

Production of an Eco-Cement by Clinker Substitution by the Mixture of Calcined Clay and Limestone, Songololo (DR Congo)

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Abstract

Ordinary Portland Cement (OPC) is by mass the largest manufactured product on Earth, responsible for approximately 6% - 8% of global anthropogenic carbon dioxide emissions (CO₂) and 35% of industrial CO₂ emissions. On average 0.8 to 0.9 ton of CO₂ is emitted to produce one ton of OPC. In this paper, partial substitution of clinker (30% - 35%) by the calcined clay-limestone mixture was investigated in order to produce an eco-cement (LC3). Analyzes by XRF, XRD and ATG/ATD have characterized different components, determined the calcination temperature and selected the right clay which can act as effective Supplementary Cementitious Material (SCM). Mechanical tests on mortar carried out over a period of 90 days. The WBCSD/WRI "Greenhouse Gas Protocol" methodology then allowed the calculation of CO₂ emissions into the atmosphere. Three types of clay are available in the Songololo Region. The kaolinite is the principal clay mineral and its content varies from 27% to 34%. The sum of kaolinite and amorphous phase which enable clay to react with cementitious material ranges from 57% to 60%. The SiO₂ content ranges from 33% to 76%, the Alumina content from 12% to 20% so that the ratio Al₂O₃/SiO₂ is on the higher side (0.17 - 0.53). The calcination window is between 750°C and 850°C and the best clay which can act as SCM identified. The clinker's substitution reduced CO₂ emissions from 0.824 ton of CO₂ for one ton of OPC to 0.640 ton of CO₂ for one ton of LC3, means 22% less emissions. The compressive strengths developed by LC3 vary from 8.91 to 57.6 MPa (Day 1 to Day 90), exceed those of references 32.5 cement and are close to 42.5 cement. In view of the results, LC3 cement can be considered for industrial trials.

Keywords

Clay, Calcined Clay, Limestone, Cement, Eco-Cement, Songololo

1. Introduction

Concrete is the most widely used and produced building material in the world. For its implementation, it requires huge quantities of cement, about 4200 Mt per year and this production continues to increase (Cembureau, 2017; Scrivener et al., 2016).

Ordinary Portland Cement (OPC) is the most widely cement type used to make concrete for housing and infrastructure's development worldwide (Cembureau, 2017; Scrivener et al., 2016). Excellent material, cheap, available and easy to use, but it is responsible for significant carbon dioxide (CO₂) emissions (5% to 8% of global anthropogenic emissions and around 35% of industrial emissions). On average, 0.8 to 0.9 ton of CO₂ is emitted for the production of one ton of Ordinary Portland Cement (OPC) (Cancio Díaz, 2017; IEA, WBCSD, 2009).

Anthropogenic emissions of CO₂ to the atmosphere come from three main sources: 1) the oxidation of fossil fuels, 2) deforestation and other land-use changes, and 3) the decomposition of carbonates in the cement and lime industry (Cancio Díaz, 2017; IEA, WBCSD, 2009).

Two aspects of cement production result in CO₂ emissions. The first is decarbonation, a chemical reaction that breaks down calcite (CaCO₃), the main component of limestone, into lime (CaO) and CO₂ by adding heat to produce the main component of cement, clinker. Stoichiometry directly indicates the amount of CO₂ released for a given amount of CaO produced. The second aspect is the massive use of fossil fuels and energy for the calcination of raw material (limestone and clay) in the rotary kiln (Gartner, 2004; IEA, WBCSD, 2009).

To reduce these environmental impacts, several solutions have been proposed including (Scrivener et al., 2016; Gartner, 2004; IEA, WBCSD, 2009):

- 1) Modernize the cement manufacturing process by investing in modern equipment;
- 2) Use alternative fuels to heat the rotary kiln;
- 3) Produce a clinker containing less calcite;
- 4) Develop CO₂ enrichment or capture processes;
- 5) Substitute clinker with already decarbonated industrial by-products or with other natural or heat-treated rocks.

The first four techniques require huge investments in terms of capital (Capex) and operational (Opex) and sometimes make the business less viable. The most promising option is the partial substitution of the clinker by Supplementary Cementitious Materials (SCM) (Antoni et al., 2012; Baudet et al., 2013).

Nowadays, more than 80% of the SCMs used to reduce the clinker factor in

cement are either, fly ash, blast furnace slag and silica fume, but the limited supply of these industrial by-product SCM makes it difficult to pursue this strategy. The only material available in quantity and quality capable of meeting the growing demand of the cement is clay containing kaolinite which can be calcined to produce metakaolin, an effective SCM (Scrivener et al., 2016; Cancio Díaz, 2017; Antoni et al., 2012; Marangu, 2020; Reddy & Reddy, 2021; Duchesne & Bérubé, 1994).

Fifteen years ago, a new type of ternary cement has been developed by a group of researchers from EPFL Lausanne, named Limestone Calcined Clay Cement (LC3) and composed of clinker (up to 50%), calcined clay, limestone and gypsum. The mixture of calcined clay and limestone allows higher levels of clinker substitution with production of a cement with mechanical properties similar to OPC with improvement in certain aspects of durability (Scrivener et al., 2018; Scrivener & Favier, 2015; Antoni et al., 2012).

Songololo area in DR Congo (as shown in **Figure 1**) has large and abundant clay deposit which has not yet found a large-scale industrial valorization. A small part is used in the manufacture of fired bricks for construction by villagers (roads and houses) and another part by cement manufacturers. Most of these clays are discarded and disposed of in vast landfill, thus modifying the landscape and biodiversity.

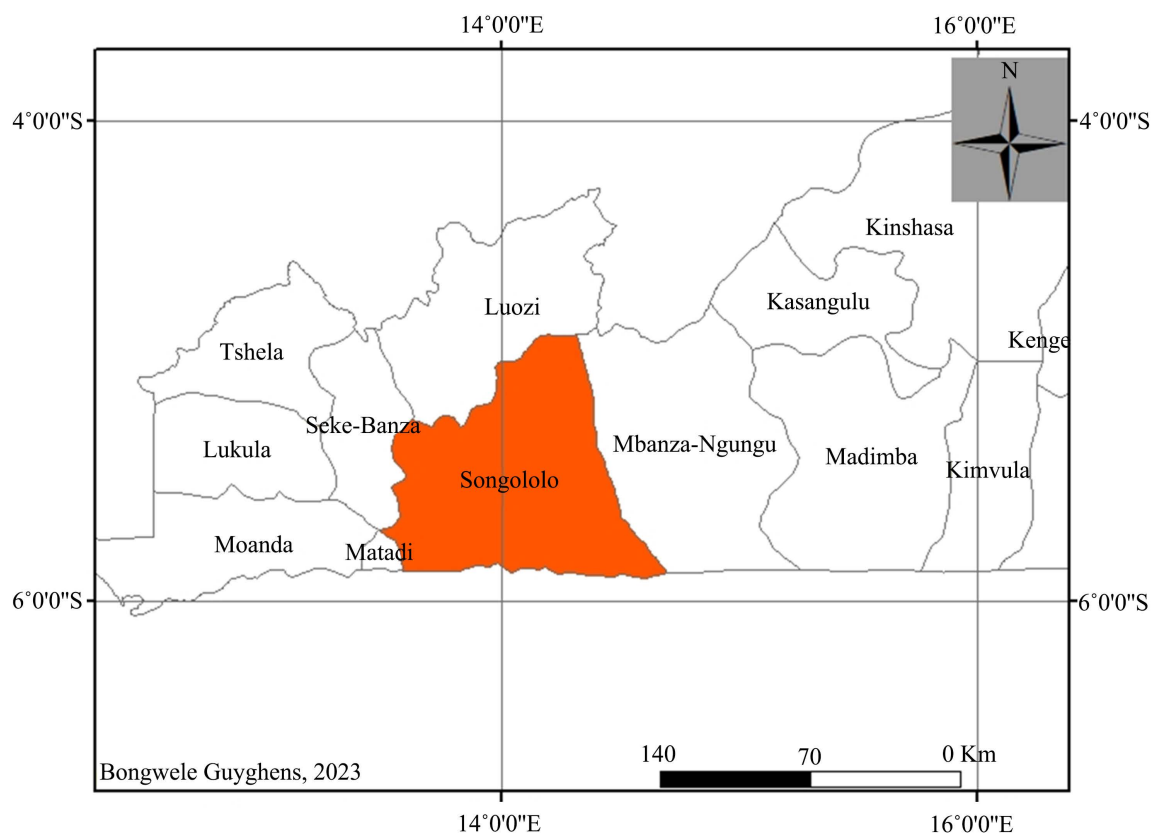


Figure 1. Kongo central province (DR Congo) showing the study location.

The Songololo rocks are aged Neoproterozoic and belong to the West-Congo Super Group, Cataractes Group (former West-Congolian) and are characterized by thick and abundant clays of ca35m on average overlapping the carbonates rocks of the Lukala Subgroup (Baudet et al., 2013).

Thus in this paper the possibility of reducing the CO₂ emissions of the cement industry by partially replacing the clinker by the mixture of limestone-kaolinitic clay of Songololo area was investigated.

2. Materials and Methods

The raw materials required to produce LC3 cement are clinker, limestone, kaolinitic clay and gypsum (Scrivener et al., 2016; Antoni et al., 2012; Duchesne & Bérubé, 1994). **Table 1** gives the proportion of each component in the formulation of the different cements. Different rocks come from the Songololo region, except for the gypsum which is imported from Angola and the clinker from the Nyumba ya akiba SA cement factory (CIMKO) in the DR Congo. These different materials are analyzed in order to select those of better quality and to establish their proportion in the formulation of LC3 cement. **Table 1** gives the proportion and **Table 2** gives the chemical composition of the different components for the mortar formulation.

2.1. X-Ray Diffractometer (XRD)

Macroscopically, three types of clays are present in the Songololo region; we gave them the codes YC, RC and LC, and they were analyzed for their mineralogical composition. The Philips PW1050 diffractometer was used for powder analysis and the Rietveld method for the calculation of mineral and amorphous phases. The operating conditions of the diffractometer are given in Frimmel (2009).

2.2. X-Ray Fluorescence Spectrometry (XRF)

The different components to prepare LC3 (clay, calcined clay, limestone, gypsum and clinker) were analyzed for their major oxide content using a Thermo Scientific X-ray fluorescence spectrometer, ARL 9900 IntelloPower series. The analysis procedure is given in (Gobbo, 2009).

Table 1. Formulation of different cements.

Cement Type	Clinker (%)	Calcined clay (%)	Limestone (%)	Gypsum (%)
CIMENT 32.5	65	0	32	3
CIMENT 42.5	84	0	13	3
LC3-60	60	20	10	5
LC3-65	65	18	13	4

Total Clinker replacement: 40% (LC3-60) and 35% (LC3-65); mass ratio between calcined clay and limestone 2:1 and 2:1.5; water/cement ratio: 0.5 for mortar study.

2.3. Thermo-Gravimetric Analysis (TGA) and Thermo-Differential Analysis (DTA)

The thermal behavior of YC clay was studied from room temperature to 1200°C using a mixed ATG-ATD device heated at a rate of 20°C/min under a dynamic N₂ atmosphere (100 cm³/min) for 15 min. This technique (thermal analysis) consists of measuring the mass variation of a sample as a function of time for a given temperature or temperature profile. Such an analysis assumes good precision for the three measurements: mass, time and temperature.

The Slope Ratio (SR) index is calculated as the ratio between the slope of the descending branch of the kaolinite dehydroxylation peak in the DTA curve (350°C - 700°C) and the slope of the ascending branch of the same peak. The DTA technique is suitable for determining the calcination temperature for complete dehydroxylation of kaolinite.

2.4. CO₂ Emissions Calculations

The World Business Council for Sustainable Development (WBCSD) methodology was used for the calculation of CO₂ emissions (IEA, WBCSD, 2009).

2.5. Compressive Strength of Mortar

The mortars were prepared according to standard EN 196-1 (British Standards EN 196-1, 2005) and the compressive strength (R_c) measured for the period ranging from 1 to 90 days.

2.6. Strength Activity Index (SAI)

Cimko 32.5 and 42.5 cements were taken as reference and the compressive strengths of LC3 cement are compared to the one developed by the reference cements during days 1, 2, 7, 28 and 90.

3. Results and Discussion

3.1. Chemical Composition

Different clays of Songololo Region were sampled and analyzed for their major oxide content. Unlike siliceous clays (SiO₂) commonly used in the cement industry for the manufacture of OPC, clays required for LC3 cement manufacture must on the other hand be rich in alumina (Al₂O₃). The chemical criteria for using clay in LC3 cement system are given in (Scrivener et al., 2018; Scrivener & Favier, 2015; Antoni et al., 2012). **Table 3** shows the results of the different oxides and the loss on ignition (LOI) of the different clays.

YC clay has good chemical properties (high Al₂O₃ and LOI content). The ratio Al₂O₃/SiO₂ is high (0.17 - 0.53), and the Fe₂O₃ content is high (5.04 - 37.08). The calcination product is red due to the oxidizing condition of the calcination but color optimization is also possible by calcining the clay under the reducing condition. This clay has a high calcination potential.

RC clay shows low chemical properties (low Al_2O_3 and LOI content). The ratio $\text{Al}_2\text{O}_3/\text{SiO}_2$ is low due to the high quartz content. The clay mineral content is only 27% and there is no amorphous phase. This clay has a low calcination potential.

LC clay has intermediate chemical properties. The ratio $\text{Al}_2\text{O}_3/\text{SiO}_2$ is good with, however, a low content of clay minerals and amorphous phase (approximately 50%). The iron content, on the other hand, is very high. The potential for color optimization should be investigated. This clay has a moderate calcination potential.

According to the criteria of (Scrivener et al., 2018; Scrivener & Favier, 2015; Antoni et al., 2012) and in view of these results, YC clay is chemically good for the manufacture of LC3 cement.

Table 2. Chemical composition (%) of limestone, gypsum, clinker, calcined clay and standard sand.

Components	Oxides								Total
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	
Limestone	0.88	0.13	0.08	54.32	1.29	0.06	0	0.01	56.77
Gypsum	1.61	0.4	0.25	31.49	0.51	40.9	0.15	0.03	75.34
Clinker	21.24	5.22	3.72	65.12	2.41	0.73	0.43	0.9	99.77
Calcined clay	57.19	22.82	8.48	0.14	1.38	0.02	3.42	0.36	93.81
Standard sand	99.41	0	0.28	0.31	0	0	0.004	0	100

Table 3. Chemical composition of clays.

Element (%)	Clay samples					
	YC 1	YC2	RC1	RC2	LC1	LC2
LOI	7.32	7.4	5.17	5.01	10.38	10.4
SiO ₂	57.38	57.5	75.03	76.2	33.91	33.95
Al ₂ O ₃	20.36	20.1	12.6	12.8	17.07	18.01
TiO ₂	1.11	1.1	0.68	0.54	0.77	0.76
Fe ₂ O ₃	9.1	9.8	5.98	5.04	37.08	36.09
Mn ₂ O ₃	0.16	0.17	0.04	0.05	0.06	0.05
CaO	0.13	0.15	0.01	0.01	0.11	0.12
MgO	1.07	1.05	0.21	0.19	0.21	0.2
P ₂ O ₅	0.32	0.4	0.14	0.15	0.31	0.35
Total	96.95	97.67	99.86	99.99	99.9	99.93
Al ₂ O ₃ /SiO ₂	0.35	0.35	0.17	0.17	0.50	0.53

3.2. Mineralogical Composition

The mineralogical composition of the different clays is summarized in **Table 4**. Kaolinite is the main clay mineral for all clays and its content ranges from 26.2% in RC clay to 37.5% in YC clay. This is less than 40%, the lower limit for the use of clays in the manufacture of LC3 cement according to (Scrivener et al., 2018; Scrivener & Favier, 2015; Antoni et al., 2012).

Quartz and muscovite are impurities in all clays and illite is only present in YC clay. Kaolinite and illite association in YC clay can be benefit for hydration process of calcined YC clay and strength development of the mortar prepare using the blend with YC clay.

Nevertheless, the sum of kaolinite and amorphous phase which enable clay to react with cementitious material ranges from 57% to 60% and is within acceptable range for calcination tests in the context of partial substitution of clinker in the cementitious system.

3.3. TGA and DTA

TGA and DTA are proven techniques for determining the kaolinite content, calcination temperature and pozzolanic activity of the calcined clays. Only YC clay was analyzed. The TG curve shows that this clay loses 1.8% of its mass between 25°C and 100°C corresponding to the loss of moisture and adsorbed water, and 8.4% of its mass between 450°C and 750°C related to the elimination of OH⁻ ions and the rearrangement of aluminum ions in its crystal structure (Frost et al., 2010; Gasparini et al., 2013). Beyond 750°C the mass of the clay remains stable. On the other hand, the DTA curve shows two significant peaks, one at 514°C corresponding to an endothermic reaction linked to dehydroxylation and the other at 985°C corresponding to an exothermic reaction linked to the crystallization of mullite (mullitization) (Aparicio & Galan, 1999; Bergaya, Theng, & Lagaly, 2006). Thus between 750°C and 985°C, the clay is in an amorphous state which corresponds to complete dehydroxylation with the formation of metakaolin.

Table 4. Mineralogical composition of the clays.

Phase (%)	Formule	Clay samples					
		YC1	YC2	RC1	RC2	LC1	LC2
Quartz	SiO ₂	30.7	30.1	68	67.3	20.4	20.1
Muscovite	KAl ₂ AlSi ₃ O ₈ (OH) ₂	3.0	2.9	2	2.3	3.1	3.0
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	36.4	37.5	25.4	26.2	31.6	30.5
Illite	(K·H ₂ O)(Al·Mg·Fe) ₂ (Si·Al) ₄ O ₁₀ [(OH) ₂ ·(H ₂ O)]	15.6	15.3	-	-	-	-
Goethite	FeOOH	4.3	4.2	3.3	4.2	27.8	28.7
Hematite	Fe ₂ O ₃	0.4	0.3	-	-	3.2	3.1
Amorphes		9.6	9.7	-	-	13.9	14.6
Total		100	100	98.7	100	100	100

The SR index characterizes the presence of defects in the crystalline structure:

For $SR = 1$, the peak is symmetrical, and the kaolinite does not have many defects, when the SR index is greater than 2, the peak is asymmetrical and the mineral has many defects in its structure (disordered structures), for therefore it can easily interact with the components of the clinker to form cementitious materials: this is the pozzolanic effect.

The SR index of YC clay is 2.2 (Table 5) and the peak is asymmetrical (Figure 2). This clay thus has pozzolanic properties and was selected for partial clinker substitution in LC3 formulations. Table 6 gives the chemical composition of the different formulations of LC3 cement compared to the reference (32.5 and 42.5 cements).

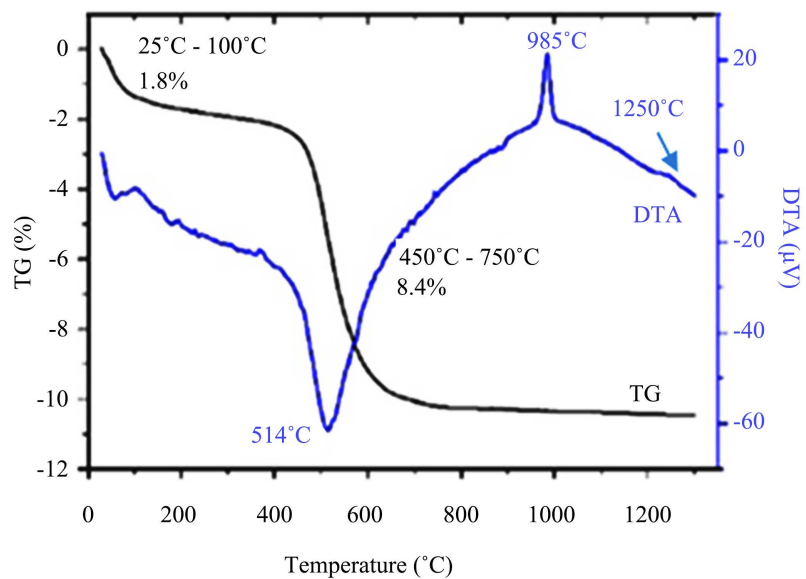


Figure 2. Thermogravimetric analysis (TG) and Differential thermal analysis (DTA) of YC clay.

Table 5. Slope Rate (SR) Index of YC clay.

Technique	SR Index	RANGE	~1	>2
DTA	2.2	Crystal structure	Order	Disorder

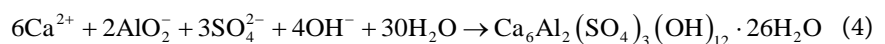
Table 6. Chemical composition of different cements (%).

Type of Cement	Oxydes (%)									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	PF	Free lime
CIMENT 32.5	15.46	3.62	2.9	65.43	1.67	0.5	0.15	1.81	13.53	2.70
CIMENT 42.5	18.67	4.42	3.43	63.68	1.80	0.6	0.19	2.18	4.29	3.56
LC3-60	23.72	7.64	4.96	50.48	1.70	0.93	0.13	2.38	8.50	2.18
LC3-65	22.61	6.91	4.57	53.32	1.73	0.83	0.13	2.56	8.65	2.17

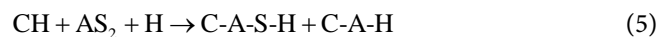
3.4. Physical Test of Cements

3.4.1. Hydration Products of LC3 Cement

The performance of a cement depends on the interaction of the different mineral phases that form during hydration. The hydration of OPC has been studied by several authors (Scrivener & Favier, 2015; Scrivener, 1984) and it depends on the the hydration of the main phases of the clinker, namely: C₃S, C₂S, C₃A and C₄AF. The main mineral phases that develop during the OPC hydration, in the presence of sulphates, are silicates and aluminates. The silicates come from the hydration of the C₃S and C₂S phases while the aluminates derive from the C₃A and C₄AF phases. The silicate phases are: 1) CSH and 2) portlandite (CH) while the aluminates are: 1) calcium trisulfoaluminate or primary ettringite (grouped under the term AFt phases) and 2) calcium monosulfoaluminate (grouped under the term Afm phases). Equations (1) - (4) show the different hydration products of Portland cement in the presence of sulphates. Besides these main phases, there are minor phases that influence the performance of cement.



Clinker can be partially substituted by SCM (AS) and allow the development of new mineral phases. Thus, the pozzolanic reaction can be written (Equation (5)) (Bich, 2005; Scrivener, 1984; Tironi et al., 2014):



In the case of LC3 cement, the presence of calcined clay (AS₂) and calcite (Cc) modifies the hydration dynamics, in addition to silicates and aluminates, hydrated calcium carbo-aluminates are formed (Scrivener et al., 2018; Scrivener & Favier, 2015; Scrivener, 1984; Antoni et al., 2012). The reaction can be written (Equation (6)):



These calcium carbo-aluminates are important in the development of cement performance because they prevent the transformation of calcium trisulfoaluminate into calcium monosulfoaluminate thus preventing the development of secondary ettringite. This improves the permeability of the concrete by preventing the reaction between the alkalis of the concrete and the reactive phases of the aggregates (ASR phenomenon), thus giving an advantage to LC3 cement for the development of infrastructures in hostile environments (sulphate and chloride attacks and high humidity) compared to OPC (Scrivener, 1984).

3.4.2. Performance of Different Cements

Table 7 shows the physical properties of different cements. LC3 cement has a normal consistency slightly higher than OPC cement, due to the high proportion

Table 7. Physical properties of the cements.

Type of cement	Normal consistency (%)	Initial setting time (Min)	Final setting time (min)	Residu (%)		Fineness Blaine (cm ² /g)	Soundness (mm)
				45μ	90μ		
32.5 CEMENT	28.5	150	230	7.4	0.1	3606	1.05
42.5 CEMENT	29	140	240	6.4	0.1	3224	1.1
LC3-60	33	190	225	14.4	0.1	6400	1.33
LC3-65	33	190	223	14.2	0.1	6430	1.35

of clay and this also impacts the setting times (initial and final). On the other hand, the Blaine fineness is far better than the OPC. The soundness of LC3 cement is between 1.33 and 1.35 and is within cement industry standards. All the values of the physical parameters are in accordance with the norms (British Standards EN 196-3:2005 + A1, 2008; British Standards EN 196-6, 2010; British Standards EN 197-1, 2000).

3.4.3. Compressive Strength (Rc)

The LC3 cement develops the Rc slightly lower than of the OPC on the first and second day. This is due to the slow hydration of LC3 cement at early age and this low reactivity can be corrected by the use of admixtures. From the day 7 (seven), the developed Rc is higher than of the OPC and this for the entire duration of the study. These resistances comply with the standard (British Standards EN 197-1, 2000). **Figure 3** highlights the strengths developed by different formulations of LC3 cement compare to the reference cement (32.5 and 42.5).

The strengths of the LC3 cement are compared to the strengths of the reference cement then the strength Activity index (SAI) is calculated (**Table 8** and **Table 9**; **Figure 4** and **Figure 5**). Compared to the reference, LC3 cement develops higher strengths compare to 32.5 cement and the strengths very close to 42.5 cement.

3.4.4. CO₂ Emissions

The parameters of the NYA Cement plant were taken as reference for the calculation of CO₂ emissions into the atmosphere. The quantities of CO₂ emitted are calculated taking into account: 1) the clinker emission factor; 2) the fuel emission factor (oil and coal) and 3) the residue from the rotary kiln (CKD). Thus, **Table 10** presents the parameters taken into account for the calculation of CO₂ emissions and **Figure 6** shows the quantities of CO₂ emitted into the atmosphere per ton of product.

CO₂ emissions into the atmosphere range from 0.850 ton CO₂ for one ton of clinker to 0.640 ton CO₂ for one ton of LC3 cement (**Figure 6**). This means that almost 210,000 ton of CO₂ can be reduced annually for 1,000,000 tons per annum plant as the case of NYA Cement plant. **Figure 6** illustrates how CO₂ emissions into the atmosphere are reduced from clinker to LC3 cement.

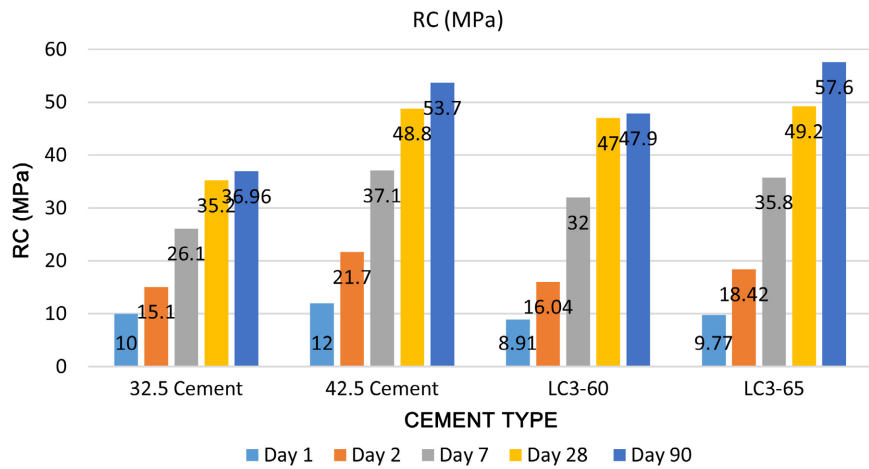


Figure 3. Compressive strength of the different cements.

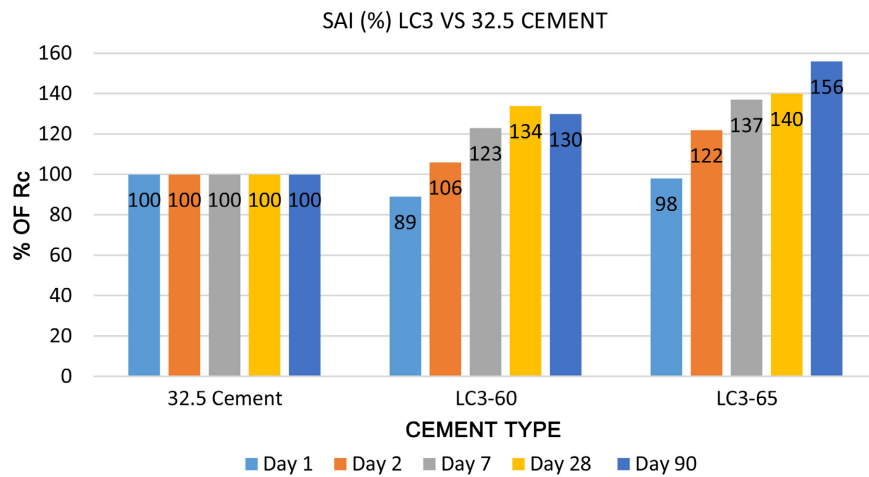


Figure 4. SAI LC3 vs cement 32.5.

Table 8. Strength Activity Index (SAI) LC3 vs cement 32.5.

IDR	Jour 1 (%)	Jour 2 (%)	Jour 7 (%)	Jour 28 (%)	Jour 90 (%)
CIMENT 32.5	100	100	100	100	100
LC3-60	89	106	123	134	130
LC3-65	98	122	137	140	156

Table 9. Strength Activity Index (SAI) LC3 vs Cement 42.5.

SAI	Jour 1 (%)	Jour 2 (%)	Jour 7 (%)	Jour 28 (%)	Jour 90 (%)
42.5 CEMENT	100	100	100	100	100
LC3-60	74	74	86	96	89
LC3-65	81	85	96	101	107

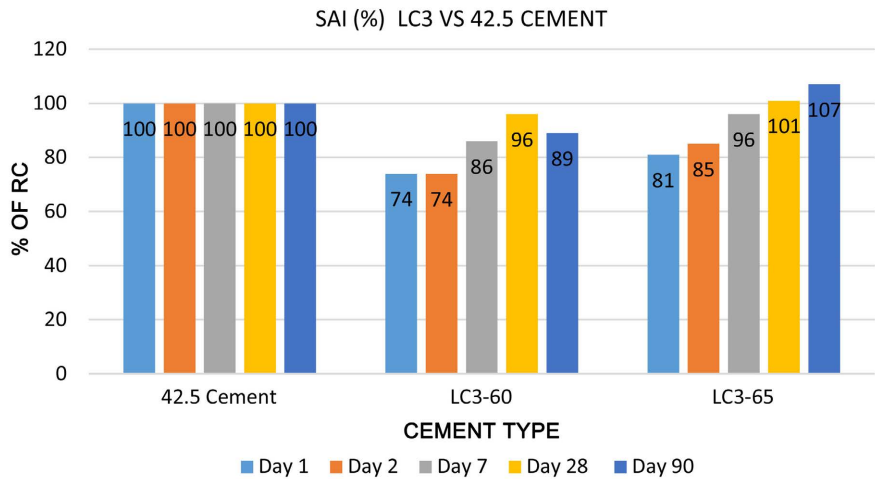


Figure 5. SAI LC3 vs cement 42.5.

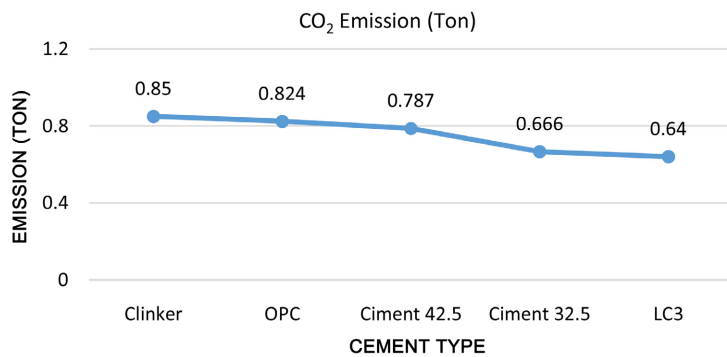


Figure 6. CO₂ emission vs cement products.

Table 10. Base calculation of CO₂ emissions.

Average CaO in clinker (%)	0.669
Ratio CO ₂ /CaO	0.785
Clinker emission factor (ton CO ₂ /ton Clinker)	0.525
Coal CO ₂ emission factor (ton CO ₂ /ton Coal/ton clinker)	0.310
Fuel CO ₂ Emission Factor (ton CO ₂ /ton Fuel/ton clinker)	0.015
CO ₂ from Combustion (Fuel et Coal) (ton CO ₂ /ton clinker)	0.325
CKD Emissions	0
Total CO ₂ Emission (ton CO ₂ /ton clinker)	0.850

4. Conclusion

Among three types of clays studied in the Songololo region, only YC clay deemed fit to the requirements for the production of LC3 cement. The kaolinite is the principal clay mineral and its content varies from 27% to 34%. The sum of kaolinite and amorphous phase which enable clay to react with cementitious material ranges from 57% - 60%. The SiO₂ content range from 33% - 76%, the Alu-

mina content from 12% to 20% so that the ratio $\text{Al}_2\text{O}_3/\text{SiO}_2$ is on the higher side (0.17 - 0.53). The clay calcination window is between 750°C and 850°C and the best clay which can act as SCM was identified. The substitution of clinker by calcined clay-limestone mixture (30% - 35%) has reduced CO_2 emissions by up to 25% compared to OPC, from 0.824 ton of CO_2 for one ton of OPC to 0.640 ton of CO_2 for one ton of LC3.

The compressive strengths (R_c) developed by LC3 vary from 8.91 to 57.6 MPa from Day 1 to Day 90, they are within the standard (**Table 10**), greatly exceed the reference 32.5 Cement and are almost similar to 42.5 Cement marketed in local market. In view of the results, the new LC3 can be considered for industrial trials.

In view of the results, the new manufactured cement (LC3) can be considered for industrial trials.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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