

EFFECT OF LIMESTONE ADDITION ON PHYSICOCHEMICAL PROPERTIES OF CEMENT: A CASE STUDY OF SOKOTO AND DANGOTE PORTLAND CEMENTS

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 *reveals* 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 *has* appreciable strength, which also decreases with addition of limestone for all the samples. Soundness test *reveals* that addition of limestone within 5-15% *will* not cause any expansion and weakening of the cement structure. The setting times for all cement types *decreased* with increasing limestone addition.

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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 18th 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 (Tsivilis *et al.*, 2002; Voglis *et 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; Bonavetti and Rahhal, 2001) and the modification of the microstructure (Kakali *et 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 CO₂ and NO₂ 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).

In 2004 the ASTM C150 standard specification for Portland cement was modified to allow the incorporation of up to a 5% **by** mass fraction of limestone in ordinary Portland cements (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 C₃S hydration rate is accelerated when the amount and fineness of limestone filler (CaCO₃) 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 (Kakali *et al.*, 2000).

The raw materials for production of such cement type is sufficiently available, requires lesser energy for production, and has less CO₂ and NO₂ emissions, It is also economical (McGrath, 2008).

It was reported that for **high** 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; Kakali *et al.*, 2000). Nehdi *et al.* (1996) showed that at 3-day tests, the compressive strength **is** 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 **contained** up to 15% limestone and for later

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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 is used with blast furnace slag, the strength increasing effect of blended limestone cement is more pronounced compared to the Ordinary Portland Cement (OPC).

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

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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 is much influenced by the degree of fineness of additions which is 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 cm²/g) influenced the time of setting so the amount of water used increased to obtain a cement with normal consistency (Mohammad and South, 2016).

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Both initial and final setting times of Portland limestone cement pastes were decreased with an increasing of 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).

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This study is thus attempting to make use of raw limestone additive in the production of ordinary Portland limestone cement. An experimental investigation is carried out to examine the impacts of

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adding raw limestone powder on the physical and chemical properties of the cement such as expansion, setting time, and compressive strength.

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2.0 MATERIALS AND METHODS

2.1 SYNTHESIZED PORTLAND CEMENT (SPC)

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

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

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

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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.

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

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

2.2 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.

2.3 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.

3.0 TESTS

3.1 COMPRESSIVE STRENGTH

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

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PROCEDURE: - 450g of cement was weighed and mixed 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 90% humidity.

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The cubes were removed from the curing room and tested on the compressive strength-testing machine. The cubes were crushed and the applied force of crushing was recorded. The compressive strength was calculated as applied force/area (kN/mm^2) (CCNN, 2003).

3.2 SETTING TIME

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

PROCEDURE: - 400g of cement sample was taken and mixed with distilled water until consistent cement past is obtained. The past 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 is repeated at interval of 5-10 minutes. If the needle stops at 5mm or just above, is the initial setting time. The VICAT needle is replaced final setting time needle, which has 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 is 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 is the time when water was added to the time were no circular mark is seen but a dot (CCNN, 2003).

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3.3 EXPANSION OR SOUNDNESS TEST

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

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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).

3.4 X-RAY ANALYSIS

X-ray analysis is 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. Percentage content of CaO, Al_2O_3 , SiO_2 , SiO_3 , Fe_2O_3 , MgO and other components were recorded and printed out by the instrument.

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4.0 RESULTS AND DISCUSSION

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 LPC with least result. DLPC also has better 2 days strength followed by LPC and then SLPC with least result. LPC has better 7 days strength followed by DLPC and then SLPC. LPC has the highest 28 days strength then DLPC and then SLPC with which has the least. It shows that LPC 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^{-2}) For LPC, SLPC And DLPC

Time (day)	1			2			7			28		
CaCO ₃	LP C	SLP	DLP C	LPC	SLP	DLP C	LP C	SLP	DLP C	LP C	SLP	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	7.40	5.9	16.5	13.5	13.1	36.9	23.6	30.8	51.2	36.9	38.1

Divide Table 1 into 3 (Tables 1, 2 and 3 for 1 day, 2 days and 3 days respectively). Draw them as bar charts with % limestone on x-axis and compressive strength on y-axis.

These results are considered as normal according to the Standard Organization of Nigeria's standard range of 10 Nmm⁻² minimum for 2 days and 42.5 Nmm⁻² minimum for 28 days. (ref ?) Therefore addition of limestone from 5%-15% has no significant effect on the early and later strength of cement, since no appreciable changes in the compressive strength were observed.

SETTING TIME

From Table 2, the result of this research work shows that the setting times of all the samples decreased with increasing limestone. The setting time of cement is controlled by amount of gypsum in the cement and increase in limestone decreases the amount of gypsum in the cement there by decreasing the setting time. As alite (C₃S) and belite (C₂S) in the cement hydrate, there is deposition of C-S-H gel with approximate composition of 3CaO.2SiO₂.3H₂O. 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).

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Table 2 Setting Times (minutes)

% Limestone	Initial setting time			Final setting time		
	LPC	SLPC	DLPC	LPC	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 result of this work shows that addition of limestone from 5%-10% has no significant effect because it falls within the standard range set by Standard Organization of Nigeria of 60 minutes minimum for initial setting time and 600 minutes maximum for final setting time (Ref ?).

SOUNDNESS TEST

The soundness test values in Table 3 show that increase in limestone addition from 5%-10% 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 10 mm maximum as set by standard Organization of Nigeria (Ref ?).

TABLE 3 Soundness (mm)

% limestone	SPC	DLPC	SLPC
0	0.50	1.00	050
5	0.50	1.00	0.50
10	0.50	1.00	0.50
15	0.50	1.00	0.50

XRF STUDIES

From Table 4, the result of the XRF, Calcium Oxide (CaO) has the highest percentage in all cement types tested. LPC 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 (SiO₂), which decreases with increasing limestone additive, and is more pronounced in SLPC followed by DLPC and then LPC.

% Limestone	0%			5%			10%			15%		
	LPC	SLP C	DLP C	LPC	SLP C	DLP C	LPC	SLP C	DLP C	LPC	SLP C	DLP C
CaO	66.80	59.22	59.90	61.10	59.16	59.79	61.60	59.03	59.57	61.90	58.92	59.34
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 ₂ O ₃	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 ₂ O ₃	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 ₂	17.73	18.76	17.95	17.08	18.06	17.76	16.76	18.00	17.38	16.25	17.87	17.12

Table 4 doesn't seem to be correct. For instance, why does the %CaO remain almost constant despite the increase in limestone? The limestone may not be chemically pure CaCO₃ as such it might contain silica, iron oxide and magnesia (clay). Personally I think Table 4 is incorrect and not necessary. Deleting doesn't affect the results.

**TABLE 4: The order of percent composition of the other oxides in the cement types are:
 $\text{Fe}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{MgO}$**

5.0 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 (of ?). Addition of limestone **does** not show any sign of weakness on the cement final structure (Tsvivilis *et al* 1999).

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