Effect of Water-Cement Ratio on the Mechanical Properties of Blended Cement Containing Bottom Ash and Limestone

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Abstract
This paper presents investigation on the effect of water requirement on compressive/ flexural strength of hardened cement mortar of ordinary portland cement (OPC) blended with 10% Limestone (L) and 10% coal bottom ash (BA) by weight (80C- 10L-10 BA). The water-cement ratio is one of the most important parameters that affect the performance (mechanical properties) of mortar, thus obtaining the best water requirement translates to the best mechanical properties. Class C bottom ash and Limestone (L) were used to partially replace Portland cement at 10% each by weight. The blended cement containing limestone and coal bottom ash and OPC were prepared at different water-cement ratios ranging from 0.35 to 0.55. Mortar mixtures were prepared for the blended cement and OPC control. 2, 7, 28, 60 days-compressive and flexural strengths of the mortar mixtures were determined. The strength results were compared to those of OPC and relative strengths are reported. It was observed that the compressive/flexural strength in comparison with the OPC control at water-cement ratio w/c = 0.4 was equivalent while at 0.45 and 0.50, the compressive strength experienced a reduction followed by compressive strength increment at 0.55. This can be attributed to the slow nature of the pozzolanic reaction which did not show effect until the water-cement ratio reached 0.55. But after 7 days, the pozzolanic reaction showed its effect with increment in flexural and compressive strength all through. At 28 days the compressive and flexural strengths were 40.85MPa and 9.34MPa respectively which were higher than OPC control for compressive and flexural strength of 33.85MPa and 8.92MPa respectively. It was observed that as the water-cement ratio was increased from 0.40 to 0.55 both blended cement and the control experienced increment in the compressive and flexural strength.

Keywords: Compressive / Flexural strength, Water-cement ratio, Bottom ash, Limestone, Ternary cement

1. Introduction

The sustainable development of the cement and concrete industries can be achieved by complete utilization of cementitious and pozzolanic by-products or Supplementary Cementitious Materials (SCM), such as coal bottom ash, rice husk ash and silica fumes, produced by thermal power plants and metallurgical industries (Ramirez and Carrasco, 2011), resulting in the increase of the performance of fresh and hardened concrete (Detwiler *et al.,* 1996). The usage of materials as both SCMs and fillers in concrete have increased remarkably in recent years (Erdoğdu *et al.,* 1999) due to economical, ecological and engineering benefits of the usage (Plessis *et al.,* 2007).
Owing to increasing demand for energy, coal burning power plants have become more prevalent globally. During coal fired electric power generation, two main types of coal combustion by products are obtained; fly coal ash and bottom coal ash (Hariharan *et al.,* 2011). Although the utilization of bottom ash either as a cement replacement material or supplementary cementitious material is not practiced due to high unburned carbon content as well as large particles size and a high porous surface, it possess pozzolanic properties, which ground, the pozzolanic properties will be enhanced (Kaya, 2010). Improvements in the compressive strength of mortars containing coal bottom ash can are explained by the chemical and physical effects of cement replaced with coal bottom ash. Chemical effect is mainly due to the pozzolanic reactions between the amorphous silica of Bottom ash and calcium hydroxide (CH) produced by the cement hydration to form calcium-silicate-hydrates. The physical (filler) effect is that Bottom ash particles increase the packing of the solid materials by filling the spaces between the cement grains in much the same way as cement fills the spaces between fine aggregates, and fine aggregates fill the spaces between coarse aggregates in concrete (Erdem and Kirca, 2008). The filler effect reduces the porosity of the transition zone and leads to a denser microstructure and improved strength of the system (Goldman and Bentur, 1993). Moreover, small particles of additions generate a large number of nucleation sites for the precipitation of the hydration products. This will accelerate the reactions and form smaller Calcium Hydroxide crystals (Isaia *et al.,* 2003)

Limestone is considered as a filler. Its incorporation with Portland cement has many advantages on early compressive strength, durability and workability (Tsivilis *et al.,* 2000). Calcite presence in the binding system determines the acceleration of the cement initial hydration especially of the tricalcium silicate (Georgescu and Saca, 2009). It increases the effective water-cement ratio as well as provide additional surface for precipitation of hydration products, thus improving hydration at early age (Soroka and Setter, 1977; Bonavetti *et al.,* 2003). During hydration of Portland cement some calcium carbonate is taken into system and reacts with the alumina phases of cement to form carboaluminates and delays or impedes the ettringite monosulphate tranformation (Menendez *et al.,* 2003). This leads to the stabilization of the ettringite and will result in an increase in the total volume of the hydration products, which might result in a decrease in porosity and thus an increase in strength (Chaipanich *et al.,* 2011). It is known that concrete strength is affected by changing the water–cement ratio and cement dosage (Yasar *et al.,* 2004). The water-cement ratio affects the durability, permeability and shrinkage cracking of a material. Future research areas can explore the incorporation of new S.C.Ms at different levels and their effects on the mechanical properties.

This paper investigates the influence of water-cement ratio on the compressive and flexural strength of ternary cement containing ordinary Portland cement (OPC) blended with 10% limestone and 10% Bottom ash. The results obtained for the compressive and flexural strength for the ternary blends were compared with ordinary Portland cement control.

2. Methodology

2.1 Preparation of the Ordinary Portland cement, Limestone and Bottom ash

Ordinary Portland cement grade 32.5R was obtained from Ashaka Cem plc, Nigeria and employed in this study. The limestone samples collected from Ashaka Cem Plc, Ashaka town, Gombe state, Nigeria were crushed and ground to powder followed by sieving with 150mm sieve. Bottom ash was obtained by burning bituminous coal sourced from Nassarawa state, Nigeria. The coal collected was burnt in a furnace at a temperature of about 950°C for 5hrs. The resultant ash at the furnace bottom were collected and sieved.

2.2 Experimental Program

The ternary cement mixture comprising of Portland cement replaced by 10% bottom ash and 10% limestone and OPC control at various water-cement ratio ranging from 0.40 to 0.55 which were tested are shown in Table 2.1. The ternary mixture and control mixture are mix 1-4 and 5-8 respectively.

Table 2.1: Quantities required for compressive and flexural strength of blended cement and OPC control

S/No	OPC (%)	BA (%)	L (%)	OPC(g)	BA(g)	L(g)	Water(ml)	Sand(g)
1	80	10	10	360	45	45.0	180.0	1350
2	80	10	10	360	45	45.0	202.5	1350
3	80	10	10	360	45	45.0	225.0	1350
4	80	10	10	360	45	45.0	247.5	1350
5	100	0	0	450	0	0.0	180.0	1350
6	100	0	0	450	0	0.0	202.5	1350
7	100	0	0	450	0	0.0	225.0	1350
8	100	0	0	450	0	0.0	247.5	1350

2.3. Experimental Procedure

Cement mortar was prepared in the laboratory at temperature of 20^{o}C and relative humidity less than 50%. Blended cement mixture were formulated by replacing OPC with 10% limestone and 10% bottom ash which was measured by weight. For blended cement pastes, the water-cement ratio was varied from 0.40 to 0.55 at interval of 0.05 for the blended cement and OPC control. The mixture was mixed and cast into 50x50x50 mm moulds. The mortar was then compacted in the mold using a standard jolting apparatus. The molds were then be kept at a relative humidity cabinet for 24 hours. The molds were then removed, de-molded; and placed in a curing tank containing distilled water. Strength tests were carried out at curing ages of 2 7, 28 and 60 days. The samples were then taken from storage tank, broken into two by bending test and each half was tested for compressive strength using Tonic Technic compression and bending machines respectively. The method comprises the determination of bending and compression strength of prismatic specimen (40mm x 40mm x 160mm) in size, using the flexural and compression machine to determine the test result.

3. Results and Discussion

3.1. Characterization of the Materials

Table 3.1 shows the XRF analysis of Ordinary Portland cement, Bottom ash and limestone. It could be seen that bottom ash comprised predominantly of three oxides: Al_2O_3, SiO_2 and Fe_2O_3. The classification of ash into classes F, C and others is done on the basis of the chemical composition of the ash. The sum total of SiO_2, Al_2O_3, and Fe_2O_3 in Bottom ash used in this study was less than 70% of the whole sample and the lime content (CaO) was less than 20%, thus this type of ash is pozzolanic in nature and can be obtained from burning older anthracite or bituminous coal producing Class F ash. Also for bituminous coal, Fe_2O_3 content ranges from 10-40% and Loss of Ignition LOI ranges from 0-15% which all fell within the literatures (www. wikipeida.org/Flyash)

Therefore, according to the ASTM C 618, 2003, the ash qualifies for classification as Class F pozzolana. The limestone comprises of average calcite content ($CaCO_3$, 54.84%) and Silicon dioxide content of 34.19%. While Ordinary Portland Cement has about 2.12 % sulphates, Bottom ash contain a high sulphate content of 6.14%. The presence of sulphates in stabilizing agents has been associated with accelerated corrosion of stabilizing bars once present (Neville, 2009). Thus, sulphate presence contributes to sulphate attack when used. Ash ties up free lime that can combine with sulfate to create destructive expansion (Freeda Christy and Tensing 2011). According Eggenberger *et al.* (2004) unburnt carbon in pozzolanic materials can serve as filler in the material being stabilized. Progress of the pozzolanic reaction of class F ash is slow.

Table 3.1: The X-ray analysis of the Ordinary Portland Cement, Bottom Ash, and Limestone

Compound	OPC (%)	Bottom Ash (%)	Limestone
SiO_2	21.01	34.19	20.789
Al_2O_3	5.98	13.37	7.021
Fe_2O_3	3.16	20.93	2.921
CaO	64.57	8.10	30.721
MgO	0.92	3.31	0.401
SO_3	2.12	6.45	0.311
K_2O	0.92	0.38	1.321
Na_2O	0.15	0.14	0.041
TiO_2	0.29	1.14	-
Mn_2O_3	0.16	0.27	0.332
P_2O_5	0.21	0.14	0.271
Cl	0.01	0.04	-
Cr_2O_3	0.49	-	-
$CaCO_3$	-	-	54.84
LSF	95.026	-	45.561
C_3S	51.960	-	-
C_2S	16.824	-	-
C_3A	10.074	-	-
C_4AF	9.198	-	-
LOI	-	11.54	35.87
Physical analysis			
< 45um		74.23	
<90um		25.24	
212um		0.53	
Surface area m^2/kg	450	532	370

3.2. Compressive and Flexural Strength

Compressive and Flexural strength were carried out at ages of 2, 7, 28 and 60 days. The average of three compressive strength specimens were estimated and were plotted against the water-blended cement ratio at constant limestone and bottom ash particle size as shown in Figure 1- 4.

Table 3.2: Compressive and Flexural strengths for blended cement after curing at 20°C at various w/c

Curing days	Compressive strength (MPa) at 0.40	Flexural strength (MPa) at 0.40	Compressive strength (MPa) at 0.45	Flexural strength (MPa) at 0.45	Compressive strength (MPa) at 0.50	Flexural strength (MPa) at 0.50	Compressive strength (MPa) at 0.55	Flexural strength (MPa) at 0.55
2	5.45	1.24	7.67	2.61	11.35	2.91	15.06	3.82
7	15.09	2.77	21.24	5.23	23.29	4.93	29.53	6.51
28	22.77	3.14	26.88	5.93	32.05	7.08	40.85	9.34
60	23.22	3.75	27.42	7.08	32.68	9.34	40.85	9.78

Table 3.3: Compressive and Flexural strengths for OPC after curing at 20°C at various w/c

Curing days	Compressive strength (MPa) at 0.40	Flexural strength (MPa) at 0.40	Compressive strength (MPa) at 0.45	Flexural strength (MPa) at 0.45	Compressive strength (MPa) at 0.50	Flexural strength (MPa) at 0.50	Compressive strength (MPa) at 0.55	Flexural strength (MPa) at 0.55
2	5.5	1.25	10.18	2.9	14.44	2.93	12.41	3.45
7	14.8	2.57	19.52	3.64	21.1	4.22	25.05	6.27
28	19.07	3.03	20.82	5.18	29.16	5.23	33.85	8.92
60	20.82	5.47	20.82	7.08	29.3	7.37	33.9	8.98

Tables 3.2 and 3.3 show reduction of the compressive and flexural strength for blended cements and Ordinary Portland cement respectively as a function of the water-cement ratio for 2,7,28 and 60 curing days respectively. The compressive and flexural strength of the blended cement increased with increment in the water-cement ratio for all ages from 2 to 60 days. The main compressive and flexural strength gain take place during the first 28 days of curing which gave similar trends with De Weerdt *et al*. (2011) work. Both strengths did not experience much change after 28 days of curing as compared within the first 28 days. However there is still a considerable strength increase between 28 and 60 days for various water-cement ratios expect for the compressive strengths obtained for water cement ratio of 0.55. The maximum 28 days compressive strength was obtained for the blended cement of 40.85MPa for water-cement ratio of 0.55. A compressive strength increase of about 27.7% was obtained between 7 and 28 days for cement replacement with 10% limestone and 10% coal bottom ash.

3.2.1: Effect of water-cement ratio on compressive and flexural strengths for blended cement and OPC control

It is known that the concrete strength is affected by the water-cement ratio and cement dosage. Figures 1-4 illustrate the compressive and flexural strengths of blended cement sample as a function of the water-cement ratio. It is clear that the strengths increases at various curing periods for all hardened cement paste with increasing water-cement ratio from 0.40 -0.55.

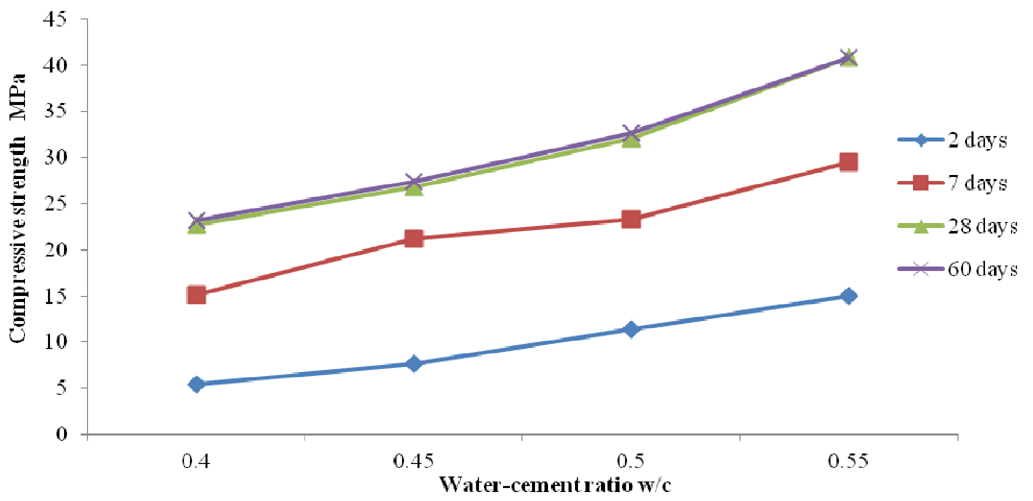

Figure 1: Effect of the water -cement ratio on Compressive strength

This can be attributed to the fact that as cement is replaced with bottom ash and limestone. According to Jaturpitakkul and Cheerat (2003) bottom ash require more water compared with mortar containing only Ordinary portland cement due to the presence of unburnt carbon. Limestone enhances the formation of calcium hydroxide at early ages because it provides nucleating sites for its growth. In addition, larger amounts of ettringite are observed at early ages with limestone addition (Barker and Cory, 1991) and of a better dispersion in water of the cement particles, which favors the hydration processes (Georgescu and Saca, 2009). As a result of the unburnt carbon causes an increased water requirement aiding hydration leading to release of the sillcate component which interacts with available additional free lime supplied by limestone dissolution. Thus producing additional calcium silicate hydrate (CSH) which is responsible for the strength.

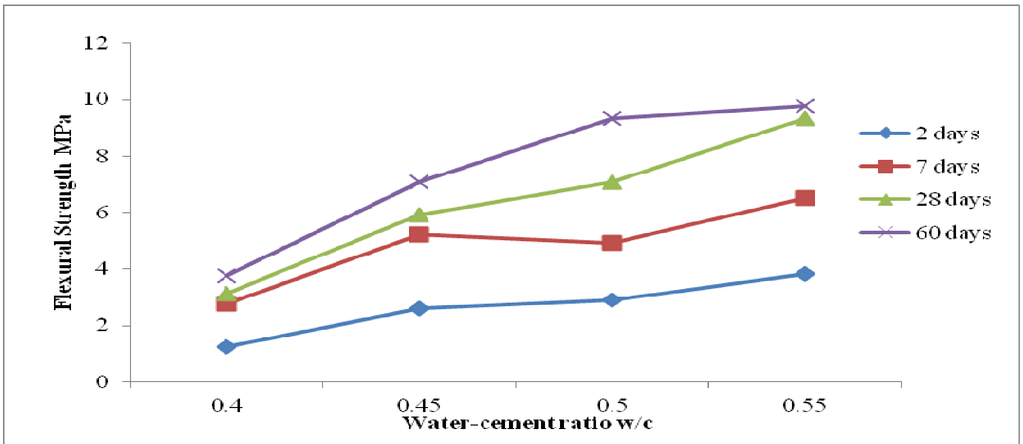

Figure 2: Effect of water cement ratio on flexural strength

The compressive strength test results at different curing ages for blended cement revealed a rapid strength gain between 2-7 days and a more gradually increase between 7- 28 days. The observed behavior may be attributed to the formation of hydration products as the reaction progressed, since pozzolanic reactions are relatively slow. Cyr *et a*l. (2006) found that the slowness of pozzolanic activity of coal ash is dependent on the amount and solubility of the amorphous silica in the material, thus lengthening the curing age to observe its positive effects. On the other hand Neville (1981) observed that formation of hydrated products could inhibit the hydration process thus leading to a reduction in the rate of hydration. Results obtained are in agreement that concrete attains approximately 70% of its 28 days strength in 7 days and 85-90% between 7 and 28 days (Assakkaf, 2004). Similar trends were experienced for flexural strength basically between 2-7 days.

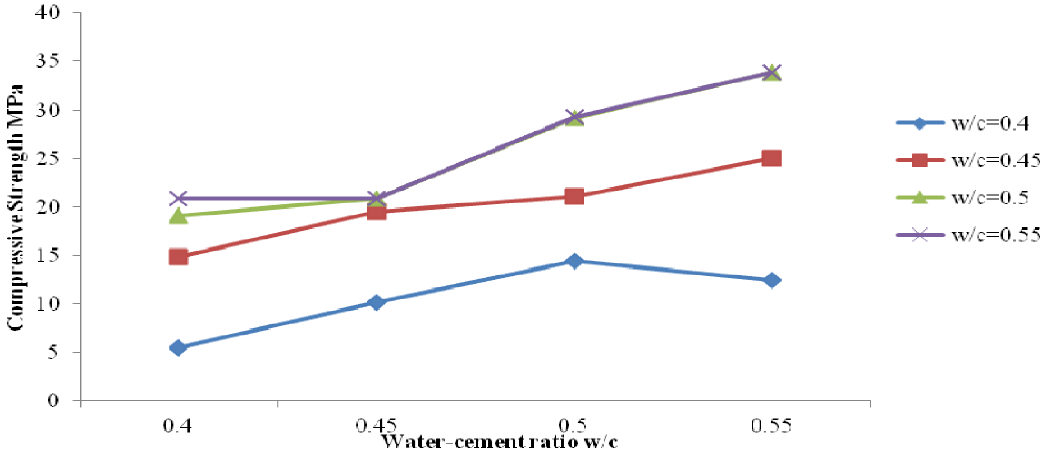

Figure 3: Effect of water-cement ratio on compressive strength of OPC

According to Neville(1981) when concrete is partially compacted, the compressive strength increases with water-cement ratio until an optimum water content is reached. It could be observed that the optimum water-cement ratio was almost reached at 0.55 as a result of constant results.

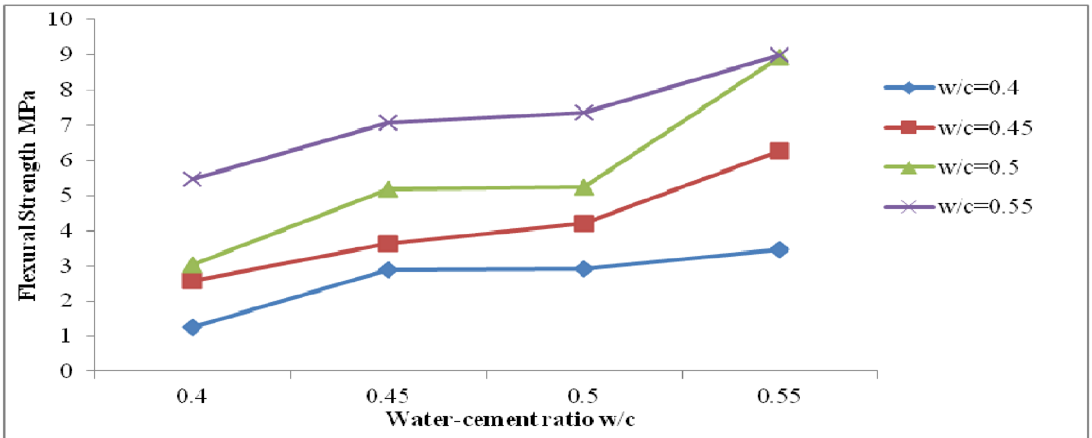

Figure 4: Effect of water-cement ratio on Flexural strength of OPC

3.2.3: Comparison between Blended cement and Ordinary Portland cement

Figures 5-8 show the effect of water-cement ratio on the compressive and flexural strength of blended cement and Ordinary Portland Cement pastes at 2, 7, 28 and 60 days of curing. It could be observed from Figures 5-8 that for the first 7 days, the blended cement strength gain compared with OPC control were similar while beyond 7 days gave better strength gain compared with the OPC control. For water-cement ratio w/c of 0.55 as shown in Figure 8, it can be observed that the compressive strengths of blended cement indicated a better strength gain in comparison with the control for all curing day.

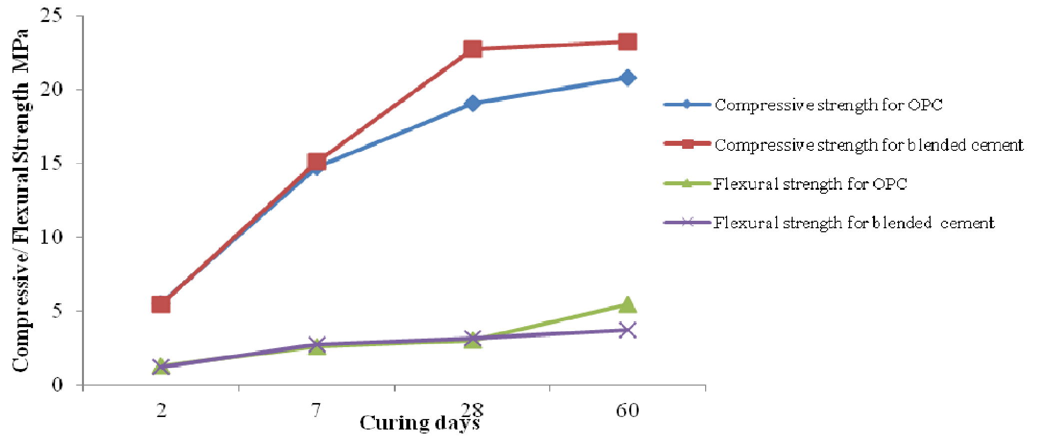

Figure 5: Strengths for blended cement and OPC at curing days at w/c = 0.4

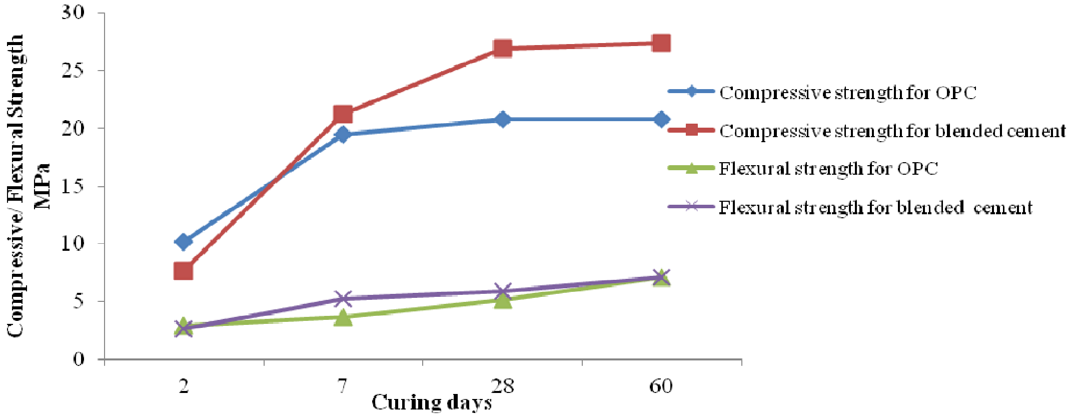

Figure 6: Strengths for blended cement and OPC at curing days at w/c =0.45

This can be attributed to the fact that bottom ash contribution in the blended cement gains strength at a slower rate in the initial period and acquires strength at faster rate beyond 28 days, due to pozzolanic action.

Also, at early age bottom ash reacts slowly with calcium hydroxide liberated during hydration of cement and does not contribute significantly to the densification of concrete matrix at early ages (Aggarwal *et al*., 2007).

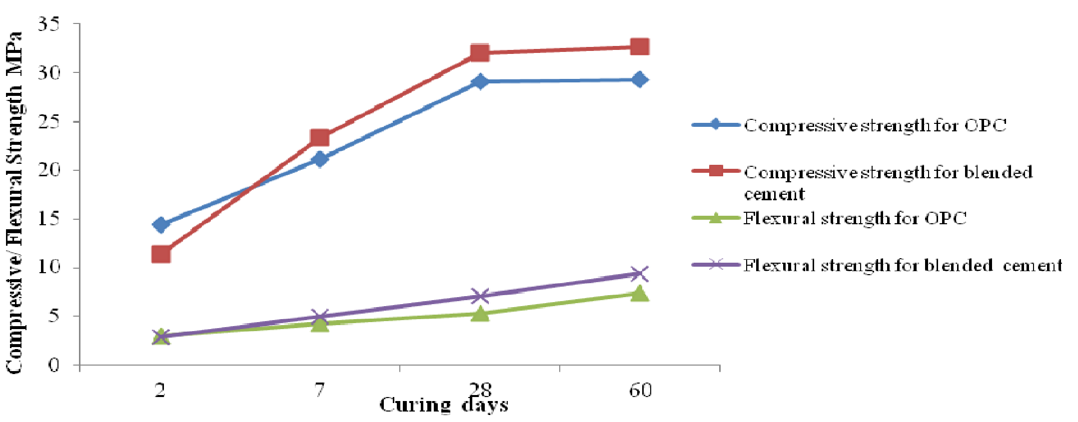

Figure 7: Strengths for blended cement and OPC at curing days at w/c = 0.5

This was in agreement with Aggarwal *et al.* (2007), that the blended cement paste did not experience any effect on the compressive strength until after 7 days. The flexural strength also experienced better strength gain for blended cement in comparison with OPC control until after 28 days. Beyond w/c = 0.4, the flexural strength improved slightly compared to the control.

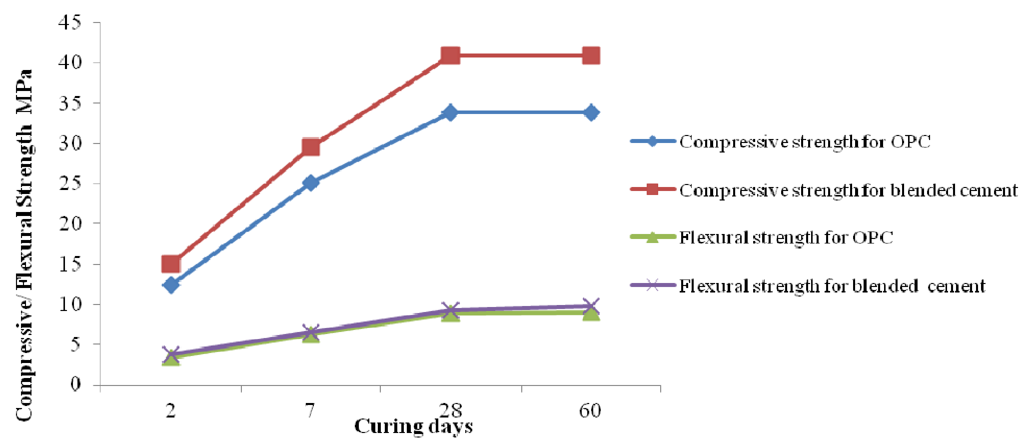

Figure 8: Strengths for blended cement and OPC at curing days at w/c = 0.55

An increase in the early strength of the mortar due to the addition of limestone can be attributed to the active participation in the hydration process and the filler effect of the fine particles of limestone thus providing sites for the nucleation and growth of hydration products leading to further increase in strength of the mortar between 2 and 28 days which is in agreement with Olgun and Yilmaz (2008).

4. Conclusion

The following conclusions

- The presence of limestone powder enhanced the early strength of the mortar due to the action of nucleation centers. Bottom ash improved the later strength due to its pozzolanic activity between the amorphous silica of bottom ash and available lime in the matrix to form calcium-silicate-hydrates with later strengths even higher than obtained with the pure Portland cement. Thus, the ternary mixture comprising of limestone and coal bottom ash and Ordinary Portland cement OPC provides higher late strengths than OPC control.
- Increase in water-cement ratio from 0.35 to 0.55 showed an increase in both flexural and compressive strengths for all curing ages. Water-cement ratio of 0.55 gave the best compressive and flexural strength for all curing ages of 40.85 and 9.78 MPa respectively. This is due to a better dispersion in water of the cement particles, which favors the hydration processes.
- Strength improvements for the ternary blends were more significant at 7 and 28 days.
- Water-cement ratio above 0.45 gave strengths lower for 2 days than for beyond 7 days for the ternary

blends compared with OPC control.

- The maximum compressive strength occurs at water-cement ratio of 0.55 with 10% bottom ash, 10% limestone content at all ages. It gave 15.06 MPa at 2 days, 29.53 MPa at 7 days, 40.85MPa at 28 days, and 40.85MPa at 60 days.
- The maximum flexural strength occurs at water-cement ratio of 0.55 with 10% bottom ash, 10% limestone content at all ages. It gave 3.82 MPa at 2 days, 6.51 MPa at 7 days, 9.34 MPa at 28 days, and 9.78 MPa at 60 days.
- From the results obtained, it suggests that incorporating Class F bottom ash and Limestone with OPC are convenient for structural use.

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