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RESEARCH ARTICLE

Optimization of Ca/Si ratio in schists to enhance the pozzolanic supplementary cementitious material for OPC blending

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Abstract

Supplementary cementitious materials (SCMs) are partial substitutes for ordinary Portland cement (OPC) to reduce cost, the production of carbon dioxide (CO_2), and fossil fuel consumption. Recent studies illustrated the effectiveness of calcined kaolinite clay as a proper partial replacement for OPC. Hence, schist-type materials containing sufficient clay contents are regarded as promising candidates for OPC replacement. This study focuses on the possible use of activated calcium carbonates ($CaCO_3$) to augment pozzolanic reactions of schists as a substitute for OPC. The use of activated calcium carbonates proved to be successful in expediting pozzolanic reactions and facilitating the formation of additional calcium aluminosilicate hydrate (C-A-S-H). In this study, the optimal strength performance for blended cement was achieved by adjusting the total carbonate content to 30 wt.% of the schist. The decision to introduce carbonate to the schist was guided by calculations determining the need for an excess of calcium ions to fully harness the potential for C-A-S-H formation. Virgin and augmented schists were activated by up to 80% of their respective potentials by heat treatment. Phase content and decomposition behavior of the active components were investigated by thermogravimetric analysis (TGA), x-ray diffraction (XRD), and scanning electron microscopy (SEM). Cement paste samples incorporating 30 wt.% replacement of OPC with activated schist SCMs were prepared. The phase distribution and compressive strengths of these samples were assessed at hydration intervals of 2, 7, 28, 50, and 90 days. Cement formulations with activated calcium-augmented SCMs exhibited compressive strength values at 109%, 101%, 96%, 95%, and 94% compared to pure cement paste at 2, 7, 28, 50, and 90 days, respectively. These values surpassed 90% of the compressive strength of pure OPC at equivalent hydration time points.

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KEYWORDS
calcined carbonate, calcined schist, cement substitute, compressive strength

1 | INTRODUCTION

The use of blended cementitious binders is increasing to minimize the ecological footprint of carbon dioxide (CO_2) generated by cement manufacturing. To reduce the total volume of ordinary Portland cement (OPC) clinker produced, various types of supplementary cementitious materials (SCMs) including industrial by-products and wastes are usually blended into binder systems. The active constituents of SCMs (mainly reactive silica and aluminosilicates—known as Pozzolans) react with the calcium hydroxide (CH) obtained from Portland cement hydration.[1–7] Together, they form calcium silicate hydrates (C-S-H), which are the main hydration products with binding properties in the hydraulic calcium silicate system. Its Ca/Si ratio ranges from 1.3 to 2.1,[8] with a mean of 1.75[9] in neat Portland cement. As for possible SCMs, the presence of significant amounts of active constituents is the main factor controlling their potential in the cement hydration process.

There are a significant number of relevant studies focusing on the use of SCMs in concrete, such as blast furnace slag, fly ash, and fumed silica.[10–16] These aluminosilicate sources are being actively used in blended cement compositions. On the other hand, clays being uniformly distributed all over the earth's crust, offer a logistical advantage over the other resources for SCMs. Consequently, calcined clays (aluminosilicate hydrates) could provide an alternative and efficient resource for reducing OPC clinker production. Schists contain the two main ingredients for cement, siliceous minerals, and a combination of calcium sources, that is, carbonates. Therefore, they are frequently used as raw materials in clinker production. However, this study illustrates that these two types of materials, when properly activated, can be used as effective SCMs for OPC.

Calcined kaolinitic clay is one of the widely investigated SCM as a partial cement substitute. This alternative use of clay-type minerals became more popular due to recent studies revealing the secrets of Roman concrete. The Roman wall concrete resists micro-cracking.[11] The key player in durability was believed to be the calcium-aluminosilicate hydrate mineral (Stratlingite) that reinforced interfacial zones in the concrete matrix.[8] Stratlingite having the chemical formula of $Ca_2Al[(OH)_6AlSiO_2$-3(OH)4-3]•2,5(H_2O) or $2CaO•Al_2O_3•SiO_2•11H_2O$ is the product of cementitious reactions between either (i) belite, aluminate gel, and calcium hydroxide; and/or (ii) alite with aluminate gel; and/or (iii) CAH_{10} and C-S-H. Stratlingite is also claimed to contribute to the early strength properties of Roman concrete. More recent studies illustrated yet another secret of Roman concrete for the revalorization of certain rocks. Romans used free lime (CaO) in their mortars that were obtained through the calcination of limestone at around 900°C. Hydration of this free lime forms calcium hydroxide (Portlandite), which dissociates to Ca^{2+} and OH^- ions in excess water. The core of the pozzolanic reactions that led to Roman mortar is the bite of the strongly alkaline portlandite solution at the destabilized Si–O–Si or Si–O–Al bonds on the surface of activated alumino-silicates (pozzolans). During this attack, alumino-silicate minerals dissociate. Their dissolved silicate and aluminate ions form cement-hydrates (i.e., C-S-H or C-A-S-H) with calcium ions from burnt Ca-carbonates.

Clay-type minerals are layered sandwich-like structures composed of octahedral aluminum hydroxide sheets and tetrahedral silicate layers. Three main classes of clays that are most frequently found in the earth's crust are kaolinite, illite, and montmorillonite.[17–19] The activation of clay minerals takes place through the de-hydroxylation of aluminum hydroxide layers. De-hydroxylation of the simplest clay structure (i.e., kaolinite) takes place in the temperature range of 400°C–750°C. In this temperature range, kaolinite will convert to a disordered and unstable structure called "metakaolin."[20–22] Similar to kaolinite, clay-type minerals in schist-type rocks attain their maximum degree of disorder in the temperature range of 700°C–800°C.[23] Walker and Pavia[21] have estimated that the optimum and safe activation ratio of clay-containing schist-type materials is associated with about 80 wt.% of the total weight loss due to the de-hydroxylation reactions. Overheating clays was shown to lead to sintering and diminished reactivity due to the recrystallization.[22–24] The reactivity and therefore the success of schist-type materials as SCMs are directly associated with the proper activation of clay content within them.[22,25–27]

Previously, *metakaolin* was mixed with virgin calcium carbonate (*calcite*) in blended cement.[24,26–28] *Calcite* reactions with the cement during hydration were claimed to give additional benefits to the hardened paste (e.g., packing effects and forming carbo-aluminates).[28–37] Furthermore, some studies focused on the decomposition

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of carbonate phases in the temperature range of 700°C–900°C.[36] The calcination of carbonates would result in free lime and carbon dioxide.[38] Heat treatments at temperatures more than 900°C cause reactions between clays and carbonate leading to metastable calcium aluminosilicates (e.g., wollastonite, anorthite, and gehlenite).[34,38–40] Traore et al. reported the formation of a calcium aluminosilicate between 820°C and 905°C.[39] Gehlenite was observed to form in the temperature range of 850°C–1000°C.[40,41] Another study reported the effectiveness of 10 wt.% calcite addition to calcined clay.[24] However, recent studies mostly focused on utilizing pozzolanic materials such as calcined clays and finely ground limestone particles as substituent materials in the cement structure and figured out the effectiveness of this blending scenario in compressive strength and durability.[24,42–44]

In this study, the effect of calcined limestone on the blended cement properties was evaluated for different amounts of activated calcium carbonate in schist SCMs. Activated clay and calcium-containing carbonate phases were shown to take part in the hydration reactions of blended Portland cement. Earlier research predominantly concentrated on utilizing untreated calcium carbonate as an SCM to impart a packing effect and partially contribute to carboaluminate formation. This study asserts that activated calcium carbonate, or Calcia, can markedly enhance the pozzolanic reaction and facilitate the formation of calcium aluminosilicate hydrate (C-A-S-H). This, in turn, is expected to result in improved mechanical properties. The role of calcined Ca-carbonate additions on the mechanical properties of blended OPC augmented with activated clays in amounts as high as 30 wt.% was illustrated.

2 | MATERIALS AND METHODS

2.1 | Materials

The schist was taken from a mining quarry in Istanbul, Turkey. The schist samples were collected using the intersectional method, where the designated area was subdivided into 10 × 10 m sections. Samples were then collected from the average particle size powders of these 10 sections. The collected schist powders were mixed to optimize the homogeneity of the samples. The raw material was ground to the same particle size as the cement powders (Blaine 3500) by the AkçanSA Cement Factory in Buyukcekmece Istanbul. The chemical composition, phase structure, and potential of the received virgin powder were evaluated with the help of the listed characterization methods. The OPC was an ENS 197-1 CEM 42.5 R type cement, which was provided by the AkcanSA Cement Mturer. The limestone ($\overline{CC}$) from the same quarry with a particle size of ≤5 μm was also provided by AkcanSA.

2.2 | Composite cement with activated schist

2.2.1 | Calcined clay cement (C^3)

The decomposition behavior of virgin schist with and without carbonate additions was investigated with the help of thermogravimetric analysis equipment (TGA; Netzsch STA 449 Jupiter Selb). Total weight losses in the sample due to decomposition reactions were measured. A safe and optimum activation level for schists augmented with calcium carbonate was determined according to the thermal decomposition behavior. A proper activation sequence requires calcination at temperatures that assure destabilization of most clay-type minerals without overheating, which may cause dead burning of clay. Calcination up to a temperature that caused about 80% of the total weight loss for each sample was selected as an optimum activation procedure.

Powders were heat-treated (calcined) up to this temperature at a heating rate of 10°C/min. The calcination method followed a stepped heating schedule. Powders (150 g) were first dehumidified at 300°C for 1 h in crucibles. Subsequently, they were taken to a temperature that would cause 80% of total weight loss and were kept there for 2 h. This last isothermal step was applied to homogenize the temperature distribution within the powders. Then, crucibles containing heat-treated materials were rapidly cooled down to room temperature by air quenching.

2.2.2 | Limestone calcined clay and calcia cement (LC^4)

The amount of calcium carbonate added to the schist powders (M sample) was varied from 0 to 30 wt.% in order to investigate the effect of calcium oxide on the strength development of composite OPC. The upper limit of calcium carbonate content was chosen as 30 wt.% in order to limit the Portlandite (CH) amount in hydrated composite cement pastes. Calcium carbonate-added schist (M_L) was subjected to the same heat treatment as C^3 powders, with the same end goal, such that the decomposition was driven to 80% of the total weight loss of the sample. This calcination temperature of augmented schists was usually higher than the temperature for the schist alone.

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2.3 | Cement paste sample preparation

Composite cement formulations were prepared by replacing 30 wt.% of OPC with activated schist-type materials with and without calcium carbonate additions. A set of cement paste samples with a water/solid ratio of 0.5 was formulated by mixing 700 g of OP cement, 300 g of one of the calcined materials, and 500 g (500 mL) of water. The samples were then cast in 40 × 40 × 40 mm molds (ASTM C348) and kept at room temperature (95% RH) for 1 day. After 24 h, the molded samples were separated from the molds, put into circulating water kept at 23°C until the day of mechanical testing. These composite cement samples were designated as M or M_L (M with 30% *CC*). The strength of C^3 and LC^4 samples was benchmarked with pure OPC paste and prepared according to the same procedure.

2.4 | Characterization

2.4.1 | Phase analysis

To determine the phase content of the schist samples, a quantitative x-ray diffraction (XRD) analysis was carried out. XRD measurements were done using a Bruker D2 phaser (Bruker AXS) diffractometer utilizing Cu-K_α ($\lambda = 1.54$ Å) radiation. The divergence slit size was fixed and was 0.5°. Samples were scanned on a rotating stage between 5° and 90° [°2θ] using a step size of 0.02 n°2θ, and 1 s time per step. Rietveld analysis was carried out to identify and quantify the amount of potentially pozzolanic and inert phases. In addition, the so-called "amorphousness" to crystallinity ratio of all samples was determined by using the same software. Calcined powders were also analyzed by XRD and compared to virgin powders to observe the outcome of the calcination process. In the case of the LC^4 powder, the comparison was performed between schist with 30 wt.% calcium carbonate and the same mixture after calcination.

To get a better handle on the quantification of phases with the help of XRD and its quantification software, a specific experiment was designed. To correct the amount of graphite in the M sample, a composite sample containing graphite and calcite with known amounts was measured and quantified. A mixture with known amounts of graphite and calcite (5 g of graphite powder was added to 95 g of calcite) was quantified using XRD. The results were used to determine a correction factor that was used for correcting the amount of graphite in the M sample.

2.4.2 | Thermal analysis

Thermal analyses of the samples were done in a temperature range between 30°C and 1000°C under nitrogen gas using simultaneous thermal analysis equipment (TGA/DTA) (NETZSCH STA 449 JUPITER). The heating rate was 10°K/min. For every run, only 50 mg of powder sample was used. Thermogravimetric analysis of each sample was able to extract important data about the decomposition temperature range of certain phases within the virgin schist powder. The amount of weight loss correlated with the potential reactivity of the schist. Based on the information extracted from the TGA, the appropriate temperatures for activating the powders were determined. For each sample, the activation temperature was the temperature associated with 80% of total weight loss due to clay and/or carbonate decomposition. Additionally, to control the effectiveness of the calcination process needed to reach the desired activation, heat-treated bulk powders were also evaluated, again by TGA.

2.4.3 | Microstructural analysis

To identify the changes that occurred during activation of the microstructure, powders before and after calcination were investigated in a scanning electron microscope (LEO Supra 35VP field emission, ZEISS) equipped with an energy dispersive x-ray microanalyzer (EDX—Roenteg, Xflash). Imaging of samples was done by an ET-type secondary electron detector having an aperture size of 30 μm. Images of powder samples were taken at different magnifications to show the overall appearance of powder morphology, as well as changes that occurred due to the activation process. In addition, EDX analysis and x-ray mapping of the samples were carried out at an accelerating voltage of 20 kV.

2.4.4 | Compressive strength test

To evaluate the effect of activated schists on the early and late strength of composite cement pastes, compression tests were done on all paste samples. The compressive strength measurement was accepted as the best indication to evaluate the potential candidates for cement substitution. This test was carried out on 40 × 40 × 40 mm composite cement paste blocks until failure compression, using a universal testing machine (MATEST E161N Servo-plus Evolution). The compressive strength tests were

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TABLE 1 Phase distribution of M schist sample.

Peak No.	Chemical phase	at.%	Crystal structure	Chemical formula
1	Quartz	38	Hexagonal	SiO_2
2	Calcite	4.7	Rhombo	$CaCO_3$
3	Ankerite	14.3	Rhombo	$Ca(Mg_{0.67}Fe_{0.33})(CO_3)_2$
4	Muscovite	19.7	Hexagonal	$(K, Na)(Al, Mg, Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$
5	Clinochlore	3.7	Monoclinic	$(Mg_{2.8}Fe_{1.7}Al_{1.2})(Si_{2.8}Al_{1.2})O_{10}(OH)_8$
6	Graphite	≈5	Hexagonal	C
7	Mg-Annite	8.77	Monoclinic	$K(Mg, Al)_{2.04}(Si_{3.34}Al_{0.66})O_{10}(OH)_2$
8	Rutile	1.32	Tetragonal	TiO_2
9	Albite	3.7	Triclinic	$NaAlSi_3O_8$
10	Pyrite	0.9	Cubic	FeS_2

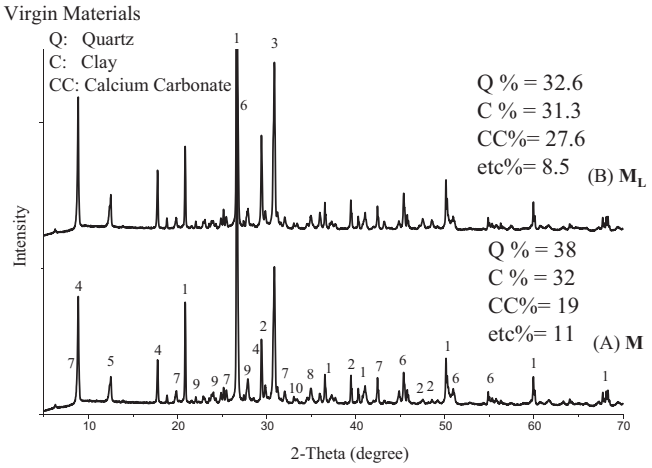

FIGURE 1 Virgin sample XRD results: (A) M, and (B) M_L.

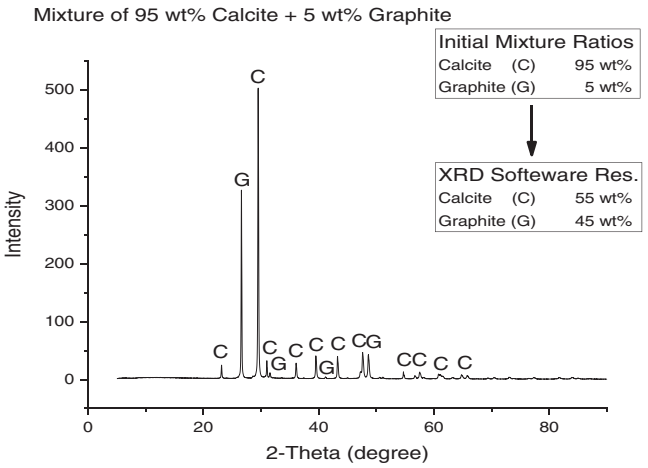

FIGURE 2 A mixture of 95 wt.% calcium carbonate and 5 wt.% graphite XRD diffractogram.

performed at 2, 7, 28, 90, and 360 days of hydration after mixing.

3 | RESULTS

3.1 | Virgin materials (before activation)

3.1.1 | Phase analysis

Schists are metamorphic rocks with various aluminosilicates and quartz as the main constituents. The exact phase composition may vary from location to location. Therefore, the phase distribution and the amounts of crystalline or amorphous content in this particular schist sample were determined by XRD analysis. Figure 1 illustrates the x-ray diffractograms of M samples with (curve b) and without (curve a) carbonate addition. Existing phases and their chemical formulae are noted in Table 1.

XRD analysis software indicated that the virgin M schist powder contained 46 wt.% crystalline and 54 wt.% amorphous amounts. The crystalline phases included quartz, calcite, ankerite, graphite, pyrite, albite (a type of feldspar mineral), and different types of clay-type minerals. The total amount of inert quartz phase (# 1) was estimated to be approximately 38 wt.% and the total clay-type content was approximately 32 wt.% (# 4, 5). The dominant clay-type phase was muscovite (# 4, 19.7 wt.%). The total amount of carbonate phases was calculated to be approximately 19 wt.% (calcite [# 2] + ankerite [# 3]). Other minor phases summed up to 11 wt.%. Table 1 lists the quantitative phase composition of the M sample. Their structural and chemical information (i.e., crystal structure and chemical formula) and weight percentages are also included.

The numbers at the peaks in Figure 2 correspond to phase ID numbers listed in Table 1.

The quantification routine of the existing XRD software indicated the amount of graphite in the sample

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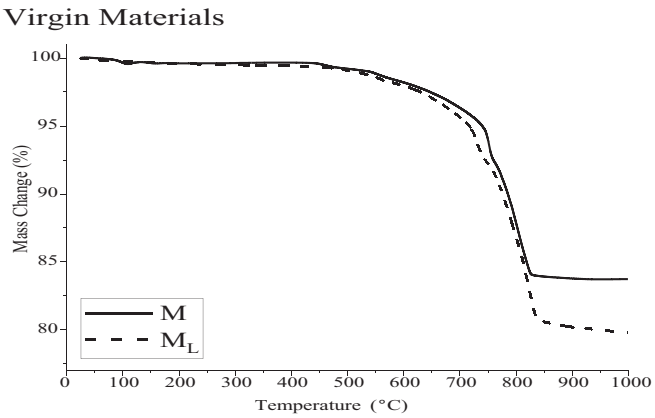

FIGURE 3 Thermogravimetric analysis of M and M_L.

to be 42.5 wt.%. This amount could not be confirmed with the other characterization techniques employed. The peculiar property of graphite was the exaggerated peak intensity in x-ray diffractograms. In order to correct the exaggerated/incorrect amount of graphite, a simple calibration experiment was conducted. The result of this experiment can be seen in Figure 2, which shows an unusually high intensity of graphite peak in a mixture of graphite and calcium carbonate, having a mixing ratio for carbonate to graphite of 95 to 5 wt.%, respectively. The quantification routine of the existing XRD software indicated the presence of 45 wt.% of graphite phases in the mixture, but it contained only 5 wt.% in reality.

Therefore, it was concluded that the actual total amount of graphite in the M schist sample could be approximately 5 wt.%. The remaining 40 wt.% of the miscalculated graphite phase amount was distributed to other existing crystalline phases proportional to their ratios as given by XRD software.

3.1.2 | Activation process

In order to determine the role of activated limestone in schist resources during pozzolanic cement hydration reactions, a schist-containing limestone was heat-treated at different temperatures. The temperatures were chosen such that clay-type minerals and limestone contained in the resource were properly activated. Too high temperatures could cause overheating and dead burning of clay, while too low temperatures may end up in wasted pozzolanic potential. In order to determine the best temperature for activation, TGA analysis was performed. The results threw light on the decomposition behavior of the samples. Figure 3 presents TGA graphs of virgin M and M_L powders for comparison. These TGA/DTGA diagrams illustrated the decomposition temperatures associated with different existing phases.

TABLE 2 Decomposition temperature intervals and total weight loss for schist or schist+carbonate powders.

Sample	Total weight loss (wt.%)	Calcination temperature (°C)
M	15.64	770
M_L	18.51	810

Low-temperature weight loss up to 300°C was related to the non-structural water existing as moisture inside the powders. The main decomposition in M and M_L samples started around 500°C, which was most likely related to the de-hydroxylation of clay-type materials. It seemed as if the crystal structures of the clay-type phases in the M sample were more stable than that of kaolinite in which the main decomposition takes place between 400°C and 600°C.[6] XRD phase analysis indicated that the schist contained 5 wt.% graphite. The existence of graphite was also obvious from the color of this sample. The graphite decomposed at approximately 700°C. The weight loss corresponding to this decomposition observed between 700°C and 750°C temperature range was 4.3 wt.%. The last decomposition (750°C–850°C) was due to the decomposition of the carbonate phases of calcite and ankerite.

Temperature ranges that corresponded to 80% of the total weight losses due to de-hydroxylation or decomposition reactions were calculated based on the TG analyses of the schist and schist plus carbonate samples (approximately 50 mg). These temperature ranges are listed in Table 2.

Later both bulk samples (150 g) were heat-treated at temperatures associated with 80% of total weight loss in a box furnace.

3.2 | Calcined materials (C^3 and LC^4)

3.2.1 | Phase analysis

The clay-phase content of the schist samples indicated that these samples had the prospects of being valuable cement substitutes. There were two different recipes to activate them as SCMs. One recipe employed their natural composition. The second recipe investigated the effect of added calcia on schist composition on cement hydration, strength, and durability. The two recipes allowed an assessment of the effectiveness of calcined clay cement (C^3) versus the potential of calcined augmented clay-carbonate mixtures (LC^4) as SCMs. Therefore, in C^3, the activated sample contained only the original schist

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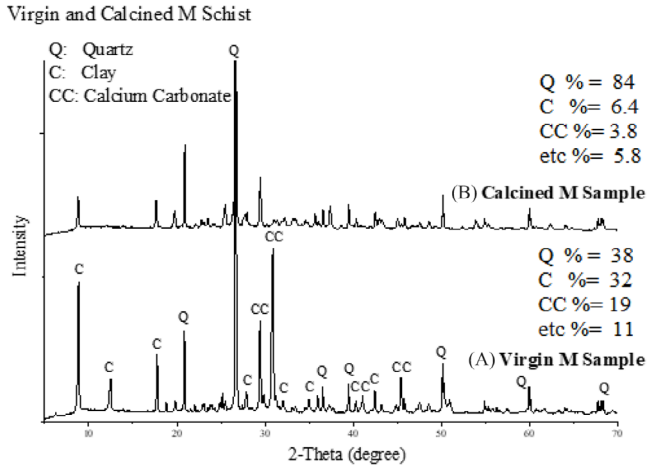

FIGURE 4 XRD diffractograms of virgin and calcined M samples: (a) virgin M, (b) calcined M.

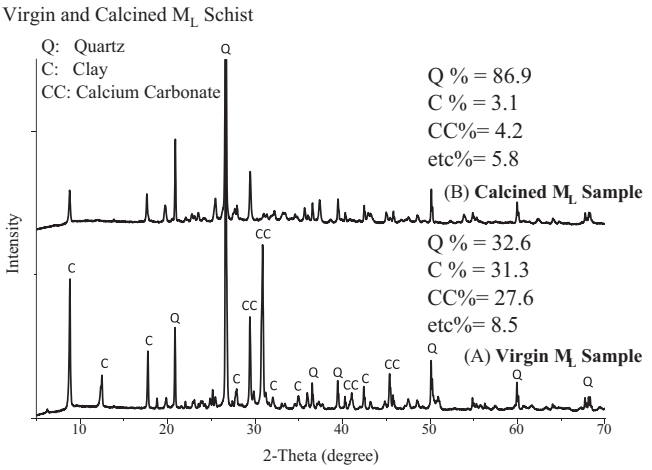

FIGURE 5 Virgin and calcined M_L sample XRD results containing added calcium carbonate: (a) virgin M_L, (b) calcined M_L.

composition without carbonate addition. On the other hand, LC^4 samples consisting of virgin powders with their carbonate content reached a maximum of 30 wt.% of the total SCM weight.

The x-ray diffractogram of all the calcined powders was analyzed and compared to the phase distributions of pre-calcined powders to observe the effects of the calcination process. Figure 4 is a diffractogram of the virgin and calcined M phases without any modification to their carbonate amount. The powder was calcined at 770°C.

Based on the Rietveld analyses of the virgin and calcined schist M, the crystalline phase amount changed from 46% to 35.1%, while the amorphous content increased by about 10% after the heat treatment. The amount of quartz was used as an internal standard, as it was an inert phase whose amount needed to be kept constant before and after the calcination. However, it seemed to have increased during the heat treatment. This apparent contradiction was due to an increase in its relative amount in the sample as some of the other phases were decomposing. The increase in the quartz amount was a misinterpretation of the data by the quantification algorithm of the XRD system. The quantification software calculated the sum of weight percentages of all existing crystalline phases as 100%. Therefore, the relative amount of the stable crystalline phases (i.e., quartz) increased due to the decomposition of non-stable crystalline phases (i.e., clays and calcium carbonate). After calcination at 770°C, the clay content of the M sample decreased from 32 to 6.4 wt.%, while the carbonate amount decreased from 19 to 3.8 wt.%. The peak intensities in the XRD pattern and the amounts of all different clay and carbonate phases were calculated from the spectra in Figure 2 and as listed in Table 1, separately.

Some other phase decompositions also took place in this temperature range, and the variation in crystalline amounts due to these decompositions was about 5.1 wt.%. Based on this quantification, the decomposition process of clay-type materials after being calcined at 770°C, reached 80% of the total weight loss as it was intended for the M schist sample. Figure 5 illustrates the x-ray spectra of virgin and calcined M_L in which the amount of carbonate phase in its composition was increased to approximately 30 wt.% by adding calcium carbonate.

The quantitative XRD analyses indicated that the crystallinity of the M_L powder with the modified carbonate amount decreased from 50.1% to 38.4%. A comparison of the spectra before and after the activation heat treatment at 810°C revealed a reduction in the intensity of certain peaks, indicating their decomposition. The weight percentage of clay-type phases changed from 31.3 to 3.1 wt.%. It indicated that more than 90% of the clay-type component decomposed. Moreover, 84% of the carbonate content was also decomposed. Therefore, according to the XRD phase quantification results, the degree of activation achieved the expected value.

3.2.2 | Activation process

To check if the targeted activation levels (80 wt.%) could be reached in large-scale heat-treatment processes, powders that were calcined in bulk amounts were subjected to thermal analysis to determine the remnant potential left in the schist samples. The figure in this section contains the TGA diagrams illustrating the weight losses in the calcined powders. These powders were heat-treated to a temperature that would correspond to 80% of activation. This temperature was estimated from TGA analysis done with a very small portion of powders. Figure 6 presents the TGA diagrams of bulk calcined M and M_L samples.

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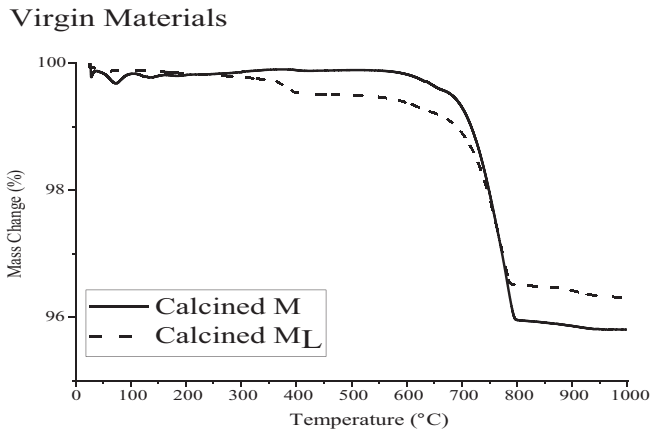

FIGURE 6 Thermogravimetric analysis of calcined M and M_L samples.

The calculated theoretical remnant weight loss for the M sample activated to 80 wt.% of its potential should have been around 3.2 wt.%. The experimentally obtained value was 3.37%, which was very close to the theoretical value. For the M_L sample, the 80% activated powder would have had 3.7 wt.% remaining weight loss (potential for further activation). The TGA results yielded 3 wt.%, which again was very close to the theoretical value.

3.3 | Microstructural analysis

The use of SEM to identify the changes occurring during calcination had two main purposes. The changes in microstructures of various minerals due to calcination were examined. In addition, the changes, if any, in the chemistry of the phases that were caused by heat treatment were studied. The SEM micrographs illustrated the particle morphological changes and reduction in size in some parts and de-crystallization (where the disappearance of prisms with ocular shapes was interpreted as such) in others. A change in the visible color of the calcined powders in comparison to the virgin materials could have been an indication of changes in phase composition in calcined powders. The color of the M sample changed to lighter gray during the calcination process. Because of the graphite content in this virgin material, the color of it was dark gray to black. The heat-treatment process caused the burning (oxidation) of graphite, and the color became a lighter gray.

The micrographs A and C belonged to the virgin powders and the micrographs B and D belonged to the calcined M schist (Figure 7). The upper micrographs A and B were lower magnification micrographs of the powders, whereas micrographs C and D were at higher magnification for the same powders.

The microstructure of the virgin M sample revealed a large fraction of plate-like particles. The particle size was approximately 50 μm. In the image of the calcined sample, the de-hydroxylated clay-type particles can be seen as ruffled-edge particles in some parts. The heat-treatment process caused the average particle size to be reduced from 35 to 11 μm.

The chemical composition of the M schist as determined by SEM/EDS is presented in Table 3. One of the critical values in the resources was the Ca/Si+Al ratio. According to the table, this value for M schist was about 0.22.

The elemental analysis of the M sample lists a variety of elements that were distributed heterogeneously. The Ca/Si ratio was approximately 0.29 in the virgin M sample. The chemical composition of the calcined M schist measured with the help of EDS is summarized in Table 4. The Ca/Si+Al ratio for the calcined sample was approximately 0.33.

The EDS result concluded that the Ca/Si ratio in the M sample after calcination increased from 0.29 to 0.44.

Platy morphologies where Al, Si, and alkali signals coincided were interpreted as clay particles. The chunky particles with similar compositions were the feldspars minerals in the schist. The co-location of Fe and S indicated pyrite particles that transformed into oxides during the calcination.

3.4 | Compressive strength evaluation

Compressive strength measurement was the simplest method to evaluate the potential of the candidates for cement substitution. The compressive strength of the calcined clay cement (C^3) and limestone calcined clay and calcia cement (LC^4) were compared. This comparison was done to discern the effect of limestone addition to schists, either as calcined carbonate (i.e., CaO) or as virgin limestone ($CaCO_3$).

Figure 8 illustrates the compressive strengths of M and M_L schist samples when they were mixed with the cement (70 wt.% OPC, 30 wt.% SCM) either as C^3 or LC^4. As a basis for comparison, the compressive strength development for 100% OPC is also shown. The success criteria for the blended cement paste were set as the 90% strength of the pure OPC control sample at 28 days.

Calcined M schist when substituted into the cement paste (C^3) resulted in significantly lower compressive strength values than for pure OPC. On the other hand, schists compositionally augmented with calcium carbonate when heat-treated properly, successfully replaced part of OPC without causing a drastic reduction in mechanical properties. Table 5 lists the strength values for C^3 and LC^4.

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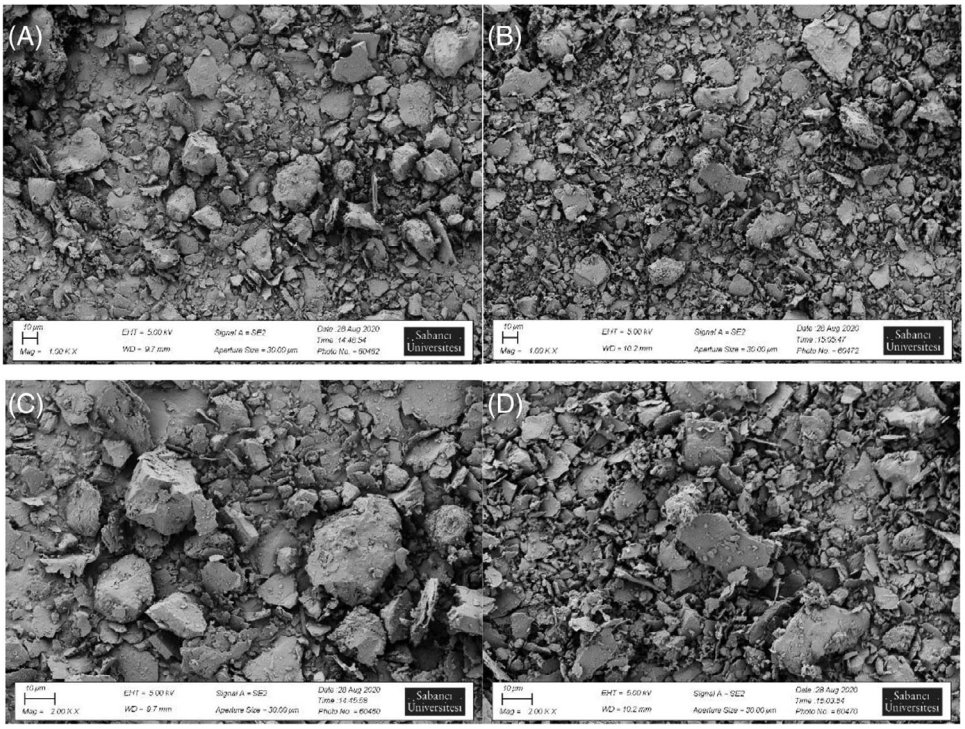

FIGURE 7 The SEM micrographs of the M schist material: virgin (A and C) and 80% heat-treated (B and D).

TABLE 3 M schist chemical composition based on EDS analysis.

Element	At. No.	Mass (%)	Mass Norm (%)	Atom (%)	abs.error (%)	rel.error (%)
Sodium	11	0.12	0.72	0.95	0.04	29.05
Magnesium	12	0.57	3.23	4.16	0.06	10.18
Aluminum	13	3.1	19.04	21.62	0.17	5.62
Silicon	14	7.83	47.96	52.4	0.36	4.59
Potassium	19	0.69	4.18	3.36	0.05	6.83
Calcium	20	2.39	14.31	11.33	0.1	4.04
Iron	26	1.49	9.21	5.07	0.07	4.62
Sulfur	16	0.06	0.4	0.39	0.03	1.57
Titanium	22	0.15	0.95	0.72	0.03	0.76

TABLE 4 Calcined M schist chemical composition based on SEM/EDS analysis.

Element	At. No.	Mass (%)	Mass Norm (%)	Atom (%)	abs.error (%)	rel.error (%)
Sodium	11	0.12	0.88	1.18	0.04	28.26
Magnesium	12	0.65	4.59	5.84	0.06	9.5
Aluminum	13	2.27	15.99	18.33	0.13	5.91
Silicon	14	6.64	46.77	51.51	0.31	4.64
Potassium	19	0.47	3.3	2.61	0.04	8.56
Calcium	20	2.95	20.78	16.04	0.11	3.8
Iron	26	0.92	6.45	3.57	0.05	5.67
Sulfur	16	0.05	0.39	0.37	0.03	50.56
Titanium	22	0.12	0.87	0.56	0.03	24.5

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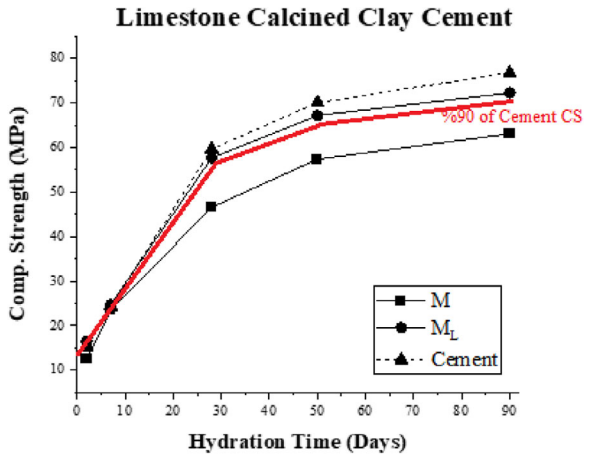

FIGURE 8 Cement, M, and M_L samples compressive strength versus time for limestone calcined clay cement and pure cement.

TABLE 5 M and M_L sample compressive strength values for calcined clay cement paste and pure cement.

Hydration time (days)	Compressive strength (MPa)		
	C^3 and LC^4		Benchmark Cement
	C^3 (M)	LC^4 (M_L)	
2	12.6	16.5	15.1
7	23.5	24.8	24.4
28	46.6	57.7	59.7
50	57.4	67.2	70.1
90	63.1	72.3	76.8

As can be seen in Table 5, the compressive strength of blended cement where 30 wt.% of OPC was substituted with M schist enhanced through the addition of 30 wt.% $\overline{CC}$ (M_L) was almost 97% of the pure cement strength after 28 days of hydration. The compressive strength for the sample without any $\overline{CC}$ additive was not satisfactory (82% of pure OPC). The main difference between these two blended cement pastes was the amount of calcined calcium carbonate contained in the SCM added to them. The most obvious reading from the results was the positive effect of extra calcia source additions to the schist on the compressive strength of blended cement.

4 | DISCUSSION

The application of calcined kaolinitic clay with some calcite impurities as an SCM has been treated in the literature before[17–20,26] Kaolinite is the simplest clay structure that can be reactivated at relatively low temperatures. Metakaolin, which is the de-hydroxylated form of clay, gave the best strength when used as a substitute also for OPC. Studies with other types of clays gave unsatisfactory results as SCMs.[37] In this study, we illustrate the possibility of activating any type of clay if proper thermal treatment is applied. Clays in nature appear as part of various rock formations. One of the most common rock formations all around the world is schists. Their potential as SCMs is closely related to their clay content. The schist-type materials with significant clay concentrations (larger than 40 wt.%) can be considered potential SCMs if a proper calcination treatment can be tailored for them. During the thermal treatment, aluminum hydroxide layers de-hydroxylate leaving active dangling bonds in the clay structure. It is these dangling bonds that facilitate the pozzolanic reactions of activated clays during cement hydration. Therefore, the higher the aluminum hydroxide content of the clay, the higher its pozzolanic reactivity.

The findings of this study illustrate that the destabilization process through thermal treatment can be optimized for the best reactivity of aluminosilicate hydrates for pozzolanic reactions: (i) Insufficient destabilization wastes the potential in the minerals and falls short of best activation. (ii) An overkill of decomposition at excess temperatures can blunt the active sites by sintering and strongly hampering the pozzolanic potential of these aluminosilicate minerals for cementitious hydration reactions.

The other component in pozzolanic reactions that react with activated clays is calcium hydroxide (CH). Normally, during cement hydration reactions, calcium hydroxide is provided by the OPC. Under the extremely alkaline condition of the hydration process, OH^- ions attack the unstable clay structures at their dangling bonds. Reactions between disintegrated aluminosilicates and calcium ions form C-S-H and C-A-S-H, the two main binders of pozzolanic cement. The available calcium ions have a twofold role in such reactions; they provide OH^- to the hydration solution, and they are the main building block of the binders. The proper dosage of reactive calcium ions for pozzolanic reactions is therefore important. Hence, schist-type rocks that may contain both clay and carbonate minerals are prime targets to be activated as SCMs.

This study evaluates the potential of a schist whose carbonate amount is varied. Both clay and carbonate contents in the schist have been activated. The success of activation has been monitored as the strength developed at various hydration times of OPC augmented with these activated schists. The bench-marking sample was pure OPC paste. The results illustrated that the cement partially substituted with virgin schist containing about 4.2 wt.% carbonate minerals, gave a compressive strength of approximately 46.6 MPa after 28 days of setting time. When M_L schist with a carbonate content of 27.6 wt.% was blended into OPC, it gave a 28-day strength of 57.7 MPa (Figure 5). The main difference between M and M_L is the Ca/Si ratio. With up to a 30 wt.% carbonate content in schist, the higher the

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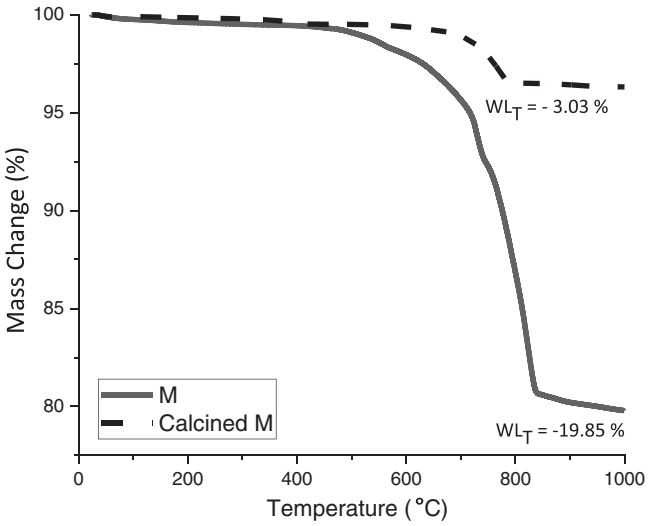

FIGURE 9 TGA graphs of M and calcined M (up to 80% of WL_T).

Ca amount the higher the strength of the schist-blended cement paste (Table 3).

The success of augmented schist as an SCM strongly depends on the design of a proper heat-treatment strategy. As graphite emerges as a sharp peak in XRD, it is not possible to quantify the accurate amount of it in the composition. According to the initial x-ray analysis, the software claimed the amount of graphite was 45 wt.%. However, the TG analysis indicated that the amount of decomposed (burnt) graphite through the temperature range of 600°C–750°C was only 5 wt.%. A control experiment with a graphite/calcite mixture in weight proportions for 5/95 wt.% illustrated that the XRD software estimated the graphite amount in this mixture to be 45 wt.% (see Figure 3). From this result, it was inferred that the real amount of graphite in the M schist sample could have been approximately 5 wt.%. In light of this realization, the 40 wt.% of miscalculated graphite phase amount in the XRD estimates was distributed to other existing crystalline phases proportional to their original weight ratios. The weight percentages reported in Table 1 represent these corrected values.

Based on the TGA analysis for virgin M schist in the previous section, the graphite decomposition takes place in a temperature range that is lower than the carbonate decomposition. Thus, the heat produced within the sample during the oxidization of graphite provided extra energy for the consequent decomposition of calcite. Figure 9 illustrates the leftover possible weight loss as 15 wt.%, indicating that the material was activated to 85% of its potential. Calcination performed at a temperature corresponding to 80% decomposition appears to exceed the intended activation amount of the M sample when performed in bulk sample quantities. This apparent mismatch between intended and realized activation may be originating from the thermal insulating properties of schist powders. The heat provided by the oxidation of graphite within the sample appeared to have a stronger impact on the bulk sample (e.g., 500 g) than in small amounts (e.g., 50 mg) used for TG analysis, as it was trapped inside the sample.

Another impurity phase in this schist sample was pyrite (FeS_2) (~1 wt.%), which would change to pyrrhotite ($Fe_{(1-x)}S$ $_{(x\ =0\ \text{to}\ 0.2)}$) or iron oxide after 780°C. Pyrite did not appear to have any drastic effect either on reactivity or on pozzolanic reactions.

The potential pozzolanic activity hidden in the amorphous content of the schist-type material must be evaluated. The estimation of the reactivity of the amorphous content is not straightforward. However, a comparison between XRD and TGA results could give an idea about it. It is believed that amorphous minerals could be reactive as pozzolans similar to the case of lava from the volcanos used in the ancient Roman concrete.[41] However, this statement could be an oversimplification of schists. To ascertain the potential reactivity of amorphous content in schist, weight loss observed in TG analysis due to de-hydroxylation of clay-type materials would be a better identification. The total weight loss due to clays (in the temperature range 400°C–700°C) in the M schist sample was approximately 5 wt.%. From this weight loss, one could conclude the total weight of crystalline as well as amorphous clay minerals in the schist. However, when one quantifies the magnitude of clay-type phases with the help of XRD, one can see only the crystalline clay content, which was 31 wt.%. The rest of the clays cause 5 wt.% weight losses due to the de-hydroxylation that must be hidden in the amorphous content of the schist. By calculating the amount of structural water in crystalline clays, one can estimate the total clay content (crystalline and amorphous) in the material. In these calculations, the ratios of different clays in the amorphous content were taken the same as in the crystalline portion of the schist. Based on these considerations, 80 wt.% of amorphous content must be activatable clays. This high amount of undetected pozzolans showed themselves also in the better-than-expected strength values of the blended cement paste prepared with this schist.

Besides activating clays, the carbonate phase in the schist materials provides a potential for hydraulic reactions in these SCMs. The partial decomposition of the carbonate phase provides on the one hand a source of Ca^{2+} ions as well as virgin carbonate, which may enter a reaction directly. As was mentioned in the literature review section,[8] an extra amount of carbonate phase could react and/or provide a filler effect. It is claimed that calcium carbonate could influence ettringite formation during the hydration process. On the other hand, decomposed

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calcium carbonate provides extra Ca^{+2} ions, which can be incorporated as C-S-H ($Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$) and C-A-S-H ($Ca_5Al_2Si_6O_{16}(OH)_2{\cdot}4H_2O$). Therefore, it was decided to limit the carbonate amount to 30 wt.% such that alongside activated aluminosilicates, active Ca ions were provided to produce more C-S-H and C-A-S-H through the pozzolanic reactions in what we called the LC^4 approach to generate SCMs for OPC. The positive influence of this approach in the strength development of blended cement paste was confirmed by the compressive strength measurements (Figure 8).

Despite the production of some amounts of carbon dioxide through the decomposition of calcium carbonate, it can be considered that, given the partial substitution of cement with calcined schist, the emissions are significantly lower compared to Portland cement production, resulting in much less pollution.

5 | CONCLUSION

This study detailed the advantages of activated carbonate additions as an excess source of calcium. The pozzolanic activity of any clay and carbonate-containing minerals can be designed according to the de-hydroxylation of clay and the de-carbonation of calcite content. Due attention has to be exercised for proper activation of schist-type materials, as there could be significant deviations between the results of lab-scale and industrial-scale activation processes for materials with very low thermal conductivity, such as schists.

The amount of carbonate in the schist could be augmented according to the Ca/(Si+Al) ratio intended within the C-S-H (C-A-S-H) formation because of the hydration reaction. Properly augmented and activated schists could be used as a potential SCM for OPC. Blended cement where OPC was replaced by up to 30 wt.% with the aforementioned SCM reached 100% strength values of pure cement paste. This suggests that it is possible to use most of the abundant or mine overburdens as SCMs.

According to the results of this study, it would be beneficial for future studies to conduct additional experimental processes to assess the adequate energy required for complete calcination. Furthermore, there is potential for the revalorization of sulfidic mine tailings, constituting over 70% of global mine tailings. This revalorization process could involve calculating the necessary calcium ions to fully exploit the pozzolanic reaction.

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