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Research Article

Clean Development Mechanism: *Laterite* as Supplementary Cementing Material (SCM) to Reduce Greenhouse Gas Emissions (GHGs)

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Abstract: Carbon dioxide (CO_2) a major Green House Gas (GHG) in the atmosphere, is believed to be largely responsible for global climate change through industrial emissions. The level of CO_2 concentration has exponentially increased from about 280 ppm at the start of the industrial revolution to about 380 ppm to date. Although Kyoto protocol has bound industrialized nations to reduce green house gas emissions by 5.2% below 1990 levels around year 2008-2012, but violation continues. The cement industry is one of the major emitter of green house gases, particularly CO_2 due to its energy intensive production process. It is estimated that approximately 1 tone of CO_2 is released during the manufacturing of each tone of Portland cement. Most of CO_2 emissions originate from burning fossil fuels and de-carbonization of limestone in a cement plant. During past several decades, the use of by-product materials in concrete, either as components of blended cements or as admixtures, has increased significantly. In this study, another alternate Supplementary Cementing Material (SCM), *Laterite* has been used with the objectives: to evaluate the performance of cement containing different percentages of *laterite* (5, 10, 15, 20, 25, and 30 %); to identify the optimum replacement percentage; and to investigate the effects of different concentrations of *laterite* on various properties of cement. For that purpose, *laterite* was tested: before blending (for elemental and mineralogical composition by using XRF, SEM and XRD): after blending (Elemental analysis using XRF, fineness test by using Blaine's air permeability test and for particle size % on 45, 90 and 200 μ sieve, respectively); and after hydration (for mineralogical analysis using SEM). Furthermore, physical tests of manufactured cement, i.e., water consistency, setting time, *Le-Chatlier*-expansion and compressive strength were also evaluated and compared with limestone and fly-ash cement blends. The results show that with the replacement level of up to 15%, the quality of cement is not disturbed. In addition, the requirement of intake of energy has also decreased (~30%). Current findings indicate that by using *Laterite*, as SCM, cement production can be increased without consuming more energy and hence reduce GHG emissions.

Keywords: Blended cement, compressive strength, fly ash, laterite, limestone, portland cement

INTRODUCTION

The concentration of Carbon dioxide (CO_2), a major green house gas, in the atmosphere has fluctuated between 180 and 310 ppm during the last 400,000 years. Over the last two centuries, the atmospheric CO_2 concentration rose from about 280 ppm at the start of the industrial revolution to 380 ppm at the start of this century **(**Turarehan and Nehdi, 2005). The high level of CO_2 concentration is believed to be largely responsible for human activities majorly industrialization. Under the Kyoto protocol, industrialized nations made binding commitments to reduce their green house gas emissions by 5.2% below 1990 levels around year 2008-2012 (Habert *et al*., 2010).

The cement industry represents a small yet significant proportion of global carbon dioxide emissions. Of the emissions produced by the cement industry, approximately 50% result from the chemical processing, 40% from the burning of fuel, 5% from transportation and the remaining 5% from electricity used in manufacturing operations (Fig. 1) (Humphreys and Mahasenan, 2000).

For this reason several emission reduction techniques in cement sector have been applied some of them are: Improvement of the energy efficiency of the process, Shifting to more energy efficient process (from wet to dry process), Replacement of high carbon fuels by low carbon fuels (from coal to natural gas), Use of alternate raw materials (replacement of limestone in

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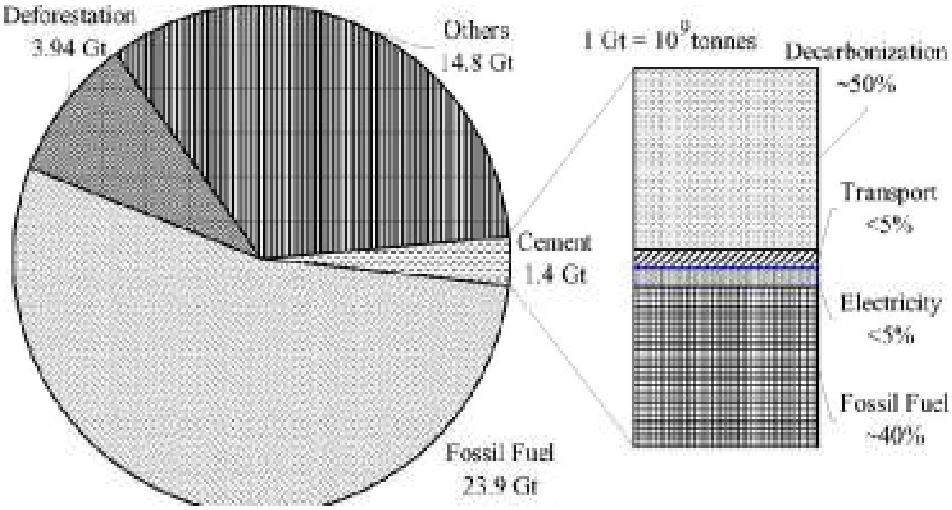

Fig. 1: Global GHG emissions (CO_2 eq.) in year 2000 and cement production (Humphreys and Mahasenan, 2000)

kiln feed), Application of low clinker/cement ratio (increasing the ratio additive/cement) and furthermore, development of blended cements, application of alternate cements (mineral polymers) and removal of CO_2 from the flue gases (Hendricks *et al*., 2004).

During the past 60 years the use of by-product materials in concrete, either as components of blended cements or as admixtures, has increased significantly (Rachel *et al*., 1996). As per ASTM C-595, the blended cements are defined as, “A hydraulic cement consisting of two or more inorganic constituents (at least one of which is not Portland cement or Portland cement clinker) which separately or in combination contribute to the strength gaining properties of the cement” (ASTM, 2003a, b). By the production of blended cement innumerable benefits could be received by the manufacturer, consumer and ultimately to all global community. It inclused: Increased plant capacity without the installation of a new kiln, reduced fuel consumption per ton of cement, Reduced CO_2 emissions per ton of cement, controlled alkali-silica reactivity even with high alkali clinker, reduced production of cement kiln dust and improved durability due to the replacement of Ca $(OH)_2$ with additional C-S-H (Rachel *et al*., 1996).

In the given scenario the use of naturally occurring or locally available material’s need has increased manifold. A new material namely *Laterite* is used for the same purpose, while some other materials like fly ash and limestone were also used for comparison purpose which are currently used and are available in the market. *Laterite* is a type of soil rich in iron and aluminium, which have been formed in hot and wet tropical areas and can be identified by rusty red colour because of iron oxides. It develops by intensive and long lasting weathering of the underlying parent rock. *Laterites* cover about one-third of the Earth's continental land area, with the majority of that in the land areas between the tropics of Cancer and Capricorn (Aleva, 1993).

The production of blended cements incorporating pozzolanic materials began in Italy in 1929. Cements containing granulated blast furnace slag have been produced in Germany, France, Luxembourg, Belgium and other countries for more than half a century (Bukki, 1986). Blended cements contains in addition to Portland cement clinker and calcium sulfate-a latently hydraulic component such as granulated blast furnace slag or Class C fly ash, or a pozzolanic component such as natural pozzolans, Class F fly ash, condensed silica fume, calcined clay, or a "filler" component such as limestone. The most common reason for blending ordinary Portland cement with these additions is economic. However, blended cements can be formulated to perform better than ordinary Portland cement. For specification purposes, Portland and blended cements are designated by type, depending on their chemical composition and/or performance requirements (Rachel *et al*., 1996).

For this study, an indigenous alternate Supplementary Cementing Materials (SCM), *Laterite*, has been used with the objectives: to evaluate the performance of cement containing different percentages of *laterite*; to identify the optimum replacement percentage; and to investigate the effects of different concentrations of *laterite* on various properties of cement.

Table 1: Experimental protocol for the compositions of the cement mixtures (wt. %)

Sample		Clinker	Gypsum	Lime stone	Fly ash	Laterite
1	OPC	95	5			
2	L-ST-5	90	5	5		
3	L-ST-10	85	5	10		
4	L-ST-15	80	5	15		
5	F-ASH-5	90	5		5	
6	F-ASH-10	85	5		10	
7	F-ASH-15	80	5		15	
8	LAT-5	90	5			5
9	LAT-10	85	5			10
10	LAT-15	80	5			15

MATERIALS AND METHODS

Materials: The raw materials used in this research were: Portland cements clinker; *laterite* and gypsum, whereas limestone and flyash were also used for comparison purposes. Portland cement clinker, limestone and gypsum were obtained from Askari Cement Ltd., Wah (Pakistan). *Laterite* was obtained from Haripur district (Pakistan) and flyash was obtained from Olympia chemical Ltd., Khushab (Pakistan).

Methods: The materials Portland cement clinker, *laterite*, gypsum, limestone and flyash specimens were first crushed in lab scale jaw crusher up to size max 05 mm and then small quantities representing whole were taken and dried for 2 h at 105±5ºC and then ground in a disc mill for 3 min to size the material less than 200 µm. The chemical analysis was then made by using X-Ray Fluorescence spectrophotometer (XRF) (PANalytical CubiX Inc., Netherlands).

Preparation of reference and blended cements: The cements used in the tests were grouped as control reference (OPC), limestone, flyash and *laterite* blended cements. Reference cement was obtained by adding 5% gypsum to the Clinker by weight and is called OPC. Limestone, flyash and *laterite* blended cement specimens were obtained by replacing the Clinker with limestone, flyash and *laterite* at various rates (5, 10 and 15%) by weight and keeping the gypsum at 5% in the composition (Table 1).

Control reference, limestone, fly-ash and *laterite* blended cement samples were ground in a laboratory type of ball mill for 1 h and 30 min. Specific surface area measurement was made by a Blaine Fineness Apparatus (Model: G-128-38-1000) manufactured by ELE International (ASTM, 2000). Particle size groups were obtained by using an Alpine Air Jet Sieves (A 200 LS model) and sieves of 90 and 200 and 45 µm residues were determined by the wet sieving method (ASTM, 2003b). Density of cement was determined by Specific Gravity Flask (Le Chatelier) H-3400, Humboldt (ASTM, 2003c).

Preparation of mortar cubes: Mortar cubes were prepared using 200 g cement, 600 g standard sand and water for each mixture as per cement water consistence (IS, 1988). At this stage, standard water demand (ASTM, 2004a), soundness and setting time (BS-EN, 1995) tests were made on the fresh mortar samples. Setting time and water demand tests were made using a Vicat Instrument (RMU 24100 Bergamo Viq Gremello 57 model). Soundness test for cement expansion was conducted on a Brass Atom (Teknik Le-Chatelier Instruments).

For the compressive strength tests (IS, 1998), the mortar samples were placed in cubical moulds (70.6 mm each side). The mortars in the moulds were vibrated for 2 min for a better placement and then kept in the moulds for 24 h at room temperature. The moulds were removed and the cubes were placed in a curing bath at 27±2ºC and removed from curing bath after 3, 7 and 28 days for compressive strength tests. The tests were done according to Pakistan Standards (2008) by using Toni Technik hydraulic press.

RESULTS AND DISCUSSION

Chemical analysis: Chemical analysis of the clinker, flyash and limestone shows that the samples results complies with the specification of Grade-53 Ordinary Portland Cement (OPC) (PS 232-2008(R) (Pakistan Standards, 2008). The results of clinker comply with the Type-1 of ASTM C150 (ASTM, 2004b), while the results of flyash comply with Class-F (ASTM C618 and BS EN 197-1) (ASTM, 2003d; BS-EN, 2000). Limestone qualifies the requirement of BS EN 197-1 and *Laterite* complies with class N natural pozzolan of ASTM C618. The result of chemical analysis is

Table 2: Chemical compositions of blending material (wt. %)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	$CaSO_4.2H_2O$
OPC clinker	21.71	5.79	3.33	64.41	1.66	0.83	0.12	0.87	
Gypsum	1.78	0.45	0.29	32.53	0.83	0.12	0	41.18	88.56
Lime stone	0.99	0.33	0.16	54.25	0.48	0.06	0.01	0.05	
Fly ash	59.27	28.01	2.66	1.64	0.19	0.22	0	0.32	
Laterite	20.50	12.36	39.76	15.33	1.96	0.08	0	0	

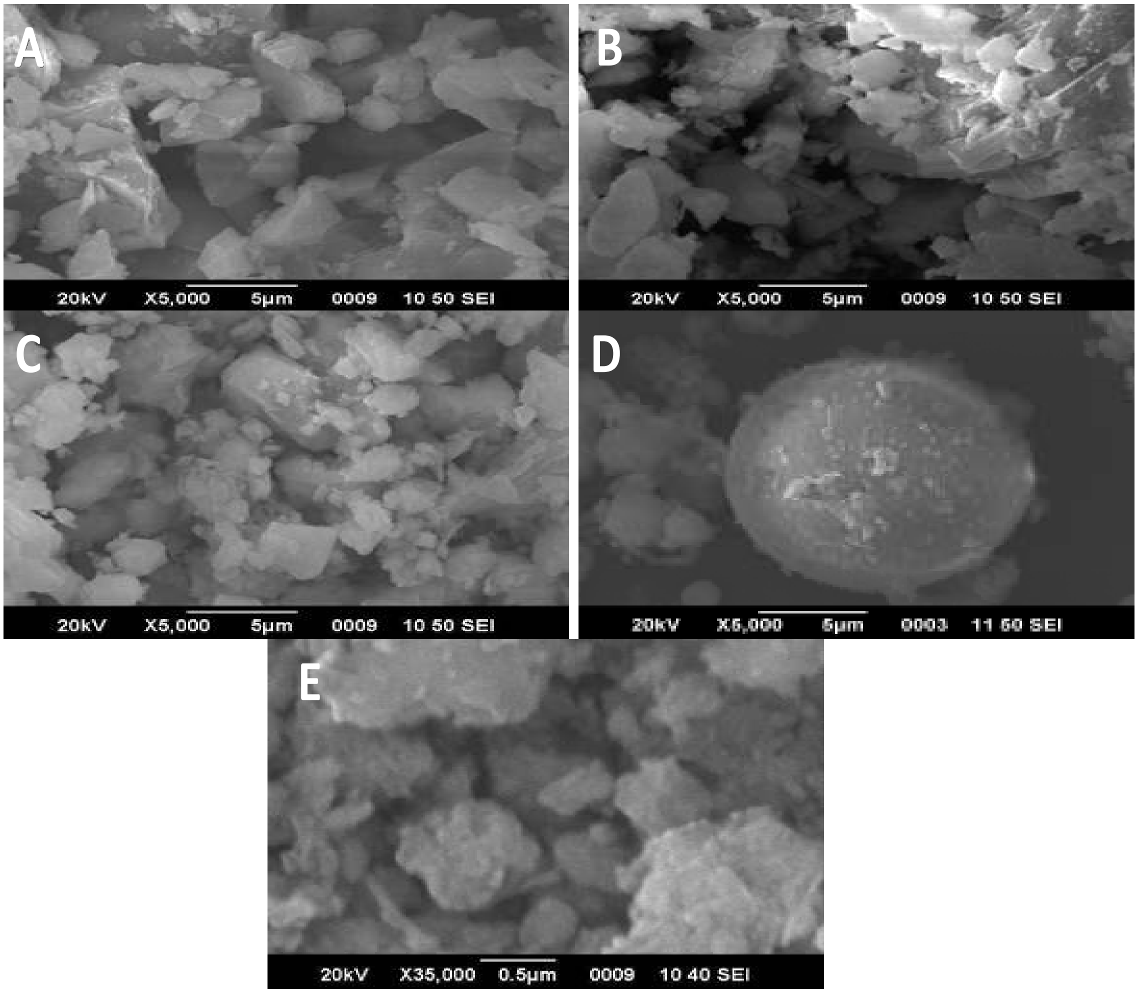

Fig. 2: SEM images of raw materials
2-A: OPC Clinker; 2-B: Gypsum; 2-C: Limestone; 2-D: Flyash; 2-E: Laterite

Table 3: Mineralogical composition of the clinker (*Bogue* calculation) (wt. %)

Mineralogical phases	C_3S	C_2S	C_3A	C_4AF
OPC clinker	50.68	24.55	9.71	10.15

given in Table 2 and the mineralogical composition of the clinker was calculated by the *Bogue* formulas as given in Table 3.

Micro-structural analysis: Microscopic structure of clinker, gypsum, *laterite*, limestone and flyash specimens are shown in Fig. 2. Samples were examined using the Analytical Scanning Electron Microscope (SEM) (JSM-6490A, JEOL, Japan), while the specimens were gold coated using Ion Sputtering Device (JFC-1500, JEOL, Japan). The Secondary Electron Images (SEI) of: clinker (Fig. 2A) shows angular crystals of alite (C_3S), rounded crystals of belite (C_2S). Figure 2B shows gypsum mineralogy while Fig. 2C depicts calcite crystals of limestone. Figure 2D shows small glass spheres of flyash and Fig. 2E shows crystals of *laterite*. The size of the shapes was in 5 μm.

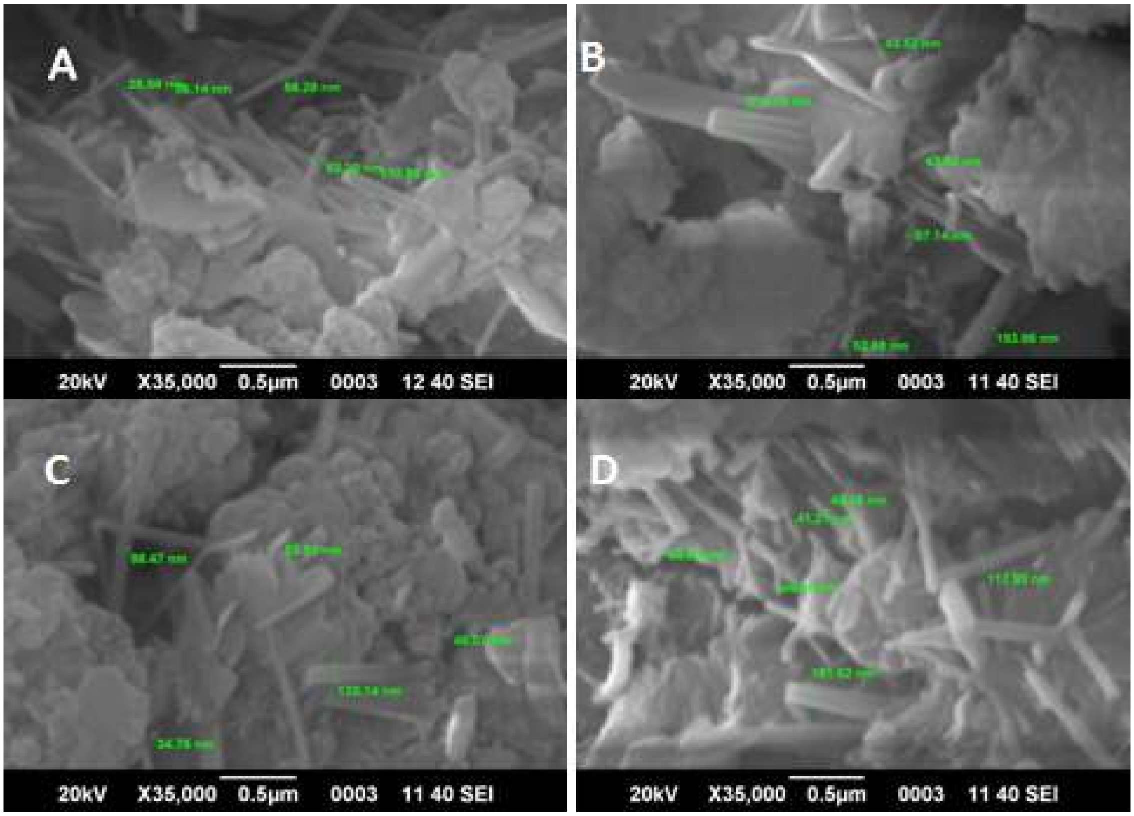

Fig. 3: SEM images of hydrated cement paste after 03 days water curing
3-A: OPC; 3-B: LST-10; 3-C: FASH-10; 3-D: LAT-10

Micro-structure of OPC, limestone and flyash cement blends at replacement level of 10% was investigated through SEM pictures after 03 days of hydration. It is clear that, the micrograph displays all hydrated products like CSH; CH and calcium silicate aluminates hydrate. Figure 3A shows the microstructure of OPC. It was found that CSH gel existed in the form of 'stand-alone' clusters, lapped and jointed together by many needle hydrates. At the same time, deposit CH crystals were distributed in the cement paste. Figure 3B, C and D) shows the microstructures of cement blends of limestone, flyash and *laterite*, respectively in all of them limestone has largest and widest needles and also gives the maximum compressive strength at that age, due to filler action of limestone, while all other images show the needles of almost same size and also have compressive strength close to each other but slightly on lower side due to slow *pozzolanic* reaction.

Density: Due to soft nature of limestone and *laterite* than clinker and smaller particle size of flyash, the density of materials with increasing replacement levels decreases. That is clearly demonstrated in Table 4. Also due to decrease in density the material required for construction on volume basis also deceased.

Table 4: Physical properties of the cement mixtures (wt. %)

	Blaine (cm^2/gm)	Residue 200 μ (%)	Residue 90 μ (%)	Residue 45 μ (%)	Density (cm^2/gm)
OPC (control)	3273	0	1.0	19.80	3.22
LST-5	3484	0	0.8	18.82	3.19
LST-10	4053	0	1.0	21.62	3.13
LST-15	4364	0	1.4	23.50	3.08
FASH-5	3345	0	1.2	18.00	3.12
FASH-10	3810	0	0.9	15.36	3.05
FASH-15	4442	0	0.6	13.27	3.00
LAT-5	4053	0	0.8	20.20	3.08
LAT-10	4154	0	0.7	22.80	3.04
LAT-15	4472	0	0.5	22.60	2.96

Fineness: Fineness of the cement increased after the addition of other supplementary cementing material. It was seen that with the addition of *laterite* as compared to limestone and flyash fineness increases more or the retention over 90 µm sieve, where as the residue on 45 µm sieves is little more causing decrease in early age strength (Table 4).

Specific surface area (blaine): Under normal conditions, *laterite* is ground finer than flyash and

Table 5: Water demand setting times and soundness of the cement mixtures

	Water consistency (%)	Initial setting time (min)	Final setting time (min)	Soundness (mm)
OPC	24.8	130	170	0.5
LST-5	23.7	140	185	0.5
LST-10	23.5	130	170	0.5
LST-15	23.2	130	170	0.5
FASH-5	24.7	155	205	0.5
FASH-10	25.1	149	201	0.5
FASH-15	25.5	146	187	0.5
LAT-5	25.8	137	172	0.5
LAT-10	25.7	132	177	0.5
LAT-15	25.4	124	178	0.5

OPC: Ordinary portland cement; LST: Limestone; FASH: Fly-ash; LAT: Laterite blend

limestone as well as OPC. *Laterite* addition in cement increased the fineness. The compressive strength as well as the other physical properties was affected by the fine grinding of cement. The results shows that the residue on 90 μm decreased but there is increased in residue on 45 μm for *laterite*, but on average the specific surface area is increased (Table 4). This indicates that residue on 45 μm is of more valuable than specific surface area, for the evaluation of early age strength. It was also seen that fineness of the all the blended cements was increased, directly proportional to the SCM addition (if the other conditions were kept constant.

Soundness (le-chatelier): CaO, MgO and SO_3 constituents of cements cause soundness effects in the concretes produced by these cements. Therefore, it is desired to have such constituents of cement as low as required. The results also supported this idea as seen in Table 5. It is expected to have a lower soundness rate since such constituents decrease with increasing diatomite amount in the blend. It can be concluded that the effect of addition of limestone, flyash and *laterite* have no contribution for the increase of Le-Chatelier expansion.

Water demand: Water demand changes according to the chemical structure, specific surface area and porosity of the cement mixtures. In blended cements, the fineness increases with addition rate (Table 4) which affects water demand. In fact, it was seen that water demand increased in all blending rates and Blaine values for flyash and *laterite* blended cement samples, whereas for limestone water demand increased (Table 5). Reason for this behavioral change of lime stone is due to its inertness or non pozzolanic nature of limestone, on contrary for flyash and *laterite* the water demand is increased due to their pozzolanic nature.

Setting time: Setting time of cements changes with particle size, specific surface area and mineralogical structure of the cement mixtures. However, in blended cement, Tri-calcium aluminate (C_3A) content decreases while the amount of gypsum remained constant. Although it is expected that setting time increases with pozzolan addition, which clearly indicated in setting time of the flyash blended cements, while setting time for *laterite* and limestone is increased but not to a larger extent (Table 5).

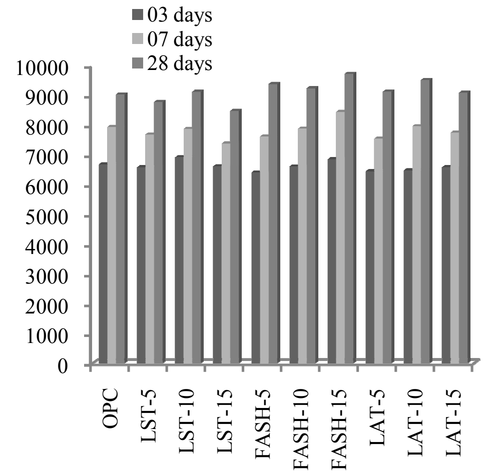

Fig. 4: Compressive strength 70.6 mm^3

Compressive strength: Since the strength of cement is a function of hydrated part, strength development is affected by mineralogical features of the clinker, pozzolanic reactions, Blaine, reactive SiO_2 ratio and water demand of the cement mixtures. Clinker phases which affect the strength values are seen in Table 2 and strength values were changed with the change in mineralogical phases due to increasing level of SCM addition (Fig. 4).

At the replacement level of 05% (Fig. 5) it was observed that there is decrease of compressive strength of flyash and *laterite* blends at early ages of 03 and 07 days due to slow pozzolanic reaction and increased at 28 days of curing. On the contrary limestone blends shows reverse of it that its strength at early ages is more than its 28 days strength. The reasons behind the above behavior are the filler effect of the fine particles of limestone, the higher clinker fineness in limestone cement blends. The strength development between 7 and 28 days seems to be good in all cements.

At the replacement level of 10% (LST-10), it is shown that with the increase in SCM contents the behavior at early ages is same as described above but the *laterite* has maximum at that replacement level at 28 days strength (Fig. 6). As the replacement level is

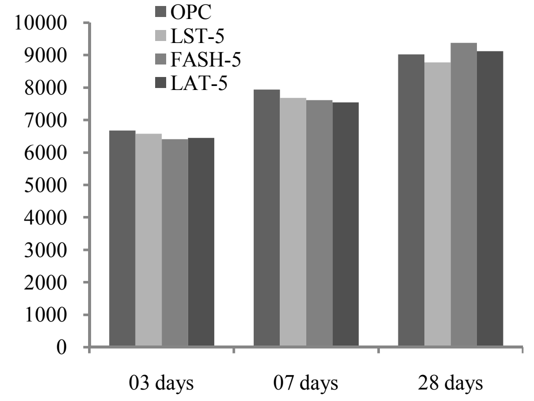

Fig. 5: Compressive strength of OPC and cement blends at the replacement level of 05%

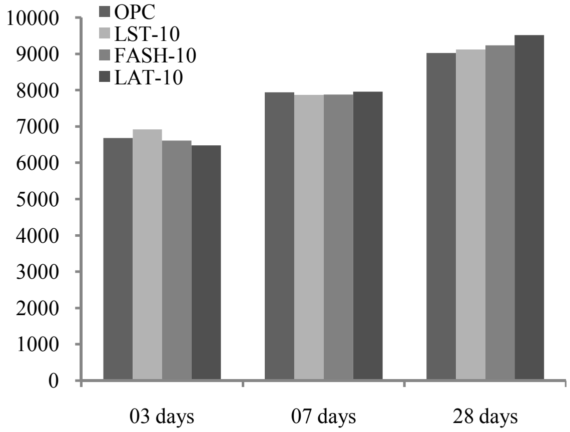

Fig. 6: Compressive strength of OPC and cement blends at the replacement level of 10%

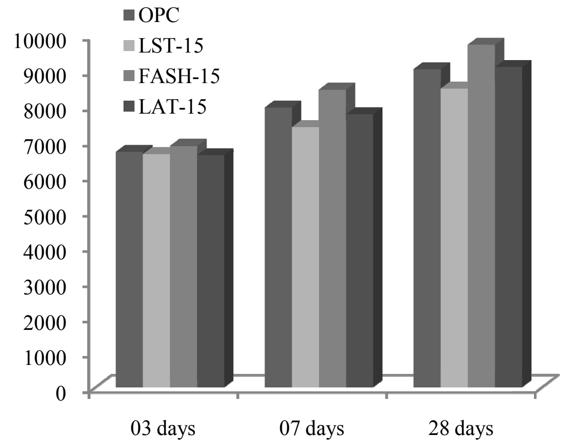

Fig. 7: Compressive strength of OPC and cement blends at the replacement level of 15%

increased to 15%, the 28 day strength of limestone blend is decreased (Fig. 7). *Laterite* blend is comparable to OPC while flyash blend showed an increase. It is indicative of the fact that further addition of limestone causes decrease of strength (Humphreys and Mahasenan, 2000). In addition, for *laterite* the % age can be even more considering that the strength was not decreased and for flyash the replacement at higher levels is still feasible which is indicated by several studies (Rachel *et al*., 1996; Hendricks *et al*., 2004; Bukki, 1986). Furthermore, the replacement level of up to 15%, the quality of cement is not disturbed but GHG emission is greatly decreased. In addition, the requirement of combustion energy is also decreased (~30%) as previously reported with other SCMs (Humphreys and Mahasenan, 2000).

CONCLUSION

Blended cements are used in USA and Europe but have not yet gained acceptance in the Pakistan due to misnomer of adulteration. However, for each 1% of cementation material used to replace clinker in Portland cement, an approximate 1% reduction in energy consumption and CO_2 emissions is achieved. It could be concluded from this study that performance of *laterite*-blended cement blends lies in between limestone and flyash cement blends, thus would be have capability to be chosen as a supplementary cementing material at the replacement level of 15% to be sure and expectedly even more. The raw form of it is advantageous in the sense that by certain modifications e.g., heat treatment and pozzolanic activity, could be increased. Introduction of blended cement needs the support of additional technical development work, government leadership and encouragement and demonstration of the performance of such products in the market.

REFERENCES

Aleva, G.J.J., 1993. The CORLAT Handbook. International Soil Reference and Information Center, Wageningen, the Netherlands.

ASTM, 2000. Test Method for Fineness of Hydraulic Cement by Air-Permeability Apparatus. ASTM C 618-03, C 150 - 04, C 188-95 (Rev. 2003) C 204-00, American Society for Testing and Materials (ASTM), USA.

ASTM, 2003a. Standard Specification for Coal Flyash and Raw or Calcined Natural Pozzolan for use in Concrete-Method No. ASTM C 618-03, American Society for Testing and Materials (ASTM), USA.

ASTM, 2003b. Method ASTM C: 430-96 (Rev, 2003) - Standard Test Method for Fineness of Hydraulic Cement by the 45-μm (No. 325) Sieve, 2003. American Society for Testing and Materials (ASTM), USA.

ASTM, 2003c. Standard Test Method for Density of Hydraulic Cement-ASTM C 618-03, C 150-04, C 188-95 (Rev. 2003), American Society for Testing and Materials (ASTM), USA.

ASTM, 2003d. Standard Terminology Relating to Hydraulic Cement-ASTM C 618-03, C 150-04, C 188-95 (Rev. 2003), C 204-00, C 219-03, American Society for Testing and Materials (ASTM), USA.

ASTM, 2004a. Test Method for Normal Consistency of Hydraulic Cement. (ASTM C 187-04, 2004) American Society for Testing and Materials (ASTM), USA.

ASTM, 2004b. Standard Specification for Portland Cement. ASTM C 618-03, C 150-04, American Society for Testing and Materials (ASTM), USA.

BS-EN (British Standards), 1995. Method No. BS EN 196-6-Determination of Setting Time and Soundness. British Standards Association, UK.

BS-EN (British Standsards), 2000. Method No. BS EN 197-1-Composition, Specifications and Conformity Criteria for Common Cements. British Standards Association, UK.

Habert, G., C. Billard, P. Rossi and N. Roussel, 2010. Cement production technology improvement compared to factor 4 objectives. Cement Concrete Res., 40(5): 820-826.

Hendricks, C.A., E. Worrell, D. Dejager, K. Blok and P. Riemer, 2004. Emission Reduction of Greenhouse Gases from the Cement Industry. Proceeding of International Conference on Greenhouse Gas Control Technologies.

Humphreys, K. and M. Mahasenan, 2000. Towards A Sustainable Cement Industry: Sub-Study on Climate Change. Retrieved from: http://www.wbcsdcement.org/ pdf/final_report8.pdf, (Accessed on: August, 2010).

IS (International Standards), 1998. (IS: 4031 (Part 6)-1988 First revision) Test Method for Compressive Strength of Hydraulic Cement 1988. Bureau of Indian Standard, New Delhi, India.

Pakistan Standards (PS), 2008. Method No. PS: 232-2008(R)-Pakistan Standard Specification for Ordinary Portland Cement (OPC), (Grades 33, 43 and 53). Ministry of Industries and Production, Pakistan, 2008.

Rachel, J.D., I.B. Javed and B. Sankar, 1996. Supplementary Cementing Materials for Use in Blended Cements. Portland Cement Association, Skokie.

Turarehan, R. and M. Nehdi, 2005. Carbon dioxide emissions and climate change: Policy implication for the cement industry. Envir. Sci. Policy, 8: 105-114.