

# EFFECT OF LIMESTONE ADDITION ON PHYSICOCHEMICAL PROPERTIES OF CEMENT: A CASE STUDY OF LABORATORY PREPARED PORTLAND CEMENT, SOKOTO PORTLAND CEMENT AND DANGOTE PORTLAND CEMENT.

## ABSTRACT

*Sokoto Ordinary Portland Cement, Dangote Ordinary Portland Cement and synthesized Portland Cement were blended with various proportions of limestone. X-Ray fluorescence (XRF) studies revealed increase in CaO concentration with addition limestone in all samples studied, while the concentration of other oxide decreases. Compressive strength decreases as limestone content increases but at lower concentration (5-15%), the cured cement had appreciable strength, which also decreases with addition of limestone for all the samples. Soundness test revealed that addition of limestone within 5-15% did not cause any expansion and weakening of the cement structure. The setting times for all cement types decreases with increasing limestone addition.*

## 1.0 INTRODUCTION

In the most general sense of the word 'cement' is a binder or a binding substance that sets and hardens independently when mixed with water. The name cement goes back to the Romans who use the term "Opus Caementitum" to describe masonry, which resembled concrete and was made from crushed rock with burnt lime as binder (Inan 2007). The volcanic ash and pulverized brick, which were added to the burnt lime to obtain hydraulic binder, were later referred to as 'cementum' and to the word cement (Taylor, 1990).

In 18<sup>th</sup> century, U.S.A production of cement relied on the processing of cement rock from various deposits, such as those in 'Resonate'. In 1824, Joseph Aspendine, an English bricklayer, patented a process for making what he called Portland cement with properties superior to its predecessors, this is the cement used in most modern constructions (Tsviliset *al.*, 2002; Vogliset *al.*, 2005).

The use of blended cements, especially those containing limestone, seems to have many technical and economic benefits (Sarkar and Ghosh, 1993; Neville, 1996; Baron and Dourve, 1987). The beneficial effect of limestone cement is questionable, pervious researches reveal that limestone cement has several impacts on the mechanism and kinetics of cement hydration; the filler effect that accelerates the hydration of Portland Clinker grains (Kuzel and Pollmann, 1991), the formation of carboaluminate (Klemm and Adams; Bonavettiand Rahhal, 2001) and the modification of the microstructure (Kakaliat *al.*, 2000).

Production of Portland limestone cement, using limestone powder additive as a partial replacement to the clinker, is a current trend in the World cement industry; especially in European countries due to its multi-faceted advantages that include: increased cement productivity, reduced production cost and environmental protection with a significant reduction of CO<sub>2</sub> and NO<sub>2</sub> emissions per ton of cement produced (Wendimu and Abebe, 2010). The recent European Standard EN 197 identifies two types of Portland limestone cements: Type II/A-L containing 6–20% and Type II/B-L containing 21–35% limestone addition. In addition, the inclusion of 5% of filler material that can be calcareous is accepted in all cements. (Wendimu and Abebe, 2010).

Literatures revealed that, in 2004 the ASTM C150 standard specification for Portland cement was modified to allow the incorporation of up to a 5% mass fraction of limestone in ordinary Portland cements ([www.jcem.vgtu.lt](http://www.jcem.vgtu.lt), 2008). The substitution of parts of cement by raw limestone powder have shown several effects on the physical and chemical properties of cement paste and hardened mortar. Most of the research investigations have emphasized that the C<sub>3</sub>S hydration rate is accelerated when the amount and fineness of limestone filler (CaCO<sub>3</sub>) content is increased due to generation of large number of nucleation sites for precipitation of the hydration products (Boubitsas, 2004). This enhanced degree of hydration at an early age reflected by the improvement of the strength of both mortars and concretes at early ages. Numerous studies on Portland limestone cement focused on the effects of limestone on the cement performance, participation of limestone in the hydration reactions and the production process specifically intergrading of clinker and limestone (Kakaliat *et al.*, 2000).

The raw materials for production of such cement type is sufficiently available, requires lesser energy for production, and has less CO<sub>2</sub> and NO<sub>2</sub> emissions, It is also economical (McGrath, 2008).

It was reported that for limestone contents over 15% mortar compressive strength reduced by increasing limestone content (Dhir *et al.* 2007; İnan 2012; Felekoğlu *et al.*, 2006; Yılmaz and Olgun 2008; Sprung and Siebel 1991; Kakaliat *et al.*, 2000). Nehdi *et al.* (1996) showed that at 3-day tests, the compressive strength **was** little affected by the substitution of 10% and 15% of cement by limestone, while it was decreased significantly for higher limestone contents. In addition, Marzouki *et al.* (2013) reported mortar compressive strength results for samples **containing** up to 15% limestone and for later ages and up to one year. It was found that the change from higher limestone content was not significant in the later ages. Hoshino *et al.* (2006) reported that when limestone cement **was** used with blast furnace slag, the strength increasing effect of blended limestone cement **was** more pronounced compared to the Ordinary Portland Cement (OPC).

Work in Brazil showed improved performance of mortars containing up to 35% limestone exposed to a sodium sulfate solution for up to 6 months (Tezuka *et al.*, 1992). Other studies showed that at 25°C, no sulfate attack was observed after a year of exposure (Kakaliat *et al.*, 2003; Torres *et al.*, 2003; Skaropoulou *et al.*, 2009). However, some researchers found that mortars **with** content of limestone from 15% to 30%, suffered from the thaumasite form of sulfate attack at low temperature of 5°C (Kakaliat *et al.*, 2003;

The delay in the time of setting can be attributed to the dilution effects resulting from clinker replacement, or to the change of the paste rheology, which can be affected by the existence of elementary carbon. (Elkhadiria. *et al.*, 2002). Batch inter-grinding cement with 0, 3, 5.5, and 8% limestone to constant specific surface showed little effect on setting time, while grinding the cement to constant residue on a 325-mesh resulted in a reduction of setting time (Hawkins, 2003; Mohammad and South, 2016).

The setting time **was** much influenced by the degree of fineness of additions which appeared to be advantageous for the decrease of both initial and final setting time of blended mixtures. It can be noted that the setting time **increased** with higher dosages of slag and limestone amounts. **This** can be explained by the low activity of **the additive**, as the increase in surface area (3500, 5000 and 11000 cm<sup>2</sup>/g) **influenced** the time of setting so water **requirement** increased to obtain a cement with normal consistence (Mohammad and South, 2016).

Both initial and final setting times **s** of Portland limestone cement pastes were decreased with an **increase in** limestone content at the same fineness. At the same level replacement, the cement pastes using small-sized limestone **showed** lower setting time than those using large-sized limestone (Mohammad and South, 2016).

This study **was** thus attempting to make use of raw limestone additive in the production of ordinary Portland limestone cement. An experimental investigation **was** carried out to examine the impacts of adding raw limestone powder on the physical and chemical properties of the cement such as **soundness**, setting time, and compressive strength.

## **2.0 THE EFFECTS OF LIMESTONE FILLERS ON CEMENT PROPERTIES**

### **2.1 FINENESS**

Limestone fillers have many effects on the cement properties due to its fineness. Inclusion of this fine material will significantly accelerate the hydration of alite and aluminates of the cement, because the particles act as nucleation sites for the formation of the hydration products. Another effect of finely divided additions is their action as fillers between the cement grains producing a denser paste and densifying the interfacial zone between the aggregate and cement paste (Neville, 1996).

### **2.2 CONSISTENCY**

The effect of limestone powder on the water requirement of OPC and blended cement has been studied extensively and a majority of findings are in favor of a better workability of mortar and lowering the water requirement for neat paste containing limestone. The improvement in the workability of paste and mortar is due to suitable texture fineness and particle size distribution of cement containing limestone (Peter, 1996).

### **2.3 SOUNDNESS**

The recent findings show that the addition of calcareous material (limestone) up to the range of 5-7% in cement mortar have smaller influence on shrinkage as compared to siliceous additives. It is also confirmed by

different investigators that there is no remarkable effect on the soundness of OPC paste with up to 10% replacement by limestone additives (Peter, 1996).

## **2.4 HYDRATION**

Many research papers on influence of limestone powder on hydration of Portland cement have reported that the  $C_3S$  hydration rate is accelerated when the amount and fineness of  $CaCO_3$  is increased. This is due to the fact that they generate a large number of nucleation sites for precipitation of the hydration products (Peter, 1996).

## **2.5 COMPRESSIVE STRENGTH**

It has been found that addition of limestone powder into cement paste and mortar increases the strength at early ages without changing the workability of mortar. It has also been investigated that blending of Portland cement with 10 -40% finely ground limestone improves the early strength (Newman and Choo, 2003). Findings of research works on the strength reveals that, irrespective of grinding methods (intergrinding or separate grinding of limestone and other materials) up to 5%, the strength of limestone cement at 3 and 7 days were slightly higher than the pure ordinary Portland cement since increase in strength is directly related to the increase in rate of hydration of cement obtained due to the addition of limestone fillers (Newman and Choo, 2003). However findings also reveal that, as the percent of substitution of limestone in OPC increases, the compressive strength development of resultant cement decreases (Newman and Choo, 2003). Grinding Studies have shown that intergrinding clinker with different proportion of limestone resulted in improved grinding behavior of clinker resulting in saving of grinding time and decrease in fuel and electric consumption cost. Thus the European cement industries allowed using mineral addition to economize the production of cement under the specified standard. It has also been proved that intergrinding have resulted in better particle size distribution for the same energy level than that of separately grinding of raw materials with clinker (Wendimu and Abebe, 2010).

## **2.5 ENVIROMENTAL IMPACT**

It has been recognized that cement industries release different gases to the atmosphere including greenhouse gas emissions, Dioxin,  $NO_2$ ,  $SO_2$ , and vibration during operating machinery and blasting in quarries. It is an established fact that 0.9 ton of  $CO_2$  is emitted per ton of cement (EN 196-6, 1989). However, there are strategies for the reduction of carbon dioxide which aimed at lowering emissions per ton of cement, even though there is inherent emission of carbon dioxide during chemical breakdown of the limestone in cement kilns during production of Portland cement clinker. One of the strategies of decreasing  $CO_2$  emission is intergrinding or blending limestone with Portland cement which offers key advantages in reduction of  $CO_2$  emissions, climate change, economic and technical benefits (Wendimu and Abebe, 2010).

## **3.0 MATERIALS AND METHODS**

### **3.1 SYNTHESIZED PORTLAND CEMENT (SPC)**

Clinker, limestone and gypsum were obtained from Sokoto cement plant. Three SPC samples were prepared with different proportions of clinker and percentage of limestone.

- i. SPC I (5% limestone)
- ii. SPC II (10% limestone)
- iii. SPC III (15% limestone)

synthesized Portland cement 1 (SPC1) with 5% limestone was prepared by using 91% clinker, 4% gypsum and 5% limestone with total weight of 2.5Kg.

2275g of crushed clinker, 100g of crushed gypsum and 125g of limestone were grinded together using laboratory mill for 1hr and sieved using 200u sieve.

SPC II and III with 10% and 15% limestone were also prepared using the same procedure above.

SPC II has 2150g, 100g and 250g of clinker, gypsum and limestone respectively.

### **3.2 SOKOTO LIMESTONE PORTLAND CEMENT (SLPC)**

SLPC I, II and III were prepared from Sokoto cement with different proportion of limestone. Sokoto limestone Portland cement I (5% limestone) was prepared by mixing 95% Sokoto cement with 5% milled limestone using an automatic mixer.

SLPC II and SLPC III were also prepared using 1:10 Sokoto cement-limestone and 15:8.5 limestone- Sokoto cement respectively.

### **3.3 DANGOTE LIMESTONE PORTLAND CEMENT (DLPC)**

DLPC I, II and III were prepared from Dangote cement with varying percentage of limestone.

Dangote limestone Portland cement I (5% limestone) was prepared by mixing 5% and 95% limestone-Dangote cement respectively using an automatic mixer.

DLPC II and III with 10% and 15% limestone were prepared by mixing 1:10 and 1.5:8.5 limestone and Dangote cement.

## **4.0 TESTS**

### **4.1 COMPRESSIVE STRENGTH**

This test **was** aimed at determining the early and later strength of cement, which is controlled, by  $C_3S$  and  $C_2S$ .

**PROCEDURE:** - 450g of cement with 225g of distilled water. **Then** 1350g of standard sand was added and mixed for 2 minutes, using an automatic mixer. The content was transferred into a greased prism mold and mounted on a jolting machine for 2 minutes. The prism was removed and cured for 24hrs in a curing chamber with temperature of about  $27^{\circ}C$  and humidity of not less than 90%.

The cubes were removed from the curing room and tested on the compressive strength-testing machine. The cubes were crushed and the applied force was taken in kilo Newton. Comprehensive strength was calculated as applied force/area ( $KN/Cm^2$ ) (CCNN, 2003).

### **4.2 SETTING TIME**

This test was carried out to determine the time it will take the cement paste to lose **workability (plasticity)**.

**PROCEDURE:** - 400g of cement sample was taken and mixed with distilled water until consistent cement paste was obtained. The paste was transferred into a greased VICAT mould and then placed under VICAT apparatus. The plunger was released gently to penetrate the cement paste. The procedure was repeated at interval of 5-10 minutes. If the needle stops at 5mm or just above, was the initial setting time. The VICAT needle was replaced final setting time needle, which had a circular mark on the cement paste, was no longer seen but a dot, the time was recorded as final setting time. Initial setting time was the time from which water was added to the time were VICAT needle refuse to penetrate the cement paste to less than 5mm. Final setting time was the time when water was added to the time were no circular mark is seen but a dot (CCNN, 2003).

### 4.3 EXPANSION OR SOUNDNESS TEST

Determination of soundness was aimed at knowing the rate of expansion of cement, which is caused by MgO that was not fused into periclase.

**PROCEDURE:** - 200g of cement was mixed with distilled water and placed into Le-chatelier' apparatus (mould) and then place on a greased glass sheet. A rubber band was used to hold it gently and then cured for 24hrs in a curing chamber. After 24hrs curing, the sample was boiled for 1hr. The distance between the two tails of the apparatus were taken before and after boiling as  $L_1$  and  $L_2$  respectively. Expansion =  $L_2 - L_1$  (mm) (CCNN, 2003).

### 4.4 X-RAY ANALYSIS

X-ray analysis was aimed at determining the chemical composition of the clinker, gypsum and limestone.

**PROCEDURE:** - 19g of cement sample was weighed and mixed with 1g of binder (powder). A tablet (metal ring) was placed on pressing machine. The machine was pressed to about 90-100N and allowed for about 90 seconds. The tablet was removed and slotted into x-ray analyzer and then ran. CaO,  $Al_2O_3$ ,  $SiO_2$ ,  $Fe_2O_3$ , MgO and other components were recorded and printed out by the instrument.

## 5.0 RESULTS AND DISCUSSION

Cubes were prepared in accordance with methods of testing cement EN 196-1 to determine compressive strength. Tests were made with SPC, SLPC and DLPC for determining 1, 2, 7 and 28 days compressive strengths.

The summaries of mean strength test results obtained shown in table 1 shows the result of compressive strength tests on LPC, DLPC and SLPC cement samples.

The result shows that the compressive strength decreases with increasing limestone. Samples with 0% limestone have better compressive strength than 5%, 10% and 15%. The result of this research shows that DLPC has better 1-day strength followed by SLPC and then SPC with least result. DLPC also has better 2 days strength followed by SPC and then SLPC with least result. SPC has better 7 days strength followed by DLPC and then SLPC. SPC has the highest 28 days strength then DLPC and then SLPC with which has

theleast. It shows that SPC has better later strength development. Similar results were obtained by CTL and IDOL group laboratories in USA (Caldorone and Zemajtis, 2008).

TABLE 1 Compressive Strength (Nmm<sup>-2</sup>) For LPC, SLPC And DLPC

	1 DAY			2 DAY			7 DAY			28 DAY		
	SPC	SLPC	DLP C	SPC	SLPC	DLP C	SPC	SLP C	DLP C	SPC	SLP C	DLP C
0	9.7	10.8	11.4	19.7	17.1	20.6	41.2	29.1	35.6	63.3	44.6	47.5
5	8.8	9.7	8.9	19.3	15.6	17.3	40.3	27.7	34.2	56.8	40.2	44.8
10	7.9	8.3	7.4	18.5	14.3	15.1	38.8	26.2	33.4	53.6	39.6	41.5
15	7.4	7.4	5.9	16.5	13.5	13.1	36.9	23.6	30.8	51.2	36.9	38.1

Source: Laboratoty test (2018).

As the test results indicate, compressive strength of all hardened cubes increase with increase of age. The incorporation of fines having a high specific area also improves compressive strengths considerably when compared. This increment of strength is due to the increase of fineness of cement which has direct relationship with the strength development. It can also be observed that the compressive strength of hardened cubes decreases simultaneously with the increase in addition of limestone filler content for same blain fineness. These decreases in strength mainly occur due to replacement of portland cement clinker with limestone addition with different proportion causing dilution of C3S and C2S composition of Portland cement which are responsible for the strength development

These results are considered as normal according to the Standard Organization of Nigeria's standard range of 10 Nmm<sup>-2</sup> minimum for 2 days and 42.5 Nmm<sup>-2</sup> minimum for 28 days (NIS 439, 20000). Therefore addition of limestone from 5%-15% has no significant effect on the early (1,2 and 7 days) and later strength (28 days) of cement.

Below are the charts representing the compressive strength of SPC, SPLC and DLPC for 1, 2,7 and 28 days respectively

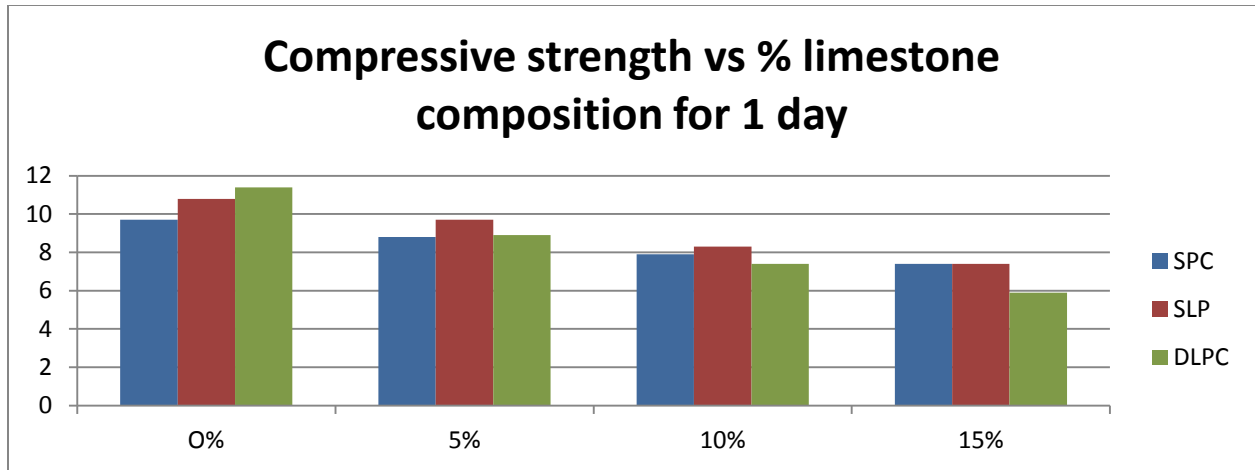


Chart 1

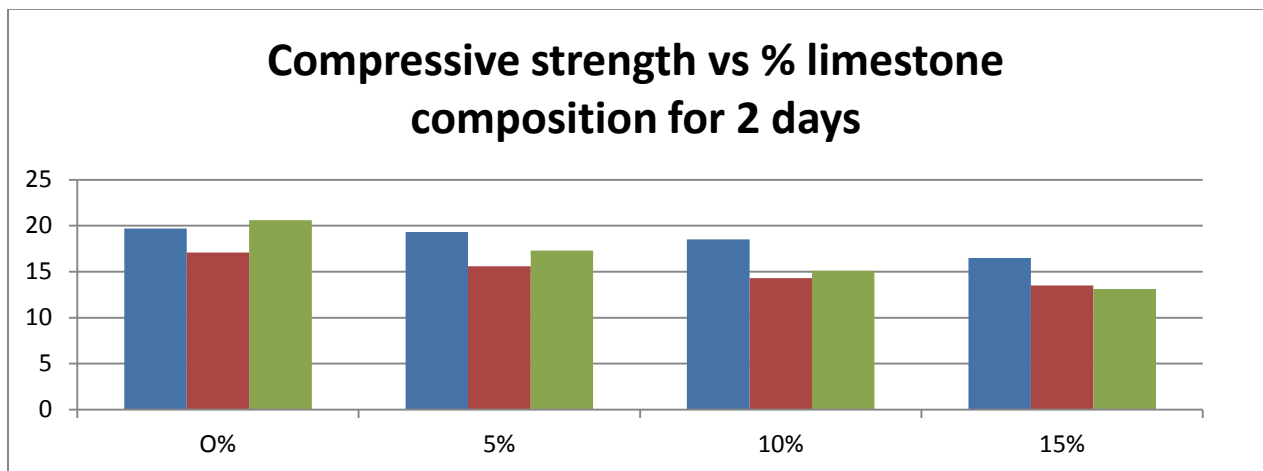


Chart 2

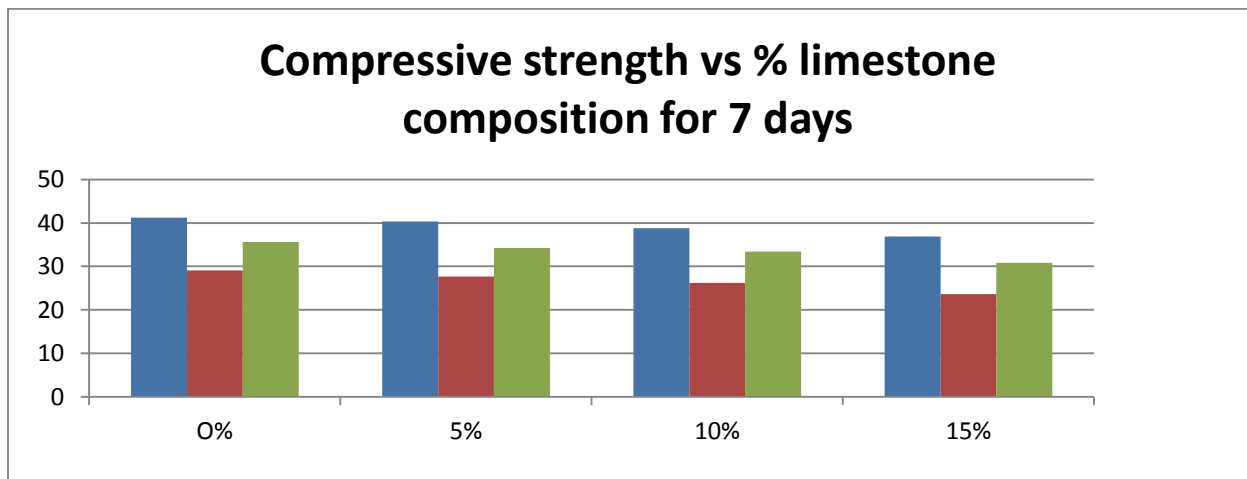


Chart 3



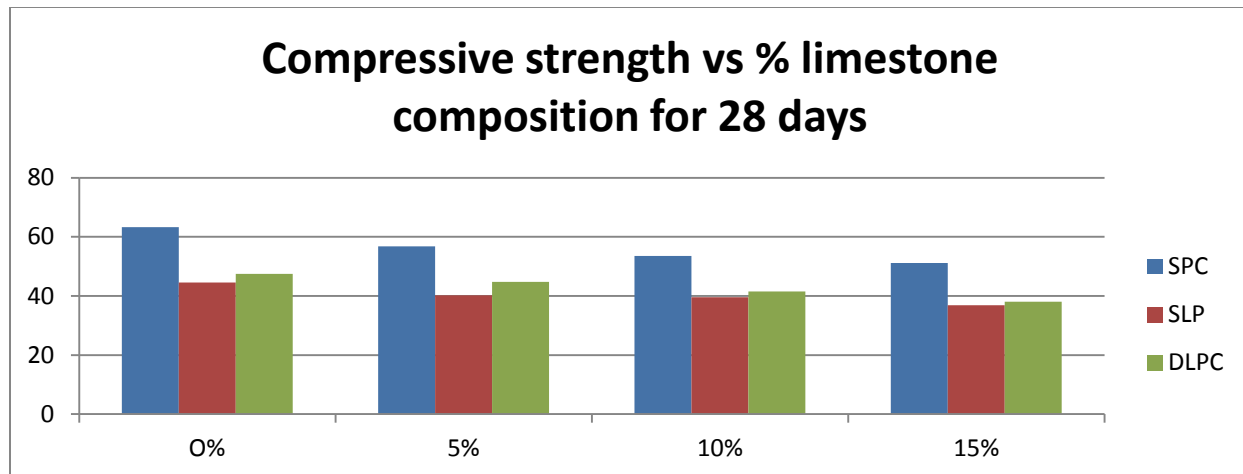


Chart 4

### SETTING TIME

From table 2, the setting times of all the samples decreased with increasing limestone additive. As alite ( $C_3S$ ) and belite ( $C_2S$ ) in the cement hydrate, there is deposition of C-S-H gel with approximate composition of  $3CaO \cdot 2SiO_2 \cdot 3H_2O$ . In the presence of limestone, the spongy mass of C-S-H gel is filled up thus causing faster setting of the cement paste (Birnin-Yauri, 1993).

Table 2 Initial & Final Setting Times (Minutes) for SPC, DLPC AND SLPC

% Limestone	Initial setting time			Final setting time		
	SPC	SLPC	DLPC	SPC	SLPC	DLPC
0	220	179	209	268	270	261
5	205	162	198	255	211	240
10	192	153	190	238	200	237
15	180	144	178	223	185	223

SPC has the highest initial setting followed by DLPC and then SLPC. The test results also indicate that, limestone addition into Portland cement decreases the initial and final setting times considerably due to dilution of  $C_3S$  and  $C_3A$  content in the cement. The result of this work shows that addition of limestone from 5%-15% has no significant effect because it falls within the standard range set by Standard Organization of Nigeria of 60 min minimum for initial setting time and 600 min maximum for final setting time (NIS 439, 2000).

Also the EN 197-1:2000 limits the initial setting times for Portland cement not to be less than 45 minutes. Ethiopian standards also specifies initial and final setting time for Portland cement (ES C.D5.202, Section 4.2.4) to be 45 minutes and 600 minutes, respectively. Comparing the obtained test results of investigation indicated in the above table, all limestone added cement produced satisfy

the requirements specified by standard organization of Nigeria, European and Ethiopian standards. Similar results were obtained by Wendimu and Abebe in 2010.

## SOUNDNESS TEST

Le-Chatlier's apparatus was used to conduct soundness test. No remarkable effects are observed on the soundness for replacement of cement clinker up to 15% by limestone additives.

The soundness test values in Table 3 shows that increase in limestone addition from 5%-15% has no effect in all the samples tested. However, SLPC and SPC have the sample expansion of 0.5 mm while DLPC has 1mm.

The results fall within the standard range of 10mm maximum as set by standard Organization of Nigeria (NIS 439, 2000).

**TABLE 3 Soundness (mm) for SPC, DLPC and SLPC**

Sample	%Limestone			
	0%	5%	10%	15%
SPC	0.5	0.5	0.5	0.5
DLPC	1	1	1	1
SLPC	0.5	0.5	0.5	0.5

This negligible soundness effect can be attributed to less content of MgO and free CaO in the raw materials, fineness of the cement, good chemical and mineralogical composition of the clinker and good burning temperature in a kiln which favor a decrease of free periclase to occur (Wendimu, 2009).

## XRF STUDIES

From Table 4, the result of the XRF, Calcium Oxide (CaO) has the highest percentage in all cement types tested. SPC had the highest percentage of CaO, followed by DLPC at 0-10% limestone addition. The second most abundant oxide in all cement types is Silicon oxide (SiO<sub>2</sub>), which decreases with increasing limestone additive, and was more pronounced in SLPC followed by DLPC and then SPC.

% Limestone	0%			5%			10%			15%		
Oxides	LPC	SLP C	DLP C	LPC	SLP C	DLP C	LPC	SLP C	DLP C	LPC	SLP C	DLP C

CaO	66.8 0	59.2 2	59.9 0	61.1 0	59.1 6	59.7 9	61.6 0	59.0 3	59.5 7	61.9 0	58.9 2	59.3 4
MgO	1.21	2.06	2.01	1.12	1.44	1.58	0.98	1.23	1.41	0.85	1.05	1.17
Fe <sub>2</sub> O <sub>3</sub>	2.82	4.33	5.87	2.80	4.18	5.63	2.79	4.03	5.29	2.75	3.92	5.07
Al <sub>2</sub> O <sub>3</sub>	3.78	4.53	3.65	3.66	4.37	3.49	3.56	4.20	3.21	3.40	3.99	3.03
SiO <sub>2</sub>	17.7 3	18.7 6	17.9 5	17.0 8	18.0 6	17.7 6	16.7 6	18.0 0	17.3 8	16.2 5	17.8 7	17.1 2

**TABLE 4: The order of percent composition of the other oxides in the cement types are: Fe<sub>2</sub>O<sub>3</sub> > Al<sub>2</sub>O<sub>3</sub> > MgO**

## 6.0 CONCLUSION

The quantity of limestone additive (5-10%) did not appear to have any significant reduction on most of the physicochemical properties of cement. The result of this study revealed the increase in CaO concentration with addition of limestone in the entire samples studied. Compressive strength decreased with increase in limestone content. Setting time had not been reduced below the ASTM and Standard Organization of Nigeria minimum value (NIS 439, 2000). Addition of limestone does not show any sign of weakness on the cement final structure (Tsviliset al/ 1999). But, mechanical properties and resistance to penetration of aggressive agents decreased as reported by Federica et al (2013).

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