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ABSTRACT

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The thick clay deposits (namely YC, RC, and LC) aged Neoproterozoic of the West-Congolian group and widely spread in the Songololo area (DR Congo), where five cement plants are erected, are examined in this paper to produce the calcined clay (metakaolin) which can be then mixed with limestone to partially substitute to the clinker in the cementitious system and make an eco-cement called Limestone Calcined Clay Cement (LC3).

The initial clay assessment based on chemical composition was carried out using the XRF method, then the phase composition using the XRD method, and finally, the Kaolinite Equivalent (KEQ) parameter to determine the kaolinite content of each clay using a laboratory oven.

Keywords: clay, calcined clay, limestone, lc3 cement, songololo.

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Nowadays, the Cement industry is relying on Supplementary Cementitious Materials (SCMs) to reduce the clinker factor, enabling the reduction of carbon dioxide (CO_2) emission into the atmosphere, but this will be a safer solution only if it's using available and abundant material as SCMs. The discovery of alternatives to conventional SCMs is a big challenge for sustainability.

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The initial clay assessment based on chemical composition was carried out using the XRF method, then the phase composition using the XRD method, and finally, the Kaolinite Equivalent (KEQ) parameter to determine the kaolinite content of each clay using a laboratory oven.

The composite cement (LC3) was prepared by mixing calcined clay, limestone, clinker, and gypsum at different clinker substitution rates. Physical analysis of the composite cement was performed, standard mortars were prepared in accordance with the Norm EN 196-1, and finally, strength development was measured at 1, 2, 7, 28, and 90 days to monitor the pozzolanic activity of the calcined clay – limestone mixture.

Among three types of clay of Songololo deposit, the results highlight that YC clay is fit, after calcination at 850°C, for use as SCM. Strength development of the mortar prepared using calcined YC clay complies with the standard EN 197-1 and is even better than the reference cement (Cimko 32.5 and Cimko 42.5). Thus, YC clay can be considered immediately for future development of LC3 cement, while further studies are recommended for LC clay. RC clay has low calcination prospects.

Keywords: clay, calcined clay, limestone, lc3 cement, songololo.

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I. INTRODUCTION

The Songololo deposits aged Neoproterozoic of West-Congolian group is characterized by thick (ca35m) clay deposits overlapping limestone or conglomerate rocks [1]. Scarce information on these clays exists, and there is no industrial valorization at a large scale. A small quantity is consumed either by the local cement industry (ca3% of the removed quantity) or by villagers in fired clay bricks production, in housing, and in road stabilization. Still, the significant quantity is rejected by the cement producers and dumped as waste in open fields leading to land and water pollution, and landscape modification.

The cement industry requires only tiny quantity of silica-rich clay to produce ordinary Portland cement (OPC), which cement is primarily consumed worldwide. Cement is a cheap material, easy to handle, and available, but, its production is responsible for high CO_2 emissions (5 to 8% of global anthropogenic emissions, and around 35% of industrial emissions). On the average, 0.8 to 0.9 tons of CO_2 are emitted to produce one ton of OPC [2].

Many techniques have been developed in order to tackle this environmental issue, but in this paper the partial substitution of clinker with the calcined clay-limestone mixture is emphasized by investigating Songololo clay deposits and their potential utilization as SCM in LC3 composite cement.

The Figure 1 shows the study location.

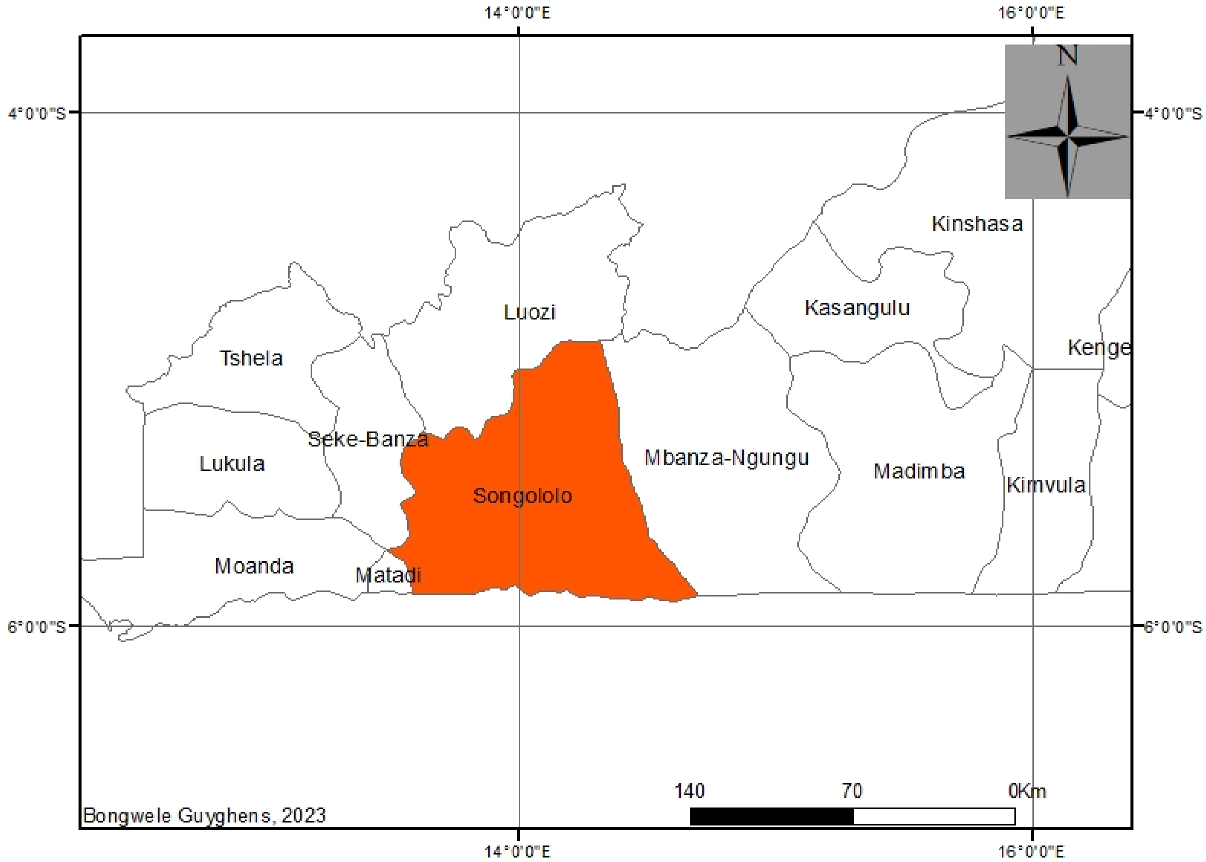

Figure 1: Kongo central Province, DR Congo showing study location [1]

1.1 Clay Minerals

Clay minerals are sheet minerals composed of repetitive tetrahedral silicate (T) and octahedral aluminate (O) layers. They are often referred to in the literature as 1:1 (T-O) and 2:1 (T-O-T) minerals.

Minerals 1:1 comprise two groups: (i) the kaolin group, which includes kaolinite, dickite, nacrite, halloysite, and hisingerite, while (ii) the second group includes, among others, lizardite, antigorite, chrysotile, caryopilite, pyrosmalite, and serpentine [3].

Minerals 2:1 form a broad group that includes pyrophyllite, talc, micas, illites, smectites (montmorillonite), vermiculite, chlorites and minerals with a mixed layered structure [4, 5, 6, 7].

This division is far from covering the rich diversity of clay minerals, as clays also contain complex minerals in which T-O and T-O-T layers coexist and can be randomly distributed [8, 9]. To sum up, in the cement industry, three main types of clay are described: (i) kaolinite; (ii) Illite; and (iii) smectites (montmorillonites).

Kaolinite differs from other types of clays, such as illite or smectite, by its layer structure. Kaolinite is a 1:1 clay which is make of one octahedral sheet and one tetrahedral sheet, while illite and smectite are 2:1 clay. Hydrogen bonds between the tetrahedral silicate and the octahedral aluminate prevent any water to penetrate the interlayer space, characterizing kaolinite as non-swelling clay. [10, 11].

1.2 Activation of Clays

Natural clays usually have a moderate or low pozzolanic activity. To increase it, they need to be activated either by grinding [13, 14] or by heating to a temperature which can destroy the crystalline structure and create disorder, and at the same time which can avoid the recrystallization and the formation of chemically inert phases [11, 17].

The clay minerals which can be easily heat-activated are kaolinite and montmorillonite [8, 10]. During heat activation, clay minerals undergo processes of dehydroxylation and amorphisation, leading to a serious damage in the crystal structure. These bring changes in coordination of Al and Si ions, and increase both their solubility and reactivity, which is an essential condition for pozzolanic activity of clay minerals [11].

This effect is more pronounced in the case of kaolinite than in the case of group 2:1 minerals. The higher pozzolanic activity of calcined kaolinite results from the position of Al atoms after dehydroxylation process which remain exposed on the surface of the crystal structure and enable easy reaction with cement hydration products [12].

But, this is not the case for Illite and montmorillonite in which Al atoms remain inside the crystal structure after dehydroxylation process, and this don't facilitate the contact with cementitious materials during cement hydration [12]. As result, their pozzolanic activity is lower than that of calcined kaolinite [10].

Additionnally, muscovite, which belongs to the same family as illite, can be heat-activated, but unfortunately develops low pozzolanic activity compared to illite.

II. EXPERIMENTAL SET UP

The raw materials needed to produce Portland LC3 composite cement are OPC clinker, limestone, kaolinite clay, and gypsum. In this paper, the natural clay is emphasized. Macroscopically, there are three types of clay in the Songololo deposits, namely YC, RC, and LC, discriminated by their color and texture, as shown in the pictures below. The clay samples were collected and dried before being ground for activation. The clay powders were analyzed for major oxide content using a Thermo Scientific ARL 9900 series IntelloPower X-ray fluorescence spectrometer (XRF).

The different phases (mineral and amorphous) present in the clays were analyzed with a Philips PW1050 diffractometer using graphite-monochromatized Cu-Kα radiation (λ = 1.5418 Å) in the 2θ 4-65° range (step length: 0.02° 2θ, scan time: 5s; 40 kV and 20 mA) and the Rietveld method was used for quantification of the different phases.

The kaolinite equivalent parameter (KEQ) of the different clays was determined using a small laboratory oven for the kaolinite content of each clay sample. 500g of each clay was calcined at 200°C, 350°C and 850°C respectively. The residence time of the clays at these temperatures was 5 min. The optimum calcination temperature for the activation of the natural clays was adopted from Onanga et al, 2023 [1].

The composite cement was prepared by mixing calcined clay, clinker (OPC), limestone powder, and gypsum, gradually reducing the proportion of clinker in the mix (50 - 65%). Automatic mixer (1600rpm) was used to obtain a homogeneous cement.

The mortars were prepared under EN 196-1 standard, and the pozzolanic activity of the calcined clay-limestone mixture was analyzed using the indirect method by measuring the compressive strength developed by the mortars on days 1, 2, 7, 28, and 90. Different compressive strengths were compared with those developed by reference cement (Cimko 32.5 and Cimko 42.5) and then with EN 197-1 Norm. This helps to select the suitable clay for developing LC3 cement.

2.1 Tests of Eligibility of Clays for Activation Procedure

Clay is a material that is widespread throughout the world, inexpensive, and easily accessible [8]. Clays are very diverse in terms of chemical and mineralogical compositions making clay with only one type of clay mineral very rare, as [9, 11]. Thus, it is essential to analyze the different clays chemically and mineralogically in order to select which comply with LC3 requirements [18].

Diaz et al. studied clays for their use as SCMs for LC3 production and established a series of chemical criteria to select the suitable clay. Ttable 1 shows the chemical criteria for the suitability of clays in the LC3 system [72].

Table 1: Chemical acceptance of Clay for LC3 system

	Al_2O_3	Al_2O_3/SiO_2	LOI	CaO	SO_3
Suitable Cay	> 18%	> 0.3	< 7%	< 3%	< 3%

However, chemical composition itself is not enough to explain the pozzolanic activity of clays. To take into account the later, the parameter defined as kaolinite equivalent (KEQ) was determined and calculated according to Equation: [18]:

$$\%KEQ = \{[m(350\ °C) - m(850\ °C)]/[m(200\ °C) \times 0.1396]\} \times 100, \qquad \text{(Equation 1)}$$

In which m(x) is the mass of the mineral after heat treatment at a given temperature x. The suitable clay must have at least 40% KEQ.

2.2 Methods of Assessment of Pozzolanic Activity

The pozzolanic reaction occurs, in case of LC3 cement, between the aluminosilicates in the clays (Al_2O_3-$2SiO_2$) and the portlandite ($Ca\ (OH)_2$) produced by cement hydration, and the hydration products are CSH gel (CaO-SiO_2-H_2O), hydrated calcium aluminates (CAH), as well as hydrated calcium aluminosilicates of the hydrogehlenite (C_2ASH) and hydrogarnets (C_3AS_3-C_3AH_6) type. With the addition of calcite, carbo-aluminates can also be formed [19, 20, and 21]. The performance of mortar depends on the different type and the proportion of hydrated products at different ages.

The pozzolanic activity of materials is assessed either by direct or indirect methods. Direct methods are based on the measure of the portlandite ($Ca\ (OH)_2$) content and its reaction products over the time in the solution [22, 23], while indirect methods analyze the evolution of some specific parameters which can be, for example, the compressive strength of mortar specimens, the electrical conductivity of a saturated solution of portlandite [$Ca(OH)_2$] in which the material tested is placed [24, 25], or the determination of the amount of heat released in calorimetric tests [84,85]. In this paper, the pozzolanic activity of the calcined clay – limestone mixture is determined by measuring the compressive strength developed by the mortar during days 1, 2, 7, 28 and 90.

III. RESULTS AND DISCUSSION

3.1. Chemical Composition

Unlike Ordinary Portland Cement (OPC) which requires siliceous clay, the LC3 cement consumes high alumina clay, and this can be observed in the Al_2O_3 / SiO_2 ratio of the natural clays (See Table 2). YC and RC clays have high Al_2O_3 contents and less SiO_2, whereas RC clays have very high SiO_2 contents. Considering chemical acceptance limits of Diaz et al. (see Table 1) [18], YC and RC clays have good calcination potential and can be considered for future studies.

Table 2: Chemical Composition of Different Clays

Clay Samples		Chemical Composition (%)										
		SiO_2	AI_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	Mn_2O_3	P_2O_5	LOI	Al_2O_3 / SiO_2
YC	1	57,38	20,36	9,1	0,13	1,07	0,31	1,11	0,16	0,35	7,32	0,35
	2	57,5	20,34	9,8	0,15	1,05	0,29	1,11	0,17	0,4	7,4	0,35
	3	56,9	20,2	9,6	0,13	1,06	0,3	1,09	0,15	0,37	7,35	0,36
	4	57,5	20,12	9,7	0,14	1,04	0,28	1,12	0,16	0,28	7,34	0,35
RC	1	75,03	12,6	5,98	0,01	0,21	0,4	0,68	0,04	0,14	5,17	0,17
	2	76,2	12,8	5,04	0,01	0,19	0,39	0,59	0,05	0,15	5,05	0,17
LC	1	33,91	17,07	37,08	0,11	0,21	0,31	0,77	0,06	0,31	10,48	0,50
	2	33,95	18,01	36,06	0,12	0,2	0,3	0,76	0,05	0,35	10,5	0,53

The other components used in the LC3 cement system have also been analyzed, and Table 3 gives the chemical composition of these components.

Table 3: Chemical composition of different components

Component	Chemical Composition (%)								
	SiO_2	AI_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI
Limestone	4,50	0,89	0,50	50,08	2,06	0,34	0,19	0,12	42,68
Gypsum	2,28	0,63	0,42	31,01	1,93	40,63	0,20	0,07	22,85
Clinker	21,04	5,05	3,52	65,17	1,80	0,93	0,76	0,20	0,31

3.2 Phase Content

The YC clay has the highest kaolinite content (36% on average), followed by the LC clay (30% on average) and, the RC clay has the lowest (25% on average). phase content.

Nevertheless, the clay mineral content (kaolinite, illite, and muscovite) exceeds 50% in the YC clay and is only 33% and 27%, respectively, in the LC and RC clays. Also, the amorphous phase represents 9% in YC clay, 14% in RC clay, and is not present in RC clay.

Quartz is found in all clays, and its influence on mortar performance remains to be determined.

Table 4 highlights the XRD result of different clay, and Table 5 shows the Kaolinite Equivalent (KEQ) of each clay and the mass loss after calcination.

The mass loss after calcination at 850 °C varies for all clays from 11.2 to 11.5%, and this highlights the clay mineral diversity in the Songololo deposit (See Table 6).

Table 4: Mineralogical Composition YC Clay

Phase (%)	Formula	Clay Samples					
		YC1	YC2	RC1	RC2	LC1	LC2
Quartz	SiO_2	31,6	30,1	68	67,3	20,4	20,1
Muscovite	$KAl_2AlSi_3O_8(OH)_2$	3,3	2,9	2	2,3	3,1	3
Kaolinite	$Al_2Si_2O_5(OH)_4$	36,4	37,5	25,4	26,2	31,6	30,5
Illite	$(K.H_3O))Al.Mg.Fe)_2(Si.Al)_4O_{10}[(OH)_2.(H_2O)]$	16,2	15,3	-	-	-	-
Goethite	FeOOH	4,3	4,2	3,3	4,2	27,8	28,7
Hematite	Fe_2O_3	0,4	0,3	-	-	3,2	3,1
Amorphous		9,6	9,7	-	-	13,9	14,6

Table 5: KEQ of Different Clays

Sample	Initial mass (g)	Mass(g) @ 200 °C	Mass (g) @ 350°C	Mass(g) @ 850°C	K	KEQ (%)
YC 2	500	475	467,5	442,5	0,1396	37,70
YC 3	500	475	467	442,5	0,1396	36,95
YC 1	500	475	466	442,5	0,1396	35,44
RC 1	500	476	460	443	0,1396	25,58
RC 2	500	475,5	460,5	443	0,1396	26,36
RC 3	500	476	461,5	443	0,1396	27,84
LC 3	500	476	464	443,5	0,1396	30,85
LC 2	500	477,5	464	444	0,1396	30,00
LC 1	500	475,5	464	443	0,1396	31,64

Table 6: Mass lost after calcination of Clays

	Mass Loss (%)			
	Initial mass loss (%)	Mass loss (%) @ 200 °C	Mass loss (%) @ 350°C	Mass loss (%) @ 850°C
YC 2	0	5.0	6.5	11.5
YC 3	0	5.0	6.6	11.5
YC 1	0	5.0	6.8	11.5
RC 1	0	4.8	8.0	11.4
RC 2	0	4.9	7.9	11.4
RC 3	0	4.8	7.7	11.4
LC 3	0	4.8	7.2	11.3
LC 2	0	4.5	7.2	11.2
LC 1	0	4.9	7.2	11.4

Considering various recommendations in the literature concerning clays, YC clay offers good prospects for use as SCM in the LC3 system. More testing is required for LC clay, while RC clay has poor prospects.

3.3 Pozzolanic Activity

The pozzolanic activity of the mixture (calcined clay – limestone) in the cementitious system was determined by monitoring the compressive strength developed by the mortars during days 1, 2, 7, 28, and 90. Clinker used came from the Cimko cement plant, limestone from the quarry of the same company, and gypsum was imported from Angola. Table 3 shows the chemical composition of these materials and Table 7 gives the proportion of each material in the formulation of the composite cement.

Table 7: Proportion (%) of components in the cement formulation

	Proportion (%)			
	Clinker	Calcined Clay	Limestone	Gypsum
Cimko 32.5	65	0	32	3
Cimko 42.5	89	0	8	3

	Proportion (%)			
	Clinker	Calcined RC	Limestone	Gypsum
Trial 1 with RC	50	30	15	5
Trial 2 with RC	55	25	15	5

	Proportion (%)			
	Clinker	Calcined LC	Limestone	Gypsum
Trial 1 with LC	50	30	15	5
Trial 2 with LC	60	22,5	12,5	5

	Proportion (%)			
	Clinker	Calcined YC	Limestone	Gypsum
Trial 1 with YC	55	30	15	5
Trial 2 with YC	60	22,5	12,5	5
Trial 3 with YC	65	20	10	5
Trial 4 with YC	65	15	15	5

Figures 2-4 show the compressive strength of the mortars prepared with calcined YC, RC, and LC clays. These results are compared both to the reference cement (Cimko 32.5 and Cimko 42.5), and to EN 197-1 standards (Figure 5).Table 8 shows the physical performance of each formulation, and this is also compare to the reference cement. The results show that, the composite LC3 mortar under investigation complies with EN 197-1, and can also compete with the reference cement.

Table 8: Physical Analysis of Different Cements

	Consistence %	Setting time (Min)	Blaine (cm2/g)	Residue (%)		Soundness (%)
				45µ	90µ	
Cimko 32.5	31	190	5885	18,1	0,1	1,05
Cimko 42.5	30	180	5829	21	0,1	1,1
Trial 1 with RC	31	190	5885	18,1	0,1	1,5

Trial 2 with RC	30	180	5829	21	0,1	1,5
	Consistence %	Setting time (Min)	Blaine (cm2/g)	Residue (%)		Soundness (%)
				45µ	90µ	
Cimko 32.5	31	190	5885	18,1	0,1	1,05
Cimko 42.5	30	180	5829	21	0,1	1,1
Trial 1 with LC	30	180	5500	16,2	0,1	1,5
Trial 2 with LC	31	175	5462	12,5	0,1	1,4
	Consistence %	Setting time (Min)	Blaine (cm2/g)	Residue (%)		Soundness (%)
				45µ	90µ	
Cimko 32.5	31	190	5885	18,1	0,1	1,05
Cimko 42.5	30	180	5829	21	0,1	1,1
Trial 1 with YC	32	190	6019	14,3	0,1	1,4
Trial 2 with YC	32	180	6395	16,7	0,1	1,34
Trial 3 with YC	32	170	5713	16	0,1	1,33
Trial 4 with YC	32	170	5084	14,5	0,1	1,35

All physical performances of LC3 cement at different clinker substitution rates comply with EN 197-1 and are almost similar to reference cement, except for Normal Consistency (NC), which is slightly higher due to adding clay.

The initial setting time ranging from 170 to 190 minutes is close to reference cement. The Blaine fineness is higher than reference cement, which may increase compressive strength of the mortar at late age, and the soundness is within the acceptable range even at 90 days.

Please note that no chemical additives have been added to improve mortar performance.

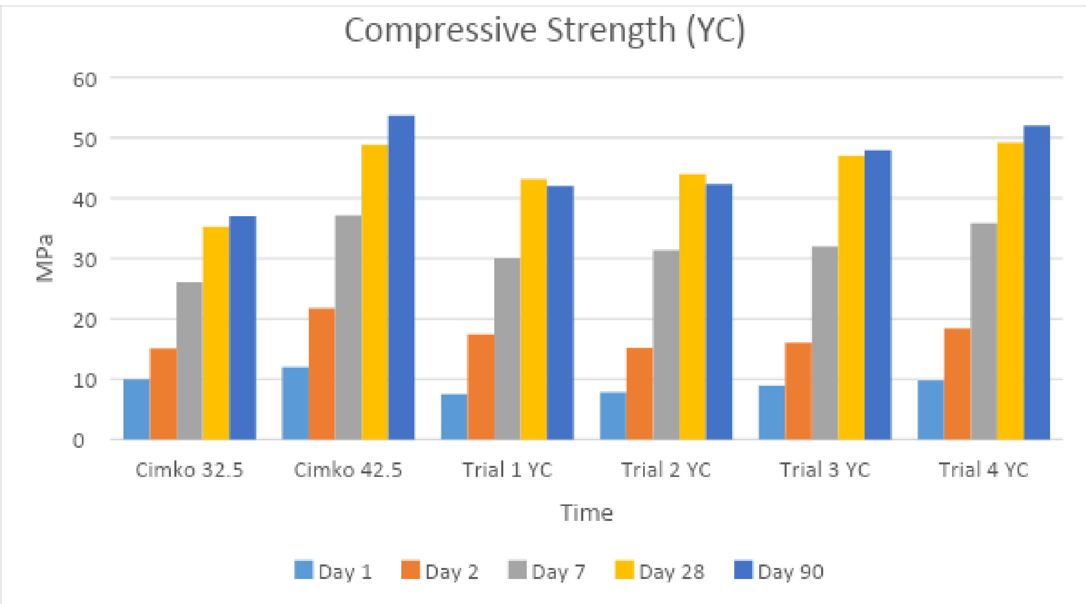

Figure 2: Compressive strength of the mortar designed using YC Clay

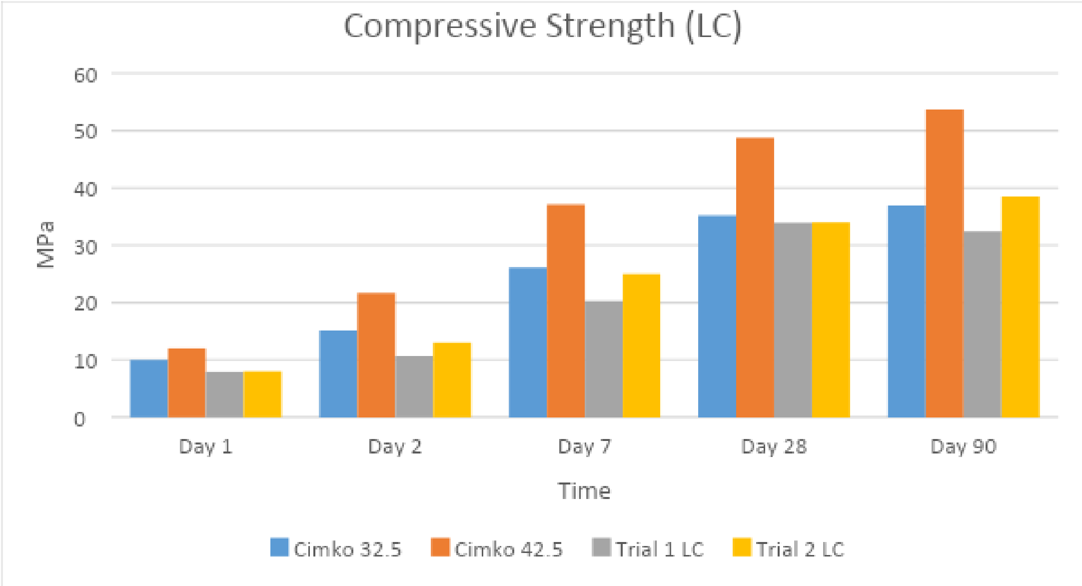

Figure 3: Compressive strength of the mortar designed using LC Clay

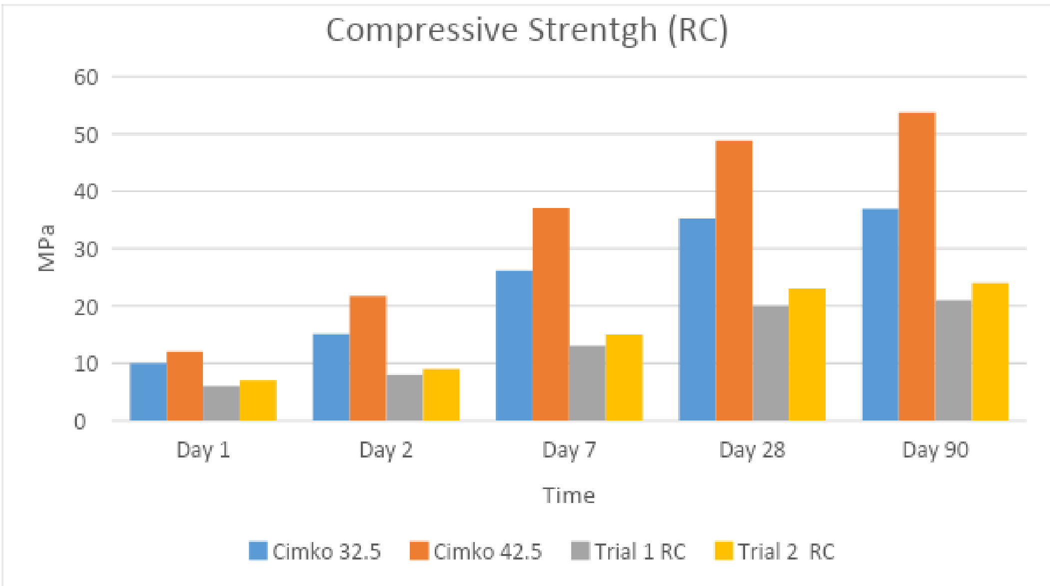

Figure 4: Compressive strength of the mortar designed using RC Clay

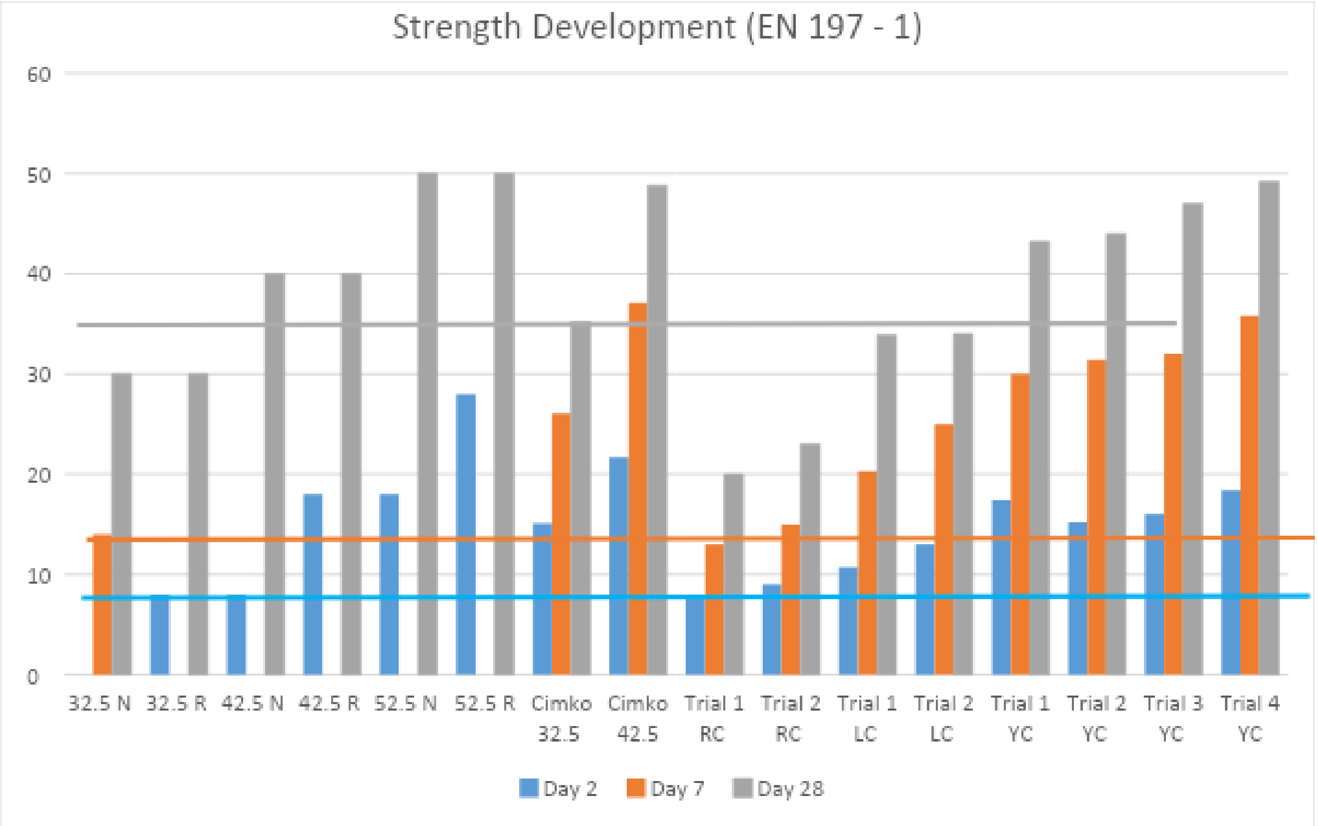

Figure 5: Compressive strength as per Norm EN 197-1 [29]

The performance of mortars prepared with calcined RC clay did not meet the requirements of EN 197-1, while mortars based on calcined LC and YC clay achieved performance in line with the requirements of the said standard.

Mortars prepared with calcined LC clay can compete with Cimko 32.5 but do not achieve the performance of Cimko 42.5, while mortars based on calcined YC clay far exceed Cimko 32.5 and can compete with Cimko 42.5.

IV. CONCLUSION

Three clay types labelled YC, RC, and LC of Songololo deposit were tested for their potential use as SCM in the LC3 cement system after calcination.

Eight clay samples were analyzed for their chemical composition using the XRF technique, the phase content (mineral and amorphous) of the natural clay were determined by XRD, and finally, the Kaolinite equivalent (KEQ) of clays determined by laboratory oven at different calcination temperatures. The composite cement (LC3) was prepared by mixing calcined clay, limestone, clinker, and gypsum at various clinker substitution rates. Reactivity of the calcined clay – limestone mixture was investigated by measuring the compressive strength developed by the mortar after 1, 2, 7, 28, and 90 days.

The results highlight that Songololo deposits are characterized by low kaolinite clays (less than 40%), but among them YC clay has the highest kaolinite (ca 37%), co-occurring with illite and smaller amount of muscovite. Rc clay consisted of low kaolinite content (about 25%) and high quartz content, and finally, the LC clay consisted of moderate kaolinite content and high iron content.

The study of pozzolanic activity of calcined clay – limestone mixture allowed us to formulate the conclusion that with clinker substitution rate (between 40 and 45%), the cementitious material with satisfactory parameters can be obtained and this offers an excellent prospect for industrial trials.

Of the three Songololo deposit clays, only the YC clay can be immediately taken into account in the formulation of LC3 cement. Further studies are recommended for LC clay, while RC clay have limited calcination potential for use as SCMs.

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