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Article

Evaluation of Kunkur Fines for Utilization in the Production of Ternary Blended Cements

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Abstract: Ternary blended cements such as limestone calcined clay cement (LC³) represent a strategic binder type for the mitigation of environmental impact associated with cement production and are estimated to reduce CO₂ emissions by about 40% compared to ordinary Portland cement (OPC). In this paper we explore the possibility of producing such ternary blends by utilizing secondary raw materials that may be locally available. Specifically, the primary limestone that is commonly used in LC³ is here substituted by quarry dust obtained by sourcing of “kunkur”, a carbonate-rich sedimentary rock (also known as caliche) that can be locally utilized for the production of ordinary OPC clinker. To optimize the blending proportions of ternary cements consisting of OPC, calcined clay and kunkur fines, a Design of Experiment (DoE) approach was implemented, with the further goal of exploring the possibility of reducing the amount of the OPC fraction to values lower than 50%. The properties of the formulated blends were assessed by a combination of techniques that comprise mechanical strength testing, XRD time-dependent quantitative phase analysis, SEM-EDS microstructural and microchemical analysis. The results suggest that ternary blended cements based on kunkur fines form hydration products, such as hemicarboaluminates, which are also observed in LC³. This shows that such a waste material can potentially be used in sustainable cement blends, however, the presence of kaolinite in the kunkur fines seems to affect the development of strength when compared to both OPC and conventional LC³.

Keywords: kunkur fines; blended cement; mixture design; circular economy

1. Introduction

The production of Portland cement leaves behind an estimated global carbon footprint of 7-10% of the global emissions [1]. This puts pressure on the global efforts to address climate change and other related environmental concerns [2]. Using alternative binders to reduce the consumption of Portland cement in concrete constructions is considered as one of the viable options to a sustainable construction industry [3,4]. The most promising achievable option is through cement dilution, i.e. by replacing a fraction of ordinary Portland cement (OPC) with powders having different degrees of reactivity, the most commons being fly ash, ground granulated blast furnace slags, calcined clay and finely ground limestone. These filler materials may be inert or reactive in the cement hydration process [3,5]. When displaying some degree of reactivity in blends with OPC, they are commonly known as Supplementary Cementitious Materials (SCMs) and have the potential to reduce the amount of emitted CO₂ per unit mass of binder [4]. With the various options in which these materials are utilized to produce the different concrete, the aspect of familiarity, versatility, strength, durability, wide availability, fire resistance, resistance to the elements, and comparatively low cost, remains key factors to be considered [6]. The use of filler materials to substitute the clinker, considerably meets these requirements [7].

Among the different possible approaches to the use of SCMs in blended cements, Limestone Calcined Clay Cement (LC³) is a promising binder, with the potential to reduce global CO₂ emissions to the atmosphere by about 40% due to clinker replacing up to about 45% [8,9]. In its most common formulation, LC³ incorporates 50 wt.% OPC clinker, 30 wt.% calcined clay (CC), 15 wt.% limestone

(LS) and 5 wt.% gypsum (Gy). Several advantages have been reported from the pilot trials implemented across the world [10–12]. According to [13], high strength LC³ binder comparable to OPC after 28 days can be produced with calcined clay having kaolinite content as low as 40%. This gives the considerable option of using impure kaolinitic clay in LC³ production [14]. Further, low-grade limestone can also be used [15–17]. The synergy between limestone and calcined clay gives a great potential of reducing the clinker fraction to about 50% [18]. Similarly, the lower demand for energy in production gives an advantage over OPC production. Optimal industrial temperatures not exceeding 900°C are needed in the calcination process [12,19,20]. Other studies also show a possible lower temperature requirement with higher pozzolanic activity when other mineral materials such as dolomite are co-calcined with clay [14,21].

Incorporation of other filler materials into similar ternary blends is also possible. This allows, for examples, industrial and agricultural wastes materials to be utilized. Such waste includes rice husk ash (RHA), broken fired bricks, and ceramic wastes among others [22–24]. Previous studies also show that the filler materials such as limestone can accelerate the early rate of hydration [2,25,26]. This effect can be accounted for by two phenomena: (1) the filler materials provide an increased surface area which then enables enhanced heterogeneous nucleation of the hydration products, and (2) enhanced water availability per unit mass of cement particles (i.e., w/c increase or dilution) [27–29]. Improved early age properties therefore leads to better performance of the binder.

Generally, most of the studies have explored the incorporation of different types of filler materials in blended cements. Several concerns such as compromise in the performance of the cement due to poor development of cementing properties have been reported before, depending on the nature and amount of the additions [30,31]. Similarly, utilization of calcined clay and further extension of clinker substitution rates were hindered by such concerns [32]. However, most challenges such as reduced workability, high water demand in concrete mixes, and delayed strength development can now be addressed by the use of superplasticizers and other admixtures [33–35]. These recent advancements expand the scope of SCMs and fillers, and their utilization in blended cements. With this realization, a better understanding of the different fillers is possible. Further, potentially viable implementation of sustainable mixture designs can be optimized to allow increased substitution of the clinker fraction [36,37].

The present study aims at investigating the potential of utilizing “kunkur”, a nodular calcium carbonate rock formed in semi-arid regions, which is also commonly known as “caliche” or “calcrete”. These are naturally cemented soils formed due to evaporation of water containing dissolved calcium carbonate [38]. They are composed of small calcite crystals, and other minerals that are commonly found in soils, and hence have found several applications in cement production and road construction [39–41].

For example, in Kenya “kunkur” has been used in cement production [42,43]. However, the fines formed by quarrying of “kunkur” have not been so far utilized as they are considered wastes and are commonly stockpiled. However, due to the significant calcite content and its wide availability in specific locations, kunkur fines may represent a suitable candidate for replacing primary limestone in ternary blends affine to LC³ cement. This study therefore explored the potential of utilizing kunkur fines in achieving higher clinker fraction substitution and improved performance of LC³ cement, using a Design of Experiments (DoE) approach.

2. Materials and Experimental Methods

2.1. Materials

OPC clinker (CL) and industrial grade gypsum powder (Gy) were used as reference materials to prepare the ternary blends. The kunkur fines (KF) and raw clay were obtained from East African Portland Cement Company (EAPCC) and Nandi County (1.3973°, 34.4489°) Kenya, respectively. Bettersizer SD (dry) particle size analyzer (LS13-320; Dandong Bettersize Instruments Ltd) was used in particle size distributions (PSD) measurements. A muffle furnace was used for calcination of clay at 800°C for 2 hours. Standard sand (CEN Standard Sand EN 196-1) was used to cast the mortars.

2.2. Methods

2.2.1. Chemical composition

The chemical composition of the sample materials was characterized using X-ray Fluorescence (XRF) (Siemens COROS OP15 HERZOG) following the standard procedure according to [44]. Laboratory grinding was carried out using a HERZOG laboratory ball mill FLS 1480, T0200 (1996) with 1480/38 RPM. The samples were then sieved to pass through the 100-micron sieve. About 12 g of the samples were mixed with a binding agent (wax) and pressed into pellets at 20T using a hand pressing machine to obtain a homogeneous pellet sample.

2.2.2. Mineralogical composition of raw materials and reacted mixes

The samples for XRD mineralogical analysis were prepared by hand grinding the samples to obtain samples of size less than 75 microns. To obtain a homogenous sample, the samples were put in a grinding jar filled with 48 zirconium oxide grinding elements. About 4 ml ethanol was added and ground using McCrone Micronizing for 5 minutes. The obtained solution was dried and flat samples were prepared through backfilling to avoid preferred orientations. This procedure was repeated for the XRD analysis of the raw samples and the reacted mixes, by a PANalytical X'Pert PRO diffractometer, in Bragg-Brentano geometry, using Cu radiation.

2.2.3. Mixture design

In the study, a three-component mixture design (simplex centroid design) was used to obtain an efficient and structured approach to examine the KF influence, potential and suitability for utilization to reduce the clinker fraction in cements. This method allows the treatment of the sample as a sum of all the components adding up to 1 (or 100%) hence the synergy effect of the variation of the ratios among the variables (KF, CC, and CL) is possible [45]. The effect of the KF on the behavior of ternary blends is screened by determining the performance of the binder in terms of compressive strength of the cast cement pastes at various curing days.

The experimental design used consists of the probed subset in the mixture space (Figure 1), where each variable is fixed at the lower and upper levels of the mixture space explored. The experimental mixture space covered a range from 40-55%, 15-30%, and 25-40% for CL, KF and CC respectively, whereas the amount of gypsum was kept constant at 5%. For reference, Portland cement with composition meeting CEM I type was prepared following the standard specified in [46]. The experiments were performed according to mixture composition for the experimental points in Figure 1 and their responses (the compressive strengths for the respective curing days) reported, based on a linear mathematical equation (Equation (1)). The equation describes the influence of the main factors (KF, CC and CL) and their interactions with respect to the response parameter Y (compressive strength):

$$= b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \quad (1)$$

In this equation, X_1 , X_2 and X_3 correspond to the amount of clinker, kunkur fines and calcined clay, normalized between 0 and 1. The value of the coefficients b_n is calculated by setting a system of seven equations, each corresponding to an experimental run, with seven unknowns.

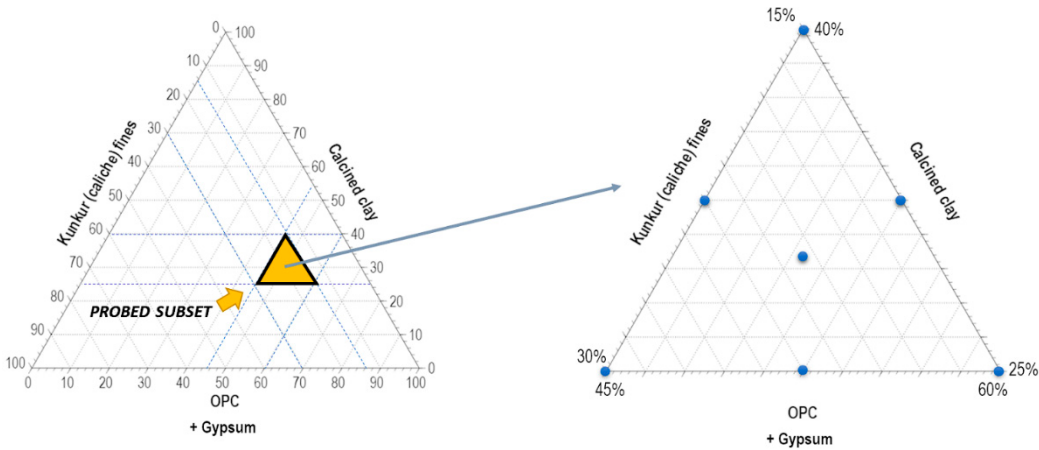


Figure 1. Graphical representation of the mixture space with points representative of the seven experiments of the mixture design.

2.2.4. Compressive strength

Cement pastes for these mixtures were prepared using potable water at a fixed water-to-cement ratio ($w/c = 0.5$) using a planetary mixer (JIKA, Eurostar) as described in [47]. The cement pastes mixes were prepared according to the proportions shown in Table 1. S1 to S7 correspond to the seven-mixture design experimental points displayed in Figure 1, whereas S8 is the OPC control mix. The pastes were cast in prisms of 1.5 cm × 1.5 cm × 6 cm and demolded after 48 hours, wrapped in a slightly wet cloth, and put in sealable plastic bags until the day of the test. The compressive strength was determined using a compressive strength test machine (Controls, Model 82-P0374) after 2, 7, and 28 days of curing.

Table 1. Mix composition (wt.%) for the prepared cement blends.

Mix	Clinker %	KF %	CC %	GY %
S1	55.0	15.0	25.0	5.0
S2	40.0	15.0	40.0	5.0
S3	40.0	30.0	25.0	5.0
S4	40.0	22.5	32.5	5.0
S5	47.5	22.5	25.0	5.0
S6	47.5	15.0	32.5	5.0
S7	45.0	20.0	30.0	5.0
S8	95.0	-	-	5.0

2.2.5. DoE model validation

To validate the modeled responses, three points from the mixture space matching cement pastes showing lower, medium, and highest (mixing proportions in Table 2) performance in terms of compressive strength in the design were prepared. After selecting the validated formulation with the highest compressive strength, an automatic mixer (AUTOMIX, Controls model no. 65-L0006/AM) was used to prepare mortars according to EN196-1. OPC paste and mortar controls were also prepared for reference.

Table 2. Mix composition (wt.%) for the prepared cement blends used for validation of the DoE model.

Mix	Clinker %	KF %	CC %	GY %
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S1'	41.0	16.0	38.0	5.0
S2'	42.0	26.0	27.0	5.0
S3'	45.0	18.0	32.0	5.0
OPC	95.0			5.0

2.2.6. Scanning Electron Microscopy (SEM)

Fragments of the samples tested for compressive strength were kept for SEM microstructural analysis. Hydration was stopped by means of solvent exchange, using ethanol. The samples were pre-polished and cast in epoxy resin, then polished to achieve a desired cross-section of the material and coated with carbon to improve conductivity during analysis. The instrument used in the study was a TESCAN SOLARIS FE-SEM, in backscattered electron (BSE) mode. Energy dispersive X-ray (EDX) was used to assess the microchemical composition of the hardened pastes.

3. Results and Discussion

3.1. Charachterization of the starting materials

The XRF chemical compositions of the materials used in the formulations are shown in Table 3. From the XRD analysis, clinker was determined to have a phase composition of 54.9% C₃S, 17.7% C₂S, 6.6% C₃A, and 10.7% C₄AF. The XRD patterns of the starting materials are shown in Figure 2.

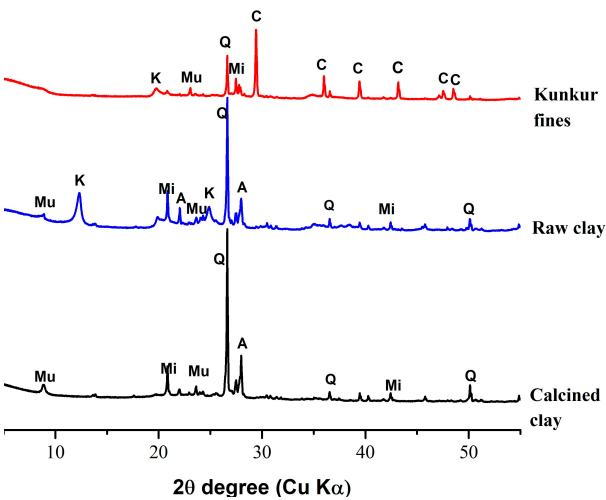


Figure 2. X-ray pattern of (top to bottom) kunkur fines, raw clay and calcined clay. A, C, K, Mi, Mu, and Q represent albite, calcite, kaolinite, microcline, muscovite and quartz.

Table 3. XRF chemical composition (wt.%) of the starting materials.

Chemical composition (w%)	Clinker	Calcined clay	Gypsum	Kunkur fines
SiO ₂	21.3	59.26	7.2	52.32
Al ₂ O ₃	6.3	29.49	1.26	9.55
Fe ₂ O ₃	3.7	4.79	0.83	7.87
CaO	62.2	0.74	29.54	14.49
SO ₃	1.5	-	40.48	0.16
MgO	3.9	2.13	0.28	3.22
K ₂ O	1.0	2.37	0.31	1.13
Na ₂ O	0.4	1.21	-	-
Cl	-	-	-	0.01
L.O. I	0.8			

From the results, the major phases observed in the kunkur fines are: calcite, kaolinite, muscovite, feldspar (microcline) and quartz, compatible with the genesis of this kind of materials, consisting of soils cemented by calcium carbonate precipitated by evaporation. The raw clay mainly consists of kaolinite and quartz, with other minor phases such as muscovite, albite and microcline. The XRD pattern of the clay calcined at 800 °C shows the disappearance of the kaolinite peaks upon structural collapse of this phase. The particle size distributions of the kunkur fines and raw clay are shown in Figure 3.

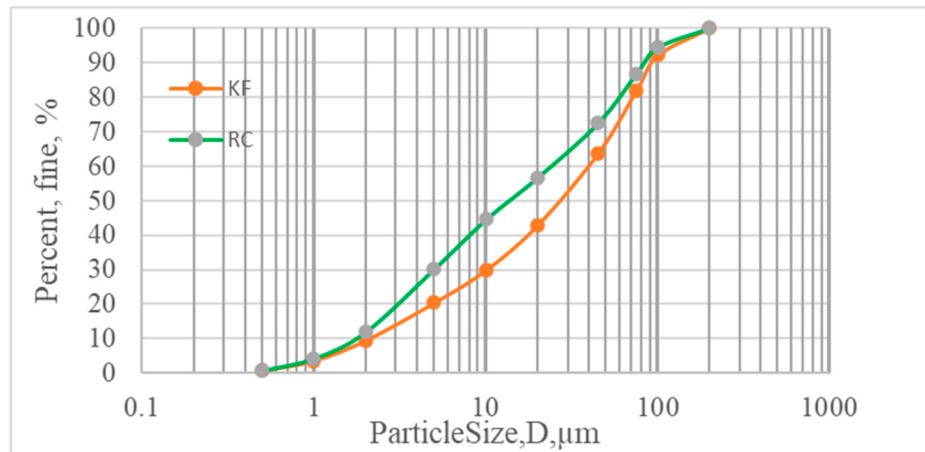


Figure 3. Particle size distribution curves of raw clay (RC) and kunkur fines (KF).

3.2. Compressive strength

The isoresponse plots of the mixture design are shown in Figure 4. These plots display the variation of the compressive strength (2, 7, 28 days) with the binder composition, obtained by interpolating the model equation (Equation (1)).

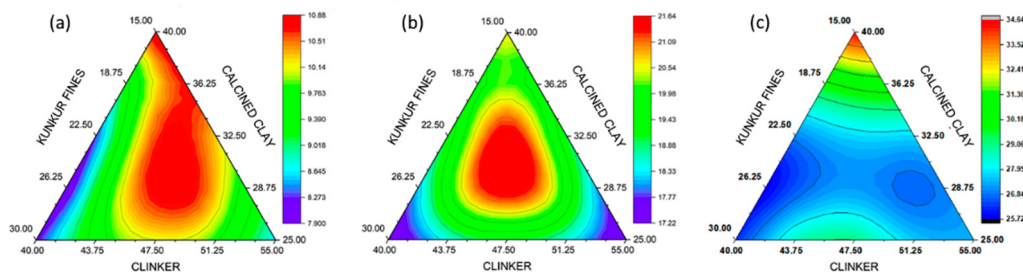


Figure 4. Isoresponse plots of the compressive strength at 2, 7 and 28 days of curing.

From the plot in Figure 4, it can be observed that the compressive strength after 2 days was majorly influenced by the presence of clinker and the calcined clay. The highest strength is predicted to be above 10 MPa. The major phases, C_3S , C_2S and C_3A undergo a faster reaction as compared to pozzolanic materials which are known to start reacting after the second day [48]. This fact can be demonstrated on day 7 where it can be observed that the influence of clinker and CC is showing a significant difference. With the additional CC the compressive strength achieved is about 20.5 MPa compared to a strength of about 17 MPa with clinker. KF is also seen to contribute to mechanical performance to some extent. The highest strength on day 7 is predicted at above 21 MPa.

Finally, at 28 days the compressive strength is observed to be influenced by the presence of the highest amount of CC present in the blend. This can be attributed to the role of the pozzolanic reaction. These observations are consistent with the previous studies that reported the reactions of metakaolin in blended cement at a later age of hydration [49]. Additionally, the major phases in the clinker react faster in the early ages leaving a smaller amount available for further reaction towards late age. This means that the amount of the hydration phases in the clinker, in this case, is slowed

hence this reaction is seen to be determined by the silicate ions in solution that react with portlandite. The highest predicted compressive strength is approximately 34 MPa for the mix consisting of 40% CL, 5% Gy, 40% CC and 15% KF. The strength predicted is lower by about 20% as compared to the control OPC, which has a mechanical strength of about 42.5 MPa.

3.3. DoE model validation

The compressive strength of the blends reported in Table 2, as well as that of the 28 days mortar samples, is displayed in Figure 5.

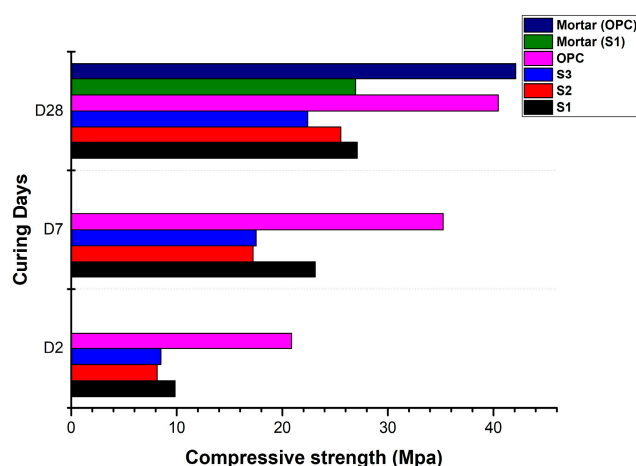


Figure 5. Experimental results for the cement paste and mortar samples compressive strengths at various curing days.

In general, these results confirm the trend predicted by the DoE model, i.e. in the studied compositional range, the strength is maximized proportional to the amount of calcined clay. The measured strengths tend to be significantly lower compared to the control OPC samples, which can be ascribed to the high level of substitution of the studied samples. The values of compressive strength measured on mortars at 28 days were in line with those measured on the corresponding cement pastes. A comparable strength attained is observed in S1' which attained a strength of 26.94 MPa in mortar whilst attaining 27.09 MPa for the case of cement paste. This was consistent for all the samples tested.

The dilution effect reduces the amount of portlandite available for pozzolanic reaction due to reduced clinker in the cement. In addition, the pozzolanic materials could not compensate for the loss in strength performance owed to the slow nature of the pozzolanic reaction which continues beyond the 28 days of curing [34]. The lower strength could further be partly attributed to the challenges with compaction experienced during casting of the blended cement mortar owed to the high water demand of the calcined clay [13]. The addition of superplasticizers (which was not envisaged in this study to avoid a too large numbers of variables in the studied system) may likely improve the strength of mortars with high content of calcined clay, as the one formulated in this study.

3.4. XRD analysis of the hardened pastes

In order to assess the role of the kinetics of formation of hydration products on the macroscopic properties of the studied mixes, XRD was performed at 2, 7 and 28 curing days. The XRD patterns of the cement pastes are presented in Figure 6 for the region of 2θ between 5° and 70° .

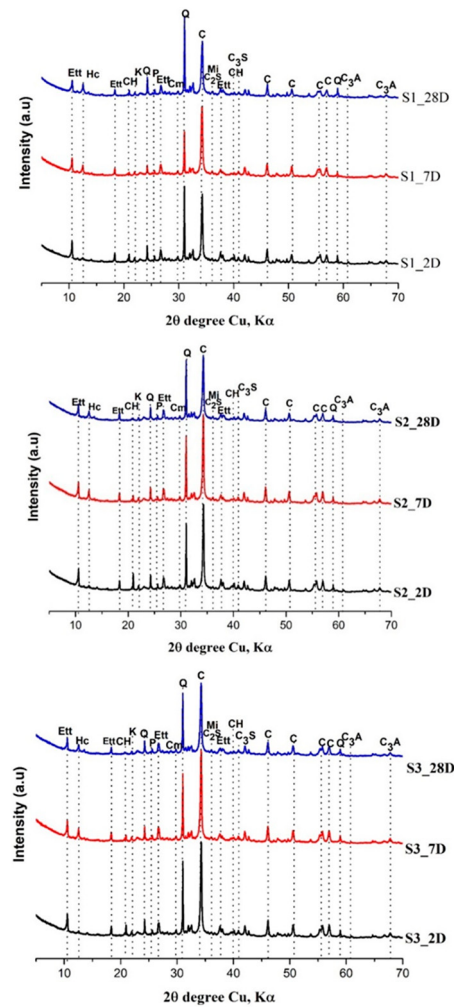


Figure 6. XRD pattern for the cement samples S1', S2' and S3' at 2, 7 and 28 days of curing. C, CH, C₃S, C₂S, C₃A, Ett, Hc, K, Mi, P and Q denote calcite, portlandite, alite, belite, aluminate, ettringite, hemicarboaluminate, kaolinite, microcline, and quartz respectively.

It can be observed that the main phases present in all samples include: clinker phases; kaolinite, quartz and microcline deriving from the kunkur fines and calcined clay; portlandite, ettringite and hemicarboaluminate as reaction product. The intensity of the calcite peaks does not vary significantly in time, suggesting that partial dissolution of the calcite present in the kunkur fines is compensated by carbonation of the reaction products [50].

Figure 7 demonstrates the difference in pozzolanic activity for S1', S2' and S3'. It can be observed that pozzolanic activity decreases from S1' to S3'. The highest activity in S1' can be attributed to the highest amount of amorphous silica from CC leading to pozzolanic reaction with CH.

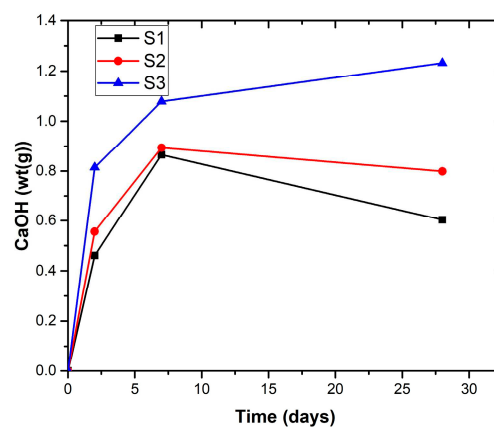


Figure 7. Pozzolanic activity of the cement paste at curing age 2, 7 and 28 days.

The other minerals including plagioclase, kaolinite, and calcite do not seem to have a significant change in their peak intensity. These materials behave to act as physical fillers. However, the formation of hemicarboaluminate (Hc) shown by the peak at $2\theta = 12.560$ indicates some extent of dissolution of calcite, which reacts with the aluminum ions released by dissolution of the amorphous alumino-silicate fraction in the CC, in agreement with previous studies [51]. The Hc peak is observed to gradually increase with curing time. According to [51] with increased curing time, beyond 28 days, the precipitation of hemicarboaluminate exerts a direct effect on pore refinement and strength development. Formation of AFm was not detected in any of the samples at all curing ages. This confirms that the formation of hemicarboaluminate stabilized ettringite and hindered the formation of monosulfate [52].

3.5. Microstructure and microchemical analysis of hardened pastes

SEM micrographs and representative EDS spectra of the hydration product matrices of the blended cement pastes containing KF and CC at 28 days of curing are shown in Figure 8. All microstructures consist of particles of unhydrated cement, calcined clay minerals, quartz, calcite and other unreacted phases in a relatively porous matrix, without significant differences between the three samples. EDS spectra acquired in matrix areas display the presence of Si, Al, Ca and S as the main elements incorporated in the hydration products. This suggests the formation of calcium silicate hydrate with uptake of Al (C-A-S-H) and ettringite as the major matrix phases.

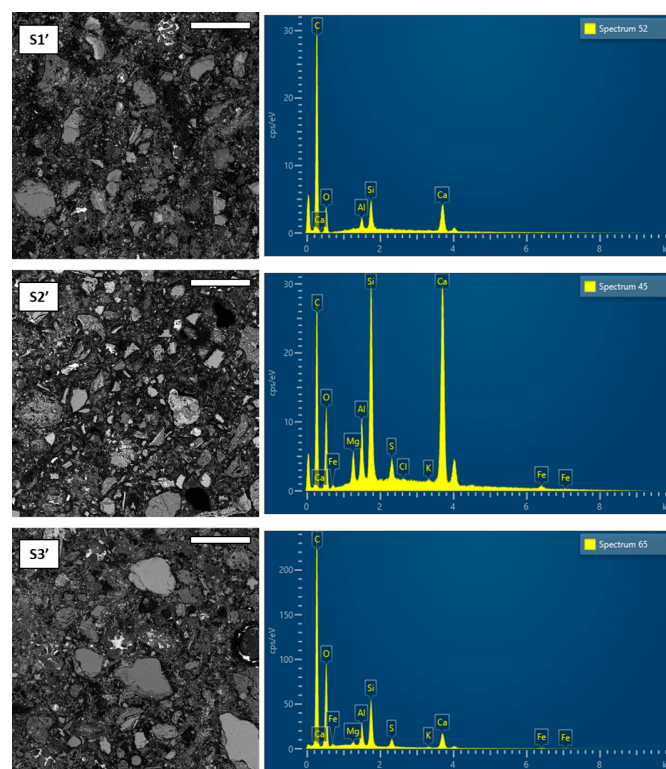


Figure 8. SEM-BSE images for samples S1', S2' and S3' (the length of the white bar corresponds to 100 μm) and example EDS spectra acquired in matrix areas, representative of the hydration products composition.

4. Conclusions

This study preliminarily assessed the possibility of utilizing kunkur fines, sourced as a waste material from quarrying of caliche used in OPC clinker production. The current results lead to the following conclusions:

1. High level of clinker substitution with calcined clay and kunkur fines was studied. The highest 28 days compressive strength for the blended cements was 30 MPa. This was a cement blend with composition consisting of 40% clinker + 5% gypsum + 40% calcined clay + 15% kunkur fines.
2. Kunkur fines can possibly substitute primary limestone in ternary blends, owing to their relatively high calcite content. The partial reactivity of this material is testified by the formation of hemicarboaluminate. However, the presence of kaolinite in the fines may hinder the overall performance, e.g. by increasing the water demand in the mix.
3. The presence of kunkur fines in the ternary blends leads to similar hydration products as those occurring in LC³ containing limestone.

However, the observed lower strength compared to OPC and standard LC³ requires that additional studies are performed to better understand the potential of kunkur fines in sustainable cements, and to elaborate strategies aimed at improving the engineering properties of such blended cements. Investigating the mechanical performance at longer curing times and the durability of blends incorporating kunkur fines will likely provide a more comprehensive view of the potential of this secondary material in sustainable cement.

Author Contributions: Conceptualization, J.M.M. and V.K.M.; methodology, J.M.M. and L.V.; formal analysis, V.K.M. and L.V.; investigation, V.K.M.; resources, J.M.M. and L.V.; writing—original draft preparation, V.K.M.; writing—review and editing, L.V., J.M.M. and C.M.M.; visualization, V.K.M. and L.V.; supervision, J.M.M., C.M.M. and L.V.; project administration, J.M.M., C.M.M. and L.V.; funding acquisition, J.M.M. and L.V. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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