.0	0.60
PPC-2-20	-	75.0	-	5.0	20.0	0.75
PPC-2-25	-	70.0	-	5.0	25.0	0.70
PPC-2-30	-	65.0	-	5.0	30.0	0.65
PPC-2-35	-	60.0	-	5.0	35.0	0.60
PPC-3-20	-	-	75.0	5.0	20.0	0.75
PPC-3-25	-	-	70.0	5.0	25.0	0.70
PPC-3-30	-	-	65.0	5.0	30.0	0.65
PPC-3-35	-	-	60.0	5.0	35.0	0.60

To investigate the impact of different clinker quality on the physical characteristics of fly ash-limestone based Portland composite cement (PCC), different cement blends were prepared using 15, 20, 25 and 30% by weight fly ash (FA), incorporating 5% by weight limestone (LST) replacing equal amount of fly ash, maintaining Blaine's fineness at $370 \pm 10 \text{ m}^2/\text{kg}$ and 3.5% SO_3 , with corresponding clinker factor 0.75, 0.70, 0.65 and 0.60 (Table 3), similar to PPC blends. These PCC samples were prepared with same methodology as discussed in preparation of PPC; initially ground clinker and gypsum for 10-minutes and then with fly ash and limestone addition for almost similar time period as discussed with PPC blends. PCC blends prepared with clinker CL-1 and 15, 20, 25 and 30% by weight fly ash and 5% by weight limestone were coded as PCC-1-15-5, PCC-1-20-5, PCC-1-25-5 and PCC-1-30-5. PCC blends prepared using different quality clinkers with 15, 20, 25% by weight fly ash, incorporating 10% by weight limestone is listed in Table 4. These cement blends; Ordinary Portland Cement (OPC), Portland Pozzolan Cement (PPC) and Portland Composite Cement (PCC) were evaluated for various physical characteristics such as water demand, initial and final setting times, compressive strengths at 1-, 3-, 7- and 28-days etc. according to the different test procedures described in Indian standard IS:4031 [Methods of Physical Tests of Hydraulic Cement: Part-2, 4, 5, 6].

Table 3: Mix design of PCC blends prepared with different doses of fly ash and 5% by weight limestone

Cement code	Constituents (weight percentage)					Clinker factor (CF)
	Portland Clinker			Gypsum (GYP)	Limestone (LST)	
	(CL-1)	(CL-2)	(CL-3)			
PCC-1-15-5	75.0	-	-	5.0	15.0	0.75
PCC-1-20-5	70.0	-	-	5.0	20.0	0.70
PCC-1-25-5	65.0	-	-	5.0	25.0	0.65
PCC-1-30-5	60.0	-	-	5.0	30.0	0.60
PCC-2-15-5	-	75.0	-	5.0	15.0	0.75
PCC-2-20-5	-	70.0	-	5.0	20.0	0.70
PCC-2-25-5	-	65.0	-	5.0	25.0	0.65
PCC-2-30-5	-	60.0	-	5.0	30.0	0.60
PCC-3-15-5	-	-	75.0	5.0	15.0	0.75
PCC-3-20-5	-	-	70.0	5.0	20.0	0.70
PCC-3-25-5	-	-	65.0	5.0	25.0	0.65
PCC-3-30-5	-	-	60.0	5.0	30.0	0.60

Table 4: Mix design of PCC blends prepared with different doses of fly ash and 10% by weight limestone

Cement code	Constituents (weight percentage)					Clinker factor (CF)
	Portland clinkers			Gypsum (GYP)	Limestone (LST)	
	(CL-1)	(CL-2)	(CL-3)			
PCC-1-15-10	70.0	-	-	5.0	15.0	0.70
PCC-1-20-10	65.0	-	-	5.0	20.0	0.65
PCC-1-25-10	60.0	-	-	5.0	25.0	0.60
PCC-2-15-10	-	70.0	-	5.0	15.0	0.70
PCC-2-20-10	-	65.0	-	5.0	20.0	0.65
PCC-2-25-10	-	60.0	-	5.0	25.0	0.60
PCC-3-15-10	-	-	70.0	5.0	15.0	0.70
PCC-3-20-10	-	-	65.0	5.0	20.0	0.65
PCC-3-25-10	-	-	60.0	5.0	25.0	0.60

3. Results and discussions

3.1 Characterization of materials

3.1.1 Portland clinkers

Chemical analysis of clinkers showed presence of usual oxide constituents; 64.81% CaO, 21.82% SiO₂ in CL-1; 65.59% CaO, 21.18% SiO₂ in CL-2; 66.10% CaO and 20.48% SiO₂ in CL-3, with 0.98, 1.25 and 1.50% free CaO (Table 5), showing their well burnt nature. Based on chemical analysis, the potential clinker phases C₃S and C₂S were estimated to be 48.20% and 26.20% for CL-1, 54.20% and 19.83% for CL-2 and 60.05% and 13.41% for CL-3 (Table 6). C₃A content in all clinker samples were estimated to be 6.30, 9.31 and 9.04%.

Table 5: Chemical analysis of materials

	CL-1	CL-2	CL-3	LST	FA	GYP
LOI	0.20	0.23	0.25	35.62	0.90	a
CaO	64.81	65.59	66.10	43.10	0.75	30.03
SiO ₂	21.82	21.18	20.48	14.43	64.00	b
Al ₂ O ₃	5.32	5.67	5.73	2.10	26.50	0.26
Fe ₂ O ₃	4.61	3.38	3.63	1.10	4.20	0.16
MgO	1.05	1.03	1.00	0.67	0.75	0.09
SO ₃	1.21	1.33	1.25	0.15	0.20	43.81
Na ₂ O	0.22	0.22	0.20	0.10	0.32	0.07
K ₂ O	0.45	0.47	0.49	0.39	0.41	0.01
Free CaO	0.98	1.25	1.50	-	-	-

a: Combined water-16.90%,

b: SiO₂+IR-8.0%,

IR-Insoluble residue

Table 6: Moduli value and potential phase composition of clinkers

Parameter	Portland clinker		
	CL-1	CL-2	CL-3
Limes Saturation Factor (LSF)	0.91	0.94	0.98
Silica modulus (SM)	2.20	2.34	2.19
Alumina modulus (AM)	1.15	1.68	1.58
Tricalcium silicate (C ₃ S)	48.20	54.20	60.05
Dicalcium silicate (C ₂ S)	26.20	19.83	13.41
Tricalcium aluminate (C ₃ A)	6.30	9.31	9.04
Tetracalcium aluminate ferrite (C ₄ AF)	14.03	10.29	11.05

3.1.2 Fly ash, limestone and gypsum

The chemical and physical characterization of fly ash (FA) showed its compliance to the requirements of Indian standard IS:3812(1)-2013 specified for fly ash for use as blending component in cement. Based on oxide constituents (Table 5), the CaCO₃ content in limestone (LST) was estimated to be 76.96%, and thus fulfilled the requirement of CaCO₃≥75% as specified in Indian standard IS:269-2015 [Ordinary Portland Cement-Specification] for limestone to be used as mineral additive in cement. The purity of gypsum was found to be about 94%, with gypsum as main mineral constituent.

3.2 Influence of Portland clinker quality on physical characteristics of OPC

The physical characteristics of ordinary Portland cements; OPC-1, OPC-2 and OPC-3 prepared with clinkers; CL-1, CL-2 and CL-3 respectively, maintaining Blaine's fineness at 310±10m²/kg showed comparable water requirement [measured according to test procedure described in IS:4031(4)-1988, Determination of Consistency of Standard Cement Paste] to prepare cement paste of normal consistency, (Table 7), but higher initial and final setting times [estimated as per IS:4031(5)-1988, Determination of Initial and Final Setting Times] in case of OPC-1 in comparison to OPC-2 and OPC-3, owing to its lower C₃A content (6.30%). Compressive strength [measured on 1:3 cement-sand mortar (200 gm cement and 600 gm sand) as per IS:4031(6)-1988, Determination of Compressive Strength of Hydraulic Binders Other Than Masonry Cement, with mould size of 70.6×70.6×70.6 mm, and water requirement determined as (P/4+3) percent combined mass of cement and sand, and where P is the percentage of water required to produce paste of standard consistency] at 1- and 3-days were found to be higher in case of OPC-2 and OPC-3 in comparison to OPC-1, and this could be attributed to higher C₃S and C₃A in clinkers CL-2 and CL-3 in comparison to CL-1, whereas 7- and 28-days strength of OPC-2 and OPC-3 were found to be lower than that of OPC-1 due to lower C₂S percentage in CL-2 and CL-3 (Table 7). Comparative evaluation of strength development of OPC-2 and OPC-3 showed no significant change, although C₃S contents were different, 54.20% and 60.05% respectively, indicating that potential phase of 54.20% C₃S and 9.3% C₃A was an optimum one and further

increase in C_3S content to 60.05% did not contribute to any further increase in compressive strength [23].

Table 7: Physical characteristics of OPC

Parameter	Ordinary Portland Cement (OPC)		
	OPC-1 [C_3S :48.20% C_3A :6.30%]	OPC-2 [C_3S :54.20% C_3A : 9.31%]	OPC-3 [C_3S :60.05% C_3A : 9.05%]
Blaine fineness (m^2/kg)	310	310	315
Consistency (%)	26.0	26.0	27.0
Setting time (minutes)			
Initial	130	90	90
Final	170	130	130
Compressive strength (MPa)			
1-day	26.8	29.8	28.6
3-days	40.5	46.2	44.0
7-days	55.7	54.9	52.5
28-days	69.6	65.9	65.9

3.3 Influence of Portland clinker quality on physical characteristics of PPC

Comparative evaluation of physical properties of PPC blends prepared with clinkers; CL-1, CL-2 and CL-3 with the addition of 20, 25, 30 and 35% by weight fly ash (Table 2) showed comparable water requirement to prepare cement paste of normal consistency, similar setting behavior and higher strength development of PPC blends at early ages (1- and 3-days) prepared with clinker CL-2 having 54.20% C_3S and 9.30% C_3A in comparison to CL-1 (C_3S :48.20%, C_3A :6.30%) at the identical level of addition of fly ash (Table 8). However, compressive strength at 7-days was found to be almost identical, whereas at 28-days, strengths of PPC blends prepared with clinker CL-1 was noticed to be more in comparison to PPC cements prepared with clinker CL-2, and this could be attributed to the higher percentage of C_3S in clinker CL-1 (Table 8). PPC blends prepared with CL-2 and CL-3, with addition of 20, 25, 30 and 35% by weight fly ash showed same trend of strength development at early as well as at later ages, corresponding to clinker factor of 0.75 and 0.60 (Fig 1), again indicating that clinker CL-2 having potential phases C_3S :54.20% and C_3A :9.30% was optimum one in the manufacture of PPC, as reported earlier [23].

Table 8: Physical characteristics of PPC blends prepared with different doses of fly ash

Cement code (Clinker factor)	Fineness (m^2/kg)	Consistency (%)	Setting time (Minutes)		Compressive strength (MPa)			
			Initial	Final	1-day	3-days	7-days	28-days
OPC-1	310	26.0	130	170	26.8	40.5	55.7	69.6
PPC-1-20 (0.75)	370	28.0	110	155	22.7	37.0	49.2	68.7
PPC-1-25 (0.70)	365	28.5	125	165	18.5	34.0	44.0	66.5
PPC-1-30 (0.65)	355	29.0	135	180	15.3	29.5	40.9	62.7
PPC-1-35 (0.60)	350	29.5	165	205	12.7	23.0	33.1	58.6
OPC-2	310	26.0	90	130	29.8	46.2	54.9	65.9
PPC-2-20 (0.75)	375	28.0	120	160	27.3	39.2	49.5	65.9
PPC-2-25 (0.70)	375	29.0	125	180	23.9	36.5	46.7	62.5
PPC-2-30 (0.65)	355	29.0	125	185	19.9	32.0	40.9	61.4
PPC-2-35 (0.60)	350	29.5	155	205	16.5	27.8	38.2	57.8
OPC-3	315	27.0	90	130	28.6	44.0	52.5	65.9
PPC-3-20 (0.75)	375	28.0	90	135	27.7	42.5	51.9	66.1
PPC-3-25 (0.70)	360	29.0	120	165	23.0	37.9	46.3	65.3
PPC-3-30 (0.65)	370	29.5	125	165	20.0	32.7	40.7	58.5
PPC-3-35 (0.60)	345	29.5	155	200	15.9	27.7	37.7	58.0

(a)

(b)

Fig 1: Trend of compressive strength development of PPC blends showing identical strength gain in PPC-2 and PPC-3 blends at clinker to cement ratio (a) 0.75 and (b) 0.60

3.4 Influence of Portland clinker quality on physical characteristics of fly ash-limestone based Portland composite cements (PCC), prepared with addition of 5% by weight limestone

Evaluation of physical characteristics of Portland composite cements prepared with different doses of fly ash and 5% by weight limestone (Table 3) showed reduction in water demand to prepare cement pastes

of normal consistency (Table 9) in comparison to their respective PPC counterparts prepared with similar clinker substitution (Table 8) i.e. PPC-1-20 vis-a-vis PCC-1-15-5 (clinker factor 0.75 in both cases), as also reported earlier by Voglis et al. (2005) [24] in fly ash/pozzolan-limestone cement system. The addition of fly ash and limestone as compositing material in Portland composite cement showed setting behaviour comparable to their respective PPC counterparts.

Comparative evaluation of mechanical strength of PCC blends prepared with addition of 15, 20, 25 and 30% by weight fly ash and 5% by weight limestone to that of PPC blends containing 20, 25, 30 and 35% by weight fly ash showed (i) marginal increase in early strength at 1- and 3-days in PCC blends prepared using clinker CL-1 (C_3S -48.20%) in comparison to respective PPC blends (ii) reduction in 1-day strength to the extent of about 18% in PCC blends prepared using clinkers CL-2 and CL-3 containing 54.20 and 60.05% C_3S in comparison to their PPC counterparts, and this could be attributed to high percentage of C_3S which accounted for early strength (iii) compressive strength at 3-days onwards was found to be comparable

in PCC and PPC blends containing similar clinker to cement ratios (iv) the later age strength at 28-days was found to be lowered due to the addition of limestone (dilution effect) (v) the level of compressive strengths of PCC blends prepared using clinkers CL-2 and CL-3 was found to be almost similar again indicating optimized C_3S content of 54.20% in clinker CL-2 in the preparation of fly ash-limestone based Portland composite cements. Improvement of early strength due to the addition of 5% by weight limestone could be attributed to improve Blaine's fineness and particle size distribution of cement and supported by Voglis et al. (2005) [24] that cements containing limestone exhibited high early strength.

Table 9: Physical characteristics of PCC blends prepared with different doses of fly ash and 5% by weight limestone

Cement code (Clinker factor)	Fineness (m^2/kg)	Consistency (%)	Setting time (Minutes)		Compressive strength (MPa)			
			Initial	Final	1-day	3-days	7-days	28-days
PCC-1-15-5 (0.75)	380	26.5	130	180	22.4	40.7	55.7	72.1
PCC-1-20-5 (0.70)	370	27.0	135	185	19.8	36.2	48.7	61.9
PCC-1-25-5 (0.65)	370	28.0	140	190	16.9	32.5	44.0	55.5
PCC-1-30-5 (0.60)	385	29.0	160	215	13.7	25.0	38.0	55.0
PCC-2-15-5 (0.75)	380	28.0	110	155	21.9	39.8	49.6	60.4
PCC-2-20-5 (0.70)	375	28.5	125	170	18.9	37.5	44.2	61.2
PCC-2-25-5 (0.65)	385	29.0	130	180	17.8	36.3	42.7	62.1
PCC-2-30-5 (0.60)	385	29.5	135	185	14.9	29.3	40.5	56.6
PCC-3-15-5 (0.75)	385	27.0	100	150	22.6	39.9	52.9	63.8
PCC-3-20-5 (0.70)	365	27.5	110	160	21.8	38.3	50.4	68.6
PCC-3-25-5 (0.65)	380	28.5	125	175	16.0	30.9	41.6	54.4
PCC-3-30-5 (0.60)	380	29.5	140	185	15.5	31.0	39.6	54.5

3.5 Influence of Portland clinker quality on physical characteristics of fly ash-limestone based Portland composite cements (PCC), prepared with addition of 10% by weight limestone

Comparative evaluation of mechanical properties of fly ash-limestone cement blends prepared using 10% by weight limestone with PCC blends prepared using 5% by weight limestone showed (i) comparable strength development in cement blends prepared using CL-1 in both 10 as well as 5% by weight limestone addition at identical clinker to cement ratios of 0.70, 0.65 and 0.60 (ii) marginally improved compressive strengths of cement blends containing 10% by weight limestone, and prepared with clinkers CL-2 and CL-3 in comparison to their counterparts containing 5% by weight limestone at similar clinker to cement ratios (iii) trend of gain in compressive strengths

was found to be comparable in cement blends prepared with clinkers CL-2 (C_3S -54.20%) and CL-3 (C_3S -60.05%) (Table 10). Piechówka-Mielnik and Giergiczny (2011) [25] reported partial replacement of silica fly ash with limestone in CEM-II/A, B-M improved early strength of cement mortars up to 7-days, and reduced significantly above 10% by weight. Giergiczny et al. (2011) [26] observed slow rate of strength increasing in first 28-days of hardening and high strength increasing after long hardening time for fly ash cement (CEM-II/B-V), in comparison to limestone cement (CEM-II/B-LL), which has different strength increasing characteristics. Therefore, in view of above discussions, it was observed that in preparation of fly ash-limestone based Portland composite cements, Portland clinker with Bogue potential phase of 54.20% C_3S and 9.3% C_3A was optimum one and further increase in C_3S to the level of 60.05% did not contribute to any further increase in strength development.

Table 10: Physical characteristics of PCC blends prepared with different doses of fly ash and 10% by weight limestone

Cement code (Clinker factor)	Fineness (m^2/kg)	Consistency (%)	Setting time (Minutes)		Compressive strength (MPa)			
			Initial	Final	1-day	3-days	7-days	28-days
PCC-1-15-10 (0.70)	385	28.5	140	185	21.3	36.1	48.0	61.9
PCC-1-20-10 (0.65)	385	29.0	145	195	17.0	30.9	42.5	58.7
PCC-1-25-10 (0.60)	385	29.5	155	200	14.4	26.0	39.0	51.2
PCC-2-15-10 (0.70)	375	27.5	110	160	24.3	42.5	52.1	62.9
PCC-2-20-10 (0.65)	380	28.0	120	165	21.2	37.1	42.7	58.8
PCC-2-25-10 (0.60)	380	28.5	140	185	19.1	32.4	40.2	56.6
PCC-3-15-10 (0.70)	385	27.0	105	150	24.5	39.3	50.5	64.9
PCC-3-20-10 (0.65)	375	28.0	110	160	21.5	35.6	44.7	59.0
PCC-3-25-10 (0.60)	375	28.5	120	175	18.2	32.5	40.3	56.6

6. Conclusions

- Potential mineral composition of Portland clinkers: CL-1; C_3S -48.20%, C_2S -14.03% and C_3A -6.30%, CL-2; C_3S -54.20%, C_2S -19.83%, C_3A -9.30%, CL-3; C_3S -60.05%, C_2S -13.41%, C_3A -9.04%, indicating their different quality in terms of Bogue calculations.
- Different PPC blends were prepared using 20, 25, 30 and 35% by weight fly ash, maintaining Blaine's fineness at $370 \pm 10 m^2/kg$ and clinker to cement ratios at 0.75, 0.70, 0.65 and 0.60.

- Ternary cement blends, fly ash-limestone based Portland composite cement (PCC) were prepared maintaining Blaine's fineness at $370 \pm 10 m^2/kg$, similar to PPC blends and maintaining identical clinker to cement ratios by incorporating 5 and 10% by weight limestone.
- Comparative evaluation of compressive strength of OPCs prepared using clinkers, clinker CL-2 (C_3S -54.20%, C_3A -9.30%) and CL-3 (C_3S -60.05%, C_3A -9.04%) showed similar strength

development at all ages indicating optimum potential composition of clinker CL-2 with 54.20% C₃S and 9.30% C₃A, and further increase in C₃S to 60.05% did not contribute to further increase in compressive strength.

- Mechanical characteristics of PPC blends prepared using different clinkers and with varying doses of fly ash indicated that clinker CL-2 (54.20% C₃S, 9.30% C₃A) provided optimum results in terms of strength gain in the manufacture of PPC.
- In the ternary fly ash-limestone based Portland composite cement, the level of compressive strengths of cement blends prepared using clinkers CL-2 (C₃S-54.20%) and CL-3 (C₃S-60.05%) was similar, again indicating the optimization of clinker CL-2 in terms of Bogue composition in manufacture of PCC blends.
- The use of ternary cement containing adequate combination of limestone and fly ash, along with optimum quality of Portland clinker can lead to an efficient use of natural resources, energy saving without compromising the quality of ternary cement blend.

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Declaration of conflict of interests

The authors declare that there is no conflict of interest. They have no known competing financial interests or personal relationship that could have appeared to influence the work reported in this paper.

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