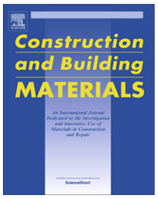
Construction and Building Materials 284 (2021) 122789

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat



Enhancement of pozzolanic activity of calcined clays by limestone powder addition

G. Argın[a], B. Uzal[b,*]

[a] Department of Sustainable Urban Infrastructure Engineering, Abdullah Gul University, Kayseri, Turkey
[b] Department of Civil Engineering, Abdullah Gul University, Kayseri, Turkey

HIGHLIGHTS

- Pozzolanic activity of calcined clays with limestone addition was investigated.
- Physical, chemical, mineralogical and pozzolanic properties were determined.
- Limestone addition enhanced the pozzolanicity of the calcined clays.
- Enhancement was attributed to nucleation effect and formation of carboaluminates.

ARTICLE INFO

Article history:
Received 27 August 2020
Received in revised form 12 January 2021
Accepted 19 February 2021
Available online 10 March 2021

Keywords:
Calcined clay
Calorimetry
Limestone powder
Pozzolanic activity
Strength activity

ABSTRACT

The influence of limestone powder addition on pozzolanic reactivity of calcined clays were investigated. Two clays containing kaolinite and halloysite in their compositions were obtained from different deposits in Turkey and physical, mineralogical, and morphological properties of the raw and calcined clay were characterized. Pozzolanic reactivity of calcined clays with and without limestone powder addition was then examined by means of lime consumption in lime-calcined clay pastes and their isothermal calorimetry as well as strength activity index test. Limestone powder addition enhanced the pozzolanic reactivity of calcined clays by increasing lime consumption and presenting higher heat of reaction released during pozzolanic activity. Limestone addition also provided benefits of reduced water requirement and increased strength activity for calcined clays. Improvements in pozzolanic reactivity and strength activity of calcined clays with limestone powder addition were attributed to nucleation effect provided by limestone particles and also formation of carboaluminate phases during pozzolanic reaction.

1. Introduction

Destruction of forests, carbonate degradation, and fossil fuel usage are the three primary sources of anthropogenic carbon dioxide emissions. The primary source of carbon dioxide emissions of Portland cement is carbonate degradation and emissions from fossil fuel use contribute to emissions. After World War II, cement production increased rapidly throughout the world. Today, concrete and cement industries are responsible for 8% of total CO_2 emissions in the world [1]. Supplementary cementitious materials (SCMs) that can be substituted with cement improves the sustainability of concrete by reducing carbon dioxide emissions [2,3]. The use of SCM also positively affects the durability and mechanical properties of mortar and concrete [4].

There is an increasing interest in SCMs due to their environmental benefits on cement and concrete industry. Although fly ash, blast furnace slag and silica fume are commonly used SCMs, there are some limitations about their availability and quality [2,5,6]. The availability problems of SCMs, which are expected to increase furtherly in time, leads to the search for alternative SCMs. Since clays are one of the most widely available minerals in the world and they have high pozzolanic activity after calcination, so calcined clays have a high potential as SCM [7]. During the calcination of clays, less energy is used compared to Portland cement production. The temperature range at which clays undergo dehydroxylation is about 600 to 850 °C whereas the production of Portland cement clinker takes place at approximately 1400 °C [8]. Especially in recent years, there are many studies on the synergistic use of calcined clays with the addition of limestone powder in blended Portland cement [7,9–14]. In these recent studies,

---

* Corresponding author at: Abdullah Gul University, Department of Civil Engineering, 38080 Kayseri, Turkey.

E-mail addresses: gizem.gorur@agu.edu.tr (G. Argın), burak.uzal@agu.edu.tr (B. Uzal).

https://doi.org/10.1016/j.conbuildmat.2021.122789

pozzolanic reactivity of calcined clays, i.e. lime consumption ability, has been examined for Portland cement-calcined clay-limestone systems. However, there is no any report in published literature focusing on the pozzolanic reactivity of calcined clays directly in plain lime-calcined clay-limestone powder systems.

The objective of this study is to investigate the pozzolanic reactivity of calcined clays with and without limestone powder addition. For this purpose, two clays with different properties were calcined at different temperatures and they were finely ground for 45 min by laboratory ball mill. The clays were then characterized in terms of their physical, thermal, chemical, mineralogical, and morphological properties. Afterward, the pozzolanic activity of calcined clays with and without limestone powder addition was studied by means of lime consumption in lime-calcined clay pastes, isothermal calorimetry, and strength activity index test. In addition, these results were supported by observing the crystalline phases formed by X-ray diffraction (XRD) analysis of the hardened lime-calcined clay pastes. The influence and role of limestone powder addition on the pozzolanic activity calcined clays were especially discussed.

2. Experimental

2.1. Materials

An ordinary Portland cement of CEMI 42.5 R type in accordance with EN197-1 standard was used as cement in the mortars prepared for the strength activity index test. Chemical composition of Portland cement (PC) is determined by X-Ray Fluorescence analysis and given in Table 1. Physical properties of the PC were also determined in accordance with relevant EN standards and given in Table 1. Clays used in the study were obtained from different regions of Turkey, Balıkesir/Düvertepe (notated as Cly1), Nigde/Hacıabdullah (notated as Cly2), in bulk form. Both clays were finely ground by a laboratory ball mill for 45 min. Their particle size distributions were determined by laser particle size analysis after grinding and shown in Table 2 with their particle diameter values where 10%, 50%, 90% of the samples are smaller than those values (d_{10}, d_{50}, d_{90}). Standard sand according to EN 196-1 is used in preparation of mortar mixtures. An analytical grade $Ca(OH)_2$ and deionized water were used in preparation of lime-calcined clay pastes. The limestone powder used in this study was obtained as finely ground commercial product (Nigtaş Corporation, Nigde/Turkey), having 99.4% $CaCO_3$ in calcite mineral form as well as impurities of 0.30% MgO, 0.1% SiO_2, 0.04% Fe_2O_3. Physical properties of limestone powder are given in Table 3 as declared by its producer. Particle diameter values of limestone powder where 50%, 97% of the samples are smaller than those values (d_{50}, d_{97}) were determined by laser particle size analysis (Table 3).

Table 1
Chemical composition and physical properties of Portland cement.

Chemical composition	(%)
SiO_2	24.28
Al_2O_3	6.53
Fe_2O_3	3.25
CaO	52.88
SO_3	3.11
MgO	3.32
Na_2O	0.81
K_2O	0.97
TiO_2	0.27
MnO	0.08
P_2O_5	0.08
Loss on ignition	4.25
Physical properties	
Specific gravity	3.13
Blaine fineness (cm^2/g)	3469
Initial setting time (min)	212
Final setting time (min)	316
Residue on 45 μm sieve (%)	4.8
Residue on 90 μm sieve (%)	0.5
Compressive strength of mortars	
2 days (MPa)	23.7
28 days (MPa)	46.5

Table 2
Particle size distribution of finely ground raw clays.

	d_{10}, μm	d_{50}, μm	d_{90}, μm
Cly1	1.2	4	62
Cly2	1.8	20	91

2.2. Methods

Finely-ground clays were calcined in porcelain crucibles by using a laboratory muffle furnace (Protherm) at various temperatures selected depending on their thermal analysis. Each sample was kept in the furnace at the specified temperature for one hour and then allowed cooling to room temperature in the furnace. Calcined clays were notated by using the clay type and calcination temperature. For instance, Cly1-400 represents the Cly1 calcined at 400 °C. The calcined clays were stored within container sealed from air contact during experimental program.

Thermal analysis of raw clays was conducted by DT-TGA instrument (DTG-60H TGA, Shimadzu) with a heating rate of 10 °C/min for the temperature range from room temperature to 1000 °C under flow rate of 150 mL/min nitrogen as purge gas. DT-TGA was also applied for calcined clays in order to determine their contents of kaolinite group minerals (kaolinite and halloysite). The amount of kaolinite group minerals in raw and calcined clays was calculated from the mass loss corresponding to dehydroxylation of kaolinite group minerals occurring between 400 and 700 °C as follows [15]:

$$w\%_{kaol/hal} = w\%_{kaol/hal-OH}\frac{M_{kaol/hal}}{2M_{water}}$$

where $M_{kaolinite/halloysite}$ (258.16 $g.mol^{-1}$) and M_{water} (18.02 $g.mol^{-1}$) indicate the molecular weight of kaolinite/halloysite and water, respectively. $w\%_{kaol/hal-OH}$ indicates mass loss during the dehydroxylation of kaolinite/halloysite approximately between 400 and 700 °C.

Chemical composition of the clays was determined by X-ray Fluorescence (XRF) technique before and after calcination by using PANalytical Axios Advanced device. XRD measurements were carried out with a diffractometer Bruker/Siemens XRD with a copper radiation CuKα = 1.54060 Å. The data were collected between 5 and 65° 2θ angles. The step size was set to 0.02° 2θ per step. The software used in the identification of phases is Diffrac. Suite Eva.

Table 3
Physical properties of limestone powder declared by its producer.

Physical properties	
Specific gravity	2.7
Particle size distribution*	
Particles > 45 μm, %	0.01
d_{50}, μm	2.7
d_{97}, μm	9.2
Particles < 2 μm, %	41
Specific surface area*, m^2/kg	1185

*By laser particle size analysis

With PDF-2 database of International Centre for Diffraction Data (ICDD). The BET surface area is carried out by the static volumetric method, with the balanced adsorption technique, using the analysis tube and the empty balance tube, with the help of the adsorbed Nitrogen gas for raw and calcined clays (Micromeritics Gemini VII). Morphology of raw and calcined clays were evaluated by scanning electron microscope (SEM) (ZEISS GeminiSEM 300). Samples were coated with 5 nm gold before analysis.

Pozzolanic reactivity of calcined clays and the effect of limestone powder addition were assessed by lime (calcium hydroxide) consumption in lime-calcined clay pastes with and without limestone powder. Lime-calcined clays pastes were prepared with 50% lime and 50% calcined clay content as solids as well as 0.55 water-to-solid ratio. Calcined clay/ limestone ratio as an important factor influencing the properties and hydration of limestone-calcined clay blended Portland cements has been suggested as an optimum value of 2/1 in several reports in published literature [7,14,16,17]. However, considering that this ratio may be different in lime-calcined clay -limestone systems containing significantly higher amount of available lime when compared to hydrated Portland cement systems, two different calcined clay/limestone ratios were tested and compared in terms of 3-day lime consumption. For this purpose, lime-calcined clay pastes with limestone powder were prepared with 10% and 20% limestone addition by weight of total solids, corresponding to calcined clay/limestone ratios of 4.5 and 2 respectively, keeping the lime:calcined clay ratio as 1:1 and water-to-solids ratio as 0.55. 10% limestone powder addition (calcined clay/limestone ratio of 4.5) was selected to use in the study since it results in 56% lime consumption at 3 days which is slightly higher than 54% lime consumption for 20% limestone addition (calcined clay/limestone ratio of 2). Consequently, lime-calcined clay-limestone powder paste experiments were conducted on paste mixtures designed with 45% lime, 45% calcined clay, and 10% limestone powder ratios.

The lime-calcined clay pastes with and without limestone powder addition were used for pozzolanic activity tests by DT-TGA analysis of hardened samples. Heat of pozzolanic reaction measurements were performed by isothermal calorimetry and examination of crystalline reaction products were conducted by XRD analysis of hardened samples.

Lime pastes were mixed by using a laboratory mixer in compliance with ASTM C305 and then stored in plastic syringes and the ends of the syringes were closed with lids to prevent moisture loss and carbonation. Plastic syringes were stored in an oven at 50 °C to accelerate pozzolanic activity till test ages.

Calcium hydroxide content in hardened lime pastes was determined by DT-TGA of samples at 3, 7, and 28-days of age for the assessment of pozzolanic activity. Hardened pastes removed from plastic syringes and then crushed to obtain particles smaller than 800 μm. The hardened pastes were removed from the syringes, crushed, and sieved to obtain particles smaller than 800 μm. The samples were then immediately analyzed thermally to avoid further hydration and carbonation by using Shimadzu DTG-60H TGA device between room temperature and 1000 °C at a heating rate of 10 °C/min. The amount of $Ca(OH)_2$ in hardened pastes was calculated from the mass loss at approximately between 420 and 470 °C corresponding to loss of water in its crystal structure, as percentage with respect to ignited mass of the paste. The lime consumption as percentage with respect to the initial amount lime in the paste mixture were finally calculated from the difference between the amount of lime at zero age and test ages.

For XRD analysis of hardened lime-calcined clay pastes, hardened samples were removed from syringes and crushed to obtain particles smaller than 0.1 mm. Samples were then analyzed at 7 and 28 days of age with Bruker/Siemens XRD instrument between 5° and 30° 2θ angles.

Isothermal calorimetry was conducted on lime-calcined clay pastes with and without limestone addition by using TAM Air Microcalorimeter device (TA Instruments) under isothermal conditions at 50 °C for 6 days. A handheld household mixer and deionized water were used to prepare lime-calcined clay pastes. The prepared samples are quickly placed in the sample holders of the isothermal calorimetry. Since ambient temperature and the ampoules placed in the calorimeter are at lower temperature than test chambers, the signal is expected to stabilize for about 60 min and records in this range are not included in the measurement. Thermal power as mW/g of calcined clay or sum of the calcined clay and limestone present in the paste was recorded for 6 days. Cumulative heat of reaction of the pastes was obtained as the area under thermal power vs. time data by integration. A summary of the experiments performed on paste is shown in Table 4.

Water requirement and strength activity index (SAI) of calcined clays with and without limestone powder addition at 7 and 28 days were determined in accordance with ASTM C311 standard method. The results were evaluated according to the requirements of ASTM C618 specifications for calcined natural pozzolans for use in concrete mixtures as SCM Control and test mortar mixtures prepared according to ASTM C311 by using standard sand were given in Table 5 with their notations. The mortar mixtures were notated with the notation of clay and -LS suffix for the mortars prepared with limestone powder addition.

3. Results and discussion

3.1. Thermal characterization

TGA analysis of raw clays were conducted up to 1000 °C, and percentage mass losses of samples as a function of temperature are shown in Fig. 1. Thermal analysis is a well-known useful method for characterization of clayey materials. Since it can provide qualitative and quantitative data regarding thermal reactions occurred in the sample at specific temperatures, especially for samples containing minerals exhibiting thermal decomposition [18].

As seen from Fig. 1, Cly1 and Cly2 demonstrated mass loss steps due to mainly of free water evaporation approximately below 110 °C and dehydroxylation occurred between 400 °C and 700 °C. This temperature range of dehydroxylation is compatible with thermal decomposition of kaolinite and halloysite as kaolinite group clay minerals. The percentage amounts of dehydroxylation with respect to dry mass of clay samples (mass at 110 °C) were determined as 97.89% and 94.7% for Cly1 and Cly2, respectively. Hence the kaolinite and/or halloysite content of Cly1 and Cly2 was calculated as 69.7% and 45.2%, respectively, by using the equation given in the methods above. The presence of kaolinite and/or halloysite in clay samples was also verified by XRD analysis below. In addition, clay samples exhibited recrystallization at approximately 1100 °C, indicated by an exothermic DTA peak, which is also thermal behavior characteristic of kaolinite group minerals [19].

The efficient temperature for calcination depends on the mineralogical structure of the clays and the energy required for the release of hydroxyl ions [20]. For this reason, calcination temperatures were determined according to the thermal analysis results of the raw clays. Based on the thermal behavior of the clay samples shown in Fig. 1, calcination temperatures used in the study were selected as 400 °C (beginning of dehydroxylation), 520 °C (middle of dehydroxylation), and 700 °C (end of dehydroxylation). Moreover, the calcination temperature of 1150 °C as above the recrystallization temperature was also applied on Cly1 in order to observe

Table 4
Summary of paste experiments.

Experiments	Materials	Mixture design	Conditions	Ages
TGA	Cly1-400–520-700Cly2-400–520-700LS*	50 %Lime-50%Cly45%Lime-45%Cly-%10LS*Water/solid: 0.55	Cured at 50 °C	3,7,28 days
XRD	Cly1-520–700Cly2-520–700LS*			7,28 days
Isothermal calorimetry				For 6 days

*LS: Limestone powder

Table 5
Mortar mixtures for water requirement and strength activity tests.

Mix notation	PC, g	Clay, g	Limestone powder, g	Sand, g	Water, g
Control	500	–	–	1375	242
Cly1-520	400	100	–		Variable by flow
Cly1-520-LS		80	20		
Cly1-700		100	–		
Cly1-700-LS		80	20		
Cly2-520		100	–		
Cly2-520-LS		80	20		
Cly2-700		100	–		
Cly2-700-LS		80	20		

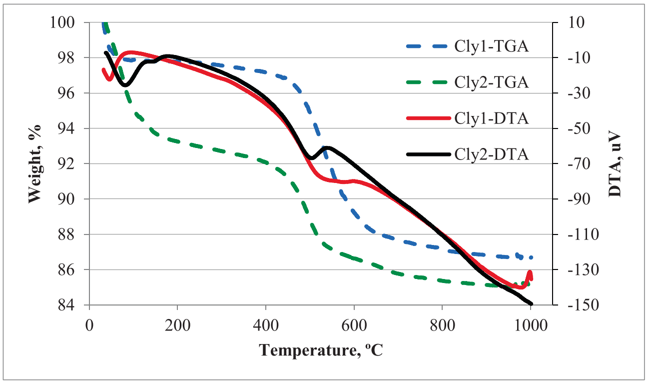


Fig. 1. TGA plot of raw clays.

the effect of recrystallization on pozzolanic reactivity of calcined clays.

The contents of kaolinite group minerals and calcined kaolinite group minerals of clay samples were determined before and after calcinations at selected temperatures by TGA analysis and the results are shown in Table 6. Kaolinite and/or halloysite content of calcined clays decreased with increasing calcination temperature. Calcination temperatures of 400 °C and 520 °C resulted in relatively higher amounts of kaolinite and/or halloysite remained in samples whereas 700 °C caused significantly lower amount of kaolinite and/or halloysite contents due to much more dehydroxylation. In addition, calcination of Cly1 at 1150 °C caused nearly complete dehydroxylation of kaolinite and/or halloysite with only 1.2% remained. Calcination temperatures below 700 °C were less effective on Cly2 for dehydroxylation when compared to Cly1, which is probably due to stronger thermal stability of halloysite at lower temperatures [21].

Table 6
Kaolinite and/or halloysite and calcined kaolinite and/or halloysite contents of clay samples.

Clay sample	Kaolinite and/or halloysite content*, %	Calcined kaolinite and/or halloysite content*, %
Cly1-raw	69.7	–
Cly1-400	66.5	3.2
Cly1-520	57.9	11.8
Cly1-700	13.9	55.8
Cly1-1150	1.2	68.5
Cly2-raw	45.2	–
Cly2-400	42.8	2.4
Cly2-520	42.4	2.8
Cly2-700	11.0	34.2

3.2. Chemical composition, XRD analysis and BET surface area

Chemical composition of raw and calcined clays was determined by XRF analysis and the results are given in Table 7. All the calcined clays, except Cly1-400, conformed the chemical composition requirements of ASTM C618 as standard specification for raw or calcined natural pozzolans to use in concrete at proper amounts of SiO_2 + Al_2O_3 + Fe_2O_3 $\geq$ 70%, SO_3 $\leq$ 4% and loss on ignition $\leq$ 10%. Comparing Cly1 and Cly2 in terms of chemical composition, it should be noted that Cly1 has higher Al_2O_3 and lower SiO_2 and Fe_2O_3 contents when compared to Cly2, which may potentially influence their pozzolanic reactivity.

XRD patterns and identified phases of the raw and calcined Cly1 and Cly2 are shown in Fig. 2 and Fig. 3, respectively. XRD pattern of raw Cly1 (Fig. 2) indicated a mineralogical composition consisting of kaolinite and quartz as crystalline minerals whereas raw Cly2 contains kaolinite and halloysite as clay minerals in addition to sanidine as well as glassy phase indicated by a raised background of the pattern between 20° to 25° 2θ angles. Therefore, the major difference between Cly1 and Cly2 in terms of their mineralogical composition qualitatively was found to be the mixed clay mineral content of Cly2 with kaolinite and halloysite in addition to existence of glassy phase.

Regarding the influence of calcination at various temperatures on XRD patterns of the clays, it was observed that calcination at 400 °C and 520 °C are not significantly influential on XRD patterns (Fig. 2 and Fig. 3). On the other hand, calcination at 700 °C resulted in almost disappeared kaolinite peaks as well as halloysite peaks with reduced intensity in XRD patterns of Cly1 and Cly2. However, the peaks corresponding to quartz and sanidine remained unchanged even at 700 °C due to their high thermal stability.

Specific surface area of the raw and calcined clays was determined by BET nitrogen adsorption method. As shown in Table 8, the BET surface area of Cly2 is significantly higher than that of Cly1; which can be attributed to the presence of halloysite in the mineralogical composition of Cly2. It is known that specific surface of halloysite with tubular shape of crystals is much more when

Table 7
Chemical composition of clays before and after calcination.

Chemical Composition (%)	Cly1-raw	Cly1-400	Cly1-520	Cly1-700	Cly2-raw	Cly2-400	Cly2-520	Cly2-700
SiO_2	55.00	56.76	57.81	58.94	59.50	61.10	59.80	62.47
Al_2O_3	28.86	28.80	28.85	31.90	24.24	24.90	25.30	25.54
Fe_2O_3	0.80	0.65	0.79	0.92	2.94	1.96	2.00	2.66
CaO	0.31	0.26	0.26	0.42	0.83	0.97	1.03	0.87
MgO	0.07	0.06	0.06	0.06	0.54	0.54	0.54	0.57
TiO_2	0.97	0.92	1.04	1.11	0.88	0.82	0.82	0.96
SO_3	0.87	0.87	0.81	1.05	0.29	0.37	0.53	0.56
Na_2O	0.02	0.01	0.01	0.01	0.46	0.02	0.02	0.56
K_2O	0.20	0.20	0.20	0.21	1.09	1.19	1.29	1.35
Loss on ignition	11.72	11.5	9.88	4.03	9.30	8.00	7.80	4.10

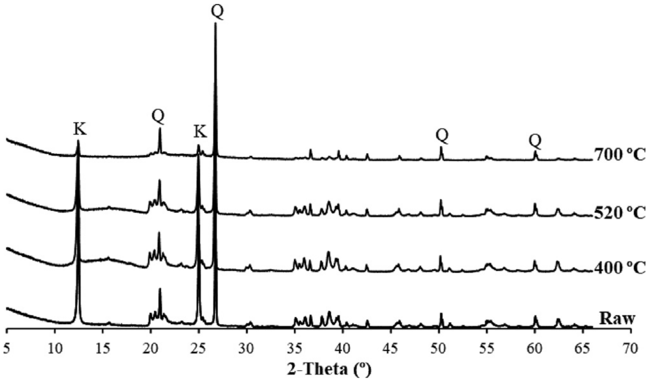


Fig. 2. XRD patterns of Cly 1 (K: Kaolinite, Q: Quartz).

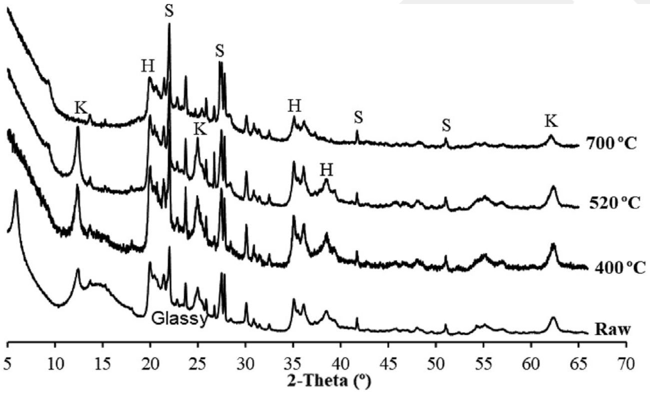


Fig. 3. XRD patterns of Cly 2 (K: Kaolinite, H: Halloysite, S: Sanidine).

compared to plate-shaped kaolinite [22–25]. Calcination of clays changed their BET surface area positively or negatively depending on calcination temperature. Calcination at 400 °C slightly increased BET surface area of both clays. Calcination of clays at 520 °C resulted in a slightly decreased specific surface area for Cly1, however, did not change it for Cly2 when compared to raw clays. On the other hand, it was observed that calcination at 700 °C decreased the surface areas of Cly1 and Cly2. Calcination of clays at relatively low temperatures causes a slight increase in BET surface areas. According to the literature, this surface area increase has been attributed to the dehydroxylation of kaolinite and the disordered of the interlayer region. On the other hand the increase in calcination temperature causes a decrease in BET surface areas as a result of the start of sintering [8,26].

Table 8
Specific surface area of raw and calcined clays.

Calcination temperature	Specific surface area, m^2/g	
	Cly1	Cly2
Raw	8.34	42.18
400 °C	8.95	46.19
520 °C	7.72	42.76
700 °C	7.56	36.89

Kakuli et al. showed that the pozzolanic activity of calcined kaolinite correlates significantly with the crystallinity of the kaolinite mineral. They also reported that well-ordered kaolinite transforms into a less reactive metakaolinite when thermally activated [27]. Although Cly 1 has a more ordered kaolinite than the Cly 2, it is not possible to directly discuss the ordering effect. This is because Cly 1 and Cly 2 are quite different mineralogical and morphological structure. Cly 2 contains kaolinite minerals as well as mineral phases such as halloysite and sanidine. This structure of Cly 2 poses difficulties in evaluating the ordering effect of the kaolinite mineral.

3.3. SEM analysis

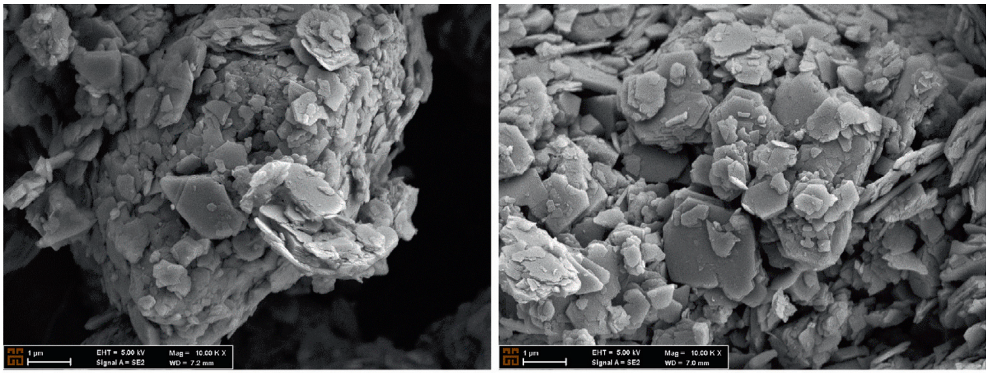
SEM micrographs of raw and calcined samples of Cly1 and Cly2 are shown in Fig. 4 and Fig. 5, respectively. In SEM micrographs, it was observed that calcination did not significantly change the morphology of the clays, which is in line with the published literature [28]. Typical kaolinite structure with hexagonal plates is clearly observed in all raw and thermally treated samples of Cly1 (Fig. 4). In addition, the kaolinite booklet structure was observed clearly in Cly1-700 at a relatively higher magnification (Fig. 4e).

On the SEM micrographs of the Cly2, a clear tubular structure was observed, which can be attributed to the morphology of halloysite reported in published literature [29,30]. SEM observations confirmed the results of XRD analysis indicating the presence of halloysite as a major crystal phase in Cly2. In addition, studies on calcination of halloysite-rich clays have shown that the tubular morphology of halloysite is preserved as long as the calcined temperature is lower than 900 °C [28].

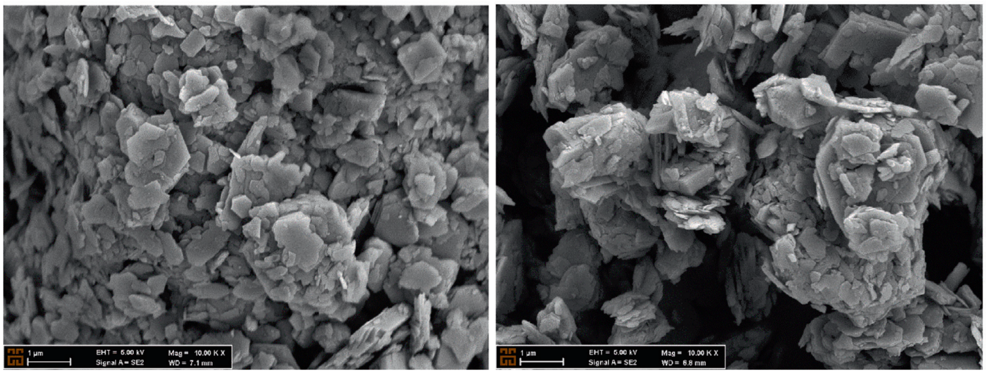
3.4. Pozzolanic reactivity

Pozzolanic reactivity of calcined clays with and without limestone powder addition were examined by means of lime consumption, heat of reaction and XRD analysis of lime-calcined clay pastes and the results are shown in Fig. 6, Fig. 7, and Fig. 8, respectively.

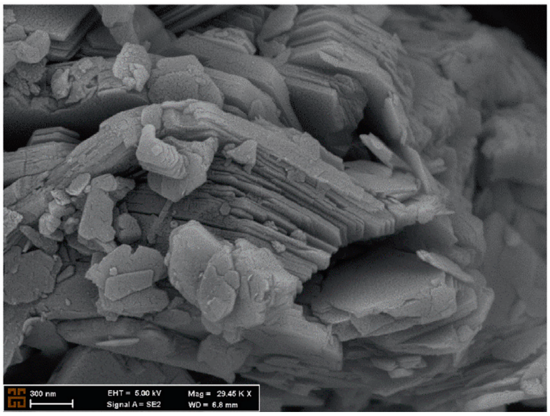
Lime consumption in lime–calcined clay pastes as a measure for the pozzolanic activity are shown in Fig. 6 as percentage of the initially available lime within the pastes. Lime consumption of calcined clays mostly increased with increasing calcination temperature and age of the samples for both of Cly1 and Cly2. Lime consumption of clays calcined at 700 °C was significantly higher than those of calcined at lower temperatures. This is clearly asso-



(a) Cly1-raw **(b) Cly1-400**



(c) Cly1-520 **(d) Cly1-700**

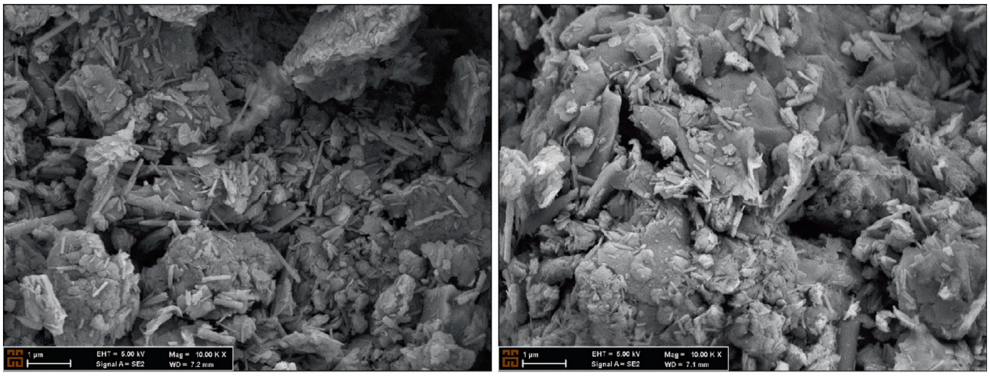


(e) Cly1-700 at high magnification

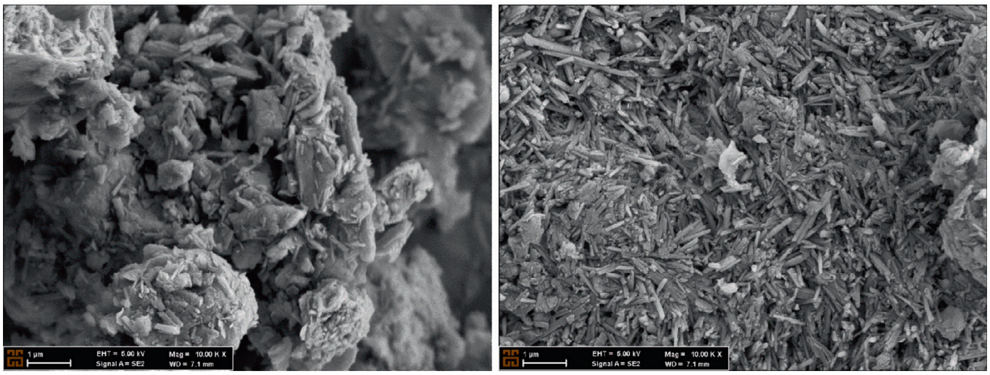
Fig. 4. SEM micrographs of Cly1 (a) Cly1-raw, (b) Cly1-400, (c) Cly1-520, (d) Cly1-700, e) Cly1-700 at high magnification.

ciated with higher content of calcined kaolinite/halloysite corresponding to calcination temperature of 700 °C (Table 6).

Comparing the lime consumption of Cly1 and Cly2 for a given calcination temperature, it was observed that Cly2 exhibited higher reactivity than Cly1 for calcination temperatures of 400 °C and 520 °C at all tested ages (Fig. 6) despite higher calcined kaolinite/halloysite content of Cly1 (Table 6). Glassy phase present in mineralogical composition of Cly2 (Fig. 3) and its significantly higher BET surface area (Table 8) could be responsible for the relatively higher reactivity of Cly2 at lower calcination temperatures. Because glassy phase content and BET surface area are known as factors affecting the pozzolanic reactivity positively [28,31]. On the other hand, pozzolanic reactivity of Cly1-700 was slightly higher than Cly2-700 due to dominant contribution of higher calcined kaolinite/halloysite content of the former. While raising the calcination temperature from 520 °C to 700 °C significantly improved the lime consumption of Cly1 (Fig. 6a), it did not increase that of Cly2 that much (Fig. 6b). This is probably due to glassy phase in mineralogical composition of Cly2 as indicated by XRD patterns (Fig. 3), which already contributes pozzolanic reactivity of Cly2 before and after calcination and reduces the marginal contribution of calcination on pozzolanic reactivity of Cly2.



(a) Cly2-raw (b) Cly2-400



(c) Cly2-520 (d) Cly2-700

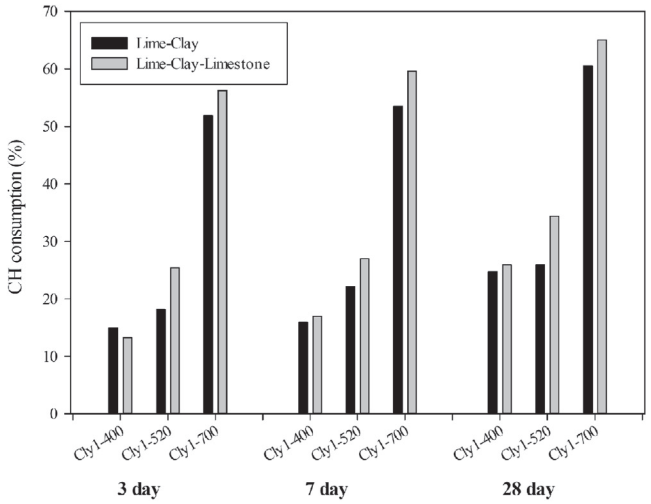
Fig. 5. SEM micrographs of Cly 2 **a)** Cly2-raw **b)** Cly2-400**c)** Cly2-520 **d)** Cly2-700.

Regarding the effect of limestone addition on pozzolanic activity of calcined clays, limestone addition obviously increased the pozzolanic reactivity of calcined clays (Fig. 6) as measured by lime consumption except for Cly1-400 exhibited comparable lime consumption. Limestone powder addition was found to be more influential to increase the lime consumption of Cly2 when compared to Cly1, especially for calcination temperatures of 400 °C and 520 °C.

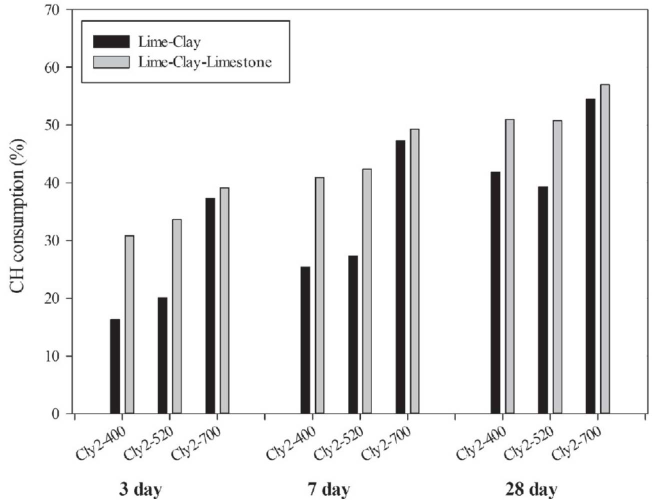
In order to understand the role of limestone powder on pozzolanic reactivity of calcined clays, isothermal calorimetry on lime-calcined clay pastes and XRD analysis of hardened pastes were also conducted for clays calcined at 520 °C and 720 °C. The clay calcined at 400 °C was not included in further experimentation due to its relatively lower pozzolanic activity. Fig. 7 shows cumulative heat release for calcined clays with and without limestone addition at the end of 144 h of age. Heat values were calculated as joule per gram of SCM consisting of calcined clay or calcined clay and limestone powder together. Suraneni and Weiss [4] have recently proposed the use of isothermal calorimetry to examine the pozzolanicity of SCMs effectively. In this novel approach, the pozzolanic activity and reaction degree are directly proportional to the cumulative heat released upon pozzolanic reaction of SCM. As seen from Fig. 7, the addition of limestone powder mostly increased the cumulative heat release, and accordingly their pozzolanic activity. Cly1-700 with limestone addition (Cly1-700-LS) showed the highest cumulative heat of reaction. It was also observed that limestone addition to clays calcined at 520 °C is highly influential on cumulative heat release of the pastes. These results agree with the trend of lime consumption data for lime-pozzolan pastes (Fig. 6) and also heat release values published in literature for calcined clays [4]. The enhancement of pozzolanic activity with the limestone addition could be attributed the nucleation effect of very fine limestone particles providing nucleation site for pozzolanic reaction products. Nucleation effect is one of the well-known mechanisms for improvement of Portland cement hydration by fine additives even in the case of inert particles [32]. A similar mechanism can also be effective on pozzolanic reaction of calcined clays with calcium hydroxide. Substantially higher influence of limestone addition on the cumulative heat release of the pastes with clays calcined at 520 °C when compared to those calcined at 700 °C can be associated with a pronounced nucleation effect in the case of a relatively lower pozzolanic activity of clays calcined at 520 °C.

Regarding to improvement of pozzolanic activity of calcined clays in the case of LS addition, formation of additional reaction products because of interaction between reactive alumina in calcined clays and calcium species could be another mechanism. It is known about limestone calcined clay cements the addition of limestone causes the formation of monocarboaluminate and hemicarboaluminate instead of the monosulfoaluminate phase that causes the formation of ettringite [33]. The use of especially high alumina containing pozzolans, such as metakaolin or calcined clays, in Portland cement systems promises potential for the formation of carboaluminate phases (both monocarboaluminate and hemicarboaluminate) indicated by XRD analysis of hardened pastes [33–35].

Fig. 8 shows the XRD patterns of lime-calcined clay pastes with and without limestone addition. Formation of carboaluminate phases was clearly observed on the XRD patterns of hardened pastes containing limestone addition especially at calcination temperature of 700 °C and age of 28 days (Fig. 8b and d). On the other



(a) Cly1



(b) Cly2

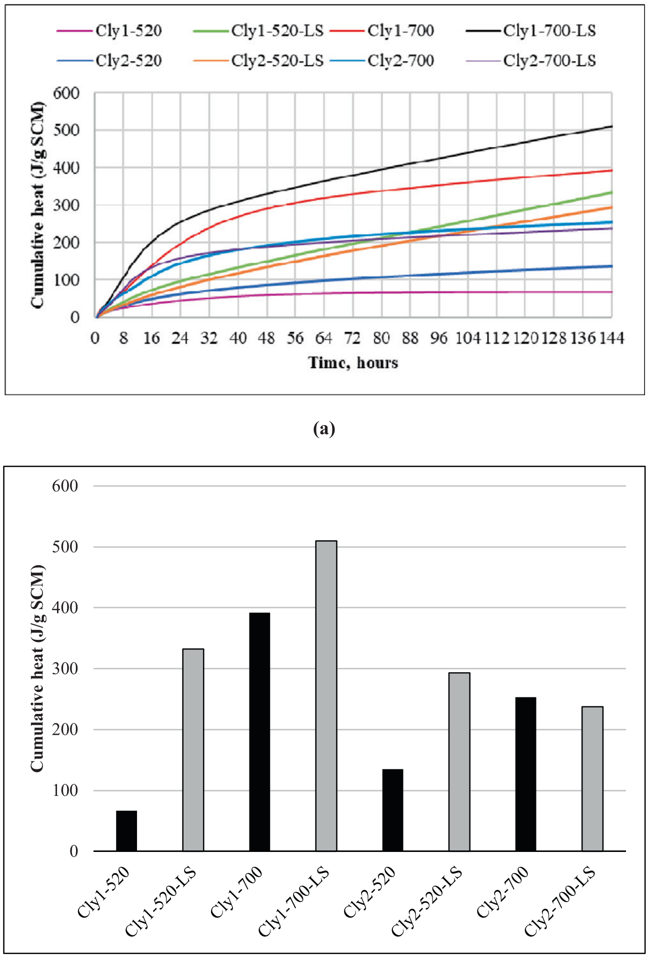
Fig. 6. Lime consumption of lime-clay pastes for a) Cly1 b) Cly2.

hand, carboaluminate formation was found to be limited in Cly1-520-LS and Cly2-520-LS samples at 28 days indicated by smaller corresponding peaks. In addition, the peaks corresponding to calcium carbonate in calcite mineral form were clear for the limestone added pastes referring to its partially inert nature remained after contributing the formation of carboaluminates to some extent.

In published literature, there are some reports emphasizing that dehydroxylation of kaolinite is partially reversible when the metakaolin rests at humid environment [36–38]. Therefore, slight kaolinite peaks detected in XRD patterns of the samples at 28 days could be attributed to formation of kaolinite in limited amounts because of rehydration of unreacted metakaolin after 7 days.

3.5. Water requirement and strength activity

Water/solid ratio (w/s) used for preparation of mortars, water requirement of calcined clays, compressive strength of mortars, and corresponding SAI values are shown in Table 9.

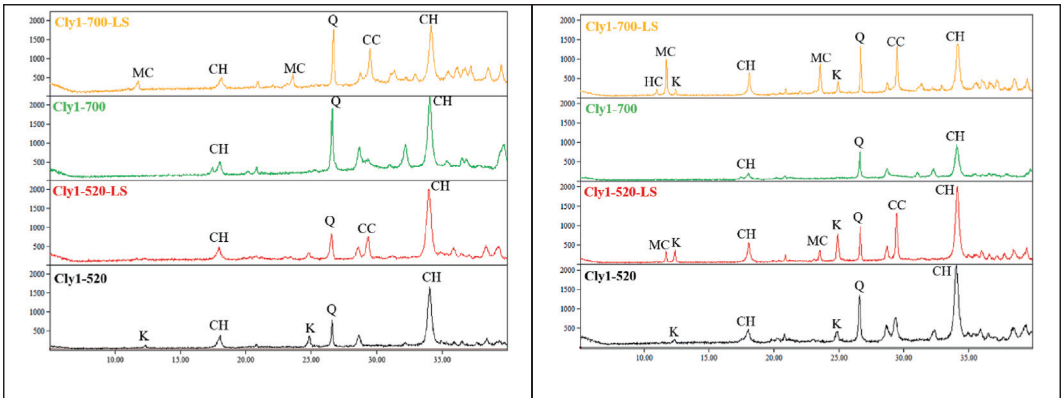


(b)

Fig. 7. a) Heat release, **b)** Cumulative heat at 144 h for lime-calcined clay and lime calcined clay-limestone pastes.

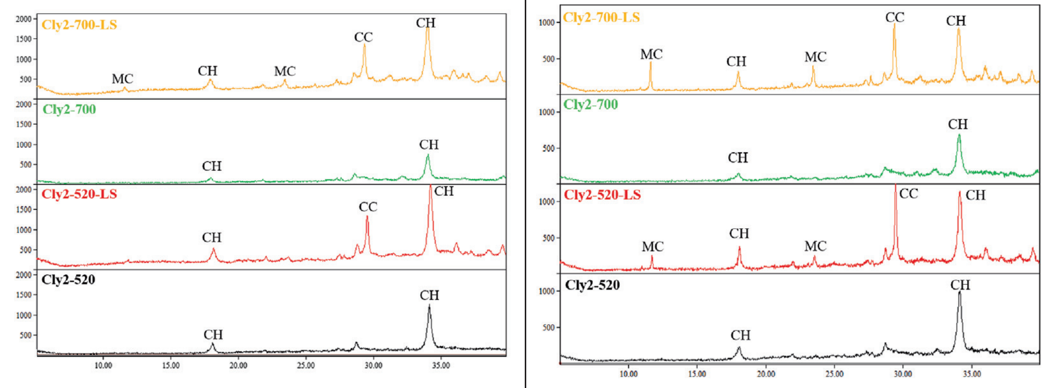
Regarding water requirement of the natural pozzolans, it is seen that the water requirement of all samples used is lower than the limit value (115%) specified by ASTM C618. In all mortars, Cly1 has a lower water requirement than Cly2. The fineness of the material, BET surface of the calcined clay, the type of the major clay mineral, and the degree of dehydroxylation are among the parameters that affect the water requirement [39]. Since the BET surface area of Cly2 is higher than Cly1, it is seen that Cly2 water requirement is also higher. When the calcined clay and calcined clay-limestone powder sample were compared, it was observed that the addition of limestone powder reduced the water requirement. This is probably due closer packing of particles (filler effect) provided by finer particle size of limestone powder (Table 2) as reported elsewhere [40]. In addition, this can also be attributed to the reduction in the weighted specific surface area of the mixture as a result of the addition of limestone powder [41].

SAI values calcined clays with and without limestone addition were between 65.4% and 83.9% at 7 days and 71.4% to 112.1% at 28 days. Considering ASTM C 618 specifying 75% or higher SAI value either at 7 days or 28 days, clays calcined at 520 °C (Cly1-520 and Cly2-520) did not meet the standard requirement in the absence of limestone addition. However, Cly1-700 and Cly2-700 exhibited considerably higher SAI values than their counterparts calcined at 520 °C, which can be associated with higher calcined kaolinite content of the samples treated at 700 °C (Table 6) and



a) Cly1 at 7 days

b) Cly1 at 28 days



c) Cly2 at 7 days

d) Cly2 at 28 days

Fig. 8. XRD patterns of hardened lime-calcined clay pastes, **a)** Cly1 at 7-day **b)** Cly1 at 28 days **c)** Cly2 at 7 days **d)** Cly2 at 28 days (K: kaolinite, CH: calcium hydroxide, Q: quartz, CC: calcium carbonate, HC: hemicarboaluminate, MC: monocarboaluminate).

Table 9
Water requirement and strength activity index of calcined clays.

Mix notation	w/s	Water requirement, %	Compressive strength, MPa		Strength activity index,%	
			7 days	28 days	7 days	28 days
Control	0.48	100	36.8	45.5	100	100
Cly1-520	0.51	105	24.1	33.6	65.5	73.8
Cly1-520-LS	0.50	103	27.1	38.3	73.6	84.2
Cly1-700	0.52	107	28.7	46.5	77.9	102.1
Cly1-700-LS	0.51	104	30.9	51.0	83.9	112.1
Cly2-520	0.54	111	24.9	32.5	67.7	71.4
Cly2-520-LS	0.53	109	27.1	35.5	73.6	78.0
Cly2-700	0.55	113	24.1	38.4	65.4	84.3
Cly2-700-LS	0.53	110	26.8	43.2	72.8	94.9

accordingly with the higher pozzolanic activity indicated by lime consumption and heat releases (Fig. 6 and Fig. 7). Comparing calcined clays Cly1 and Cly2, Cly1 exhibited higher SAI values especially at 28 days which can be attributed to combined effects of a lower water-to-solid ratio (w/s) of the mortars with Cly1 and its relatively higher pozzolanic reactivity as indicated by the lime consumption (Fig. 6). In addition, relatively more pronounced filler effect of Cly1 due to its finer particle size (Table 2) could be the other factor determining higher SAI of Cly1. Regarding the influence of glassy/vitreous phase available in Cly2, which is known as one of the factors affecting the pozzolanic reactivity and strength activity of pozzolans [42,43], variability of w/s in standard strength activity test depending on the water requirement of samples does not allow for a direct comparison between SAI values of Cly1 and Cly2.

The addition of LS increased 7-day and 28-day SAI values of all the calcined clays so that the clays calcined at 520 °C conform the minimum requirement of ASTM C 618. Increases in SAI values of calcined clays with LS addition were approximately 6 to 8 points at 7 days and 7 to 11 points at 28 days, suggesting that LS addition is more influential in enhancing 28-day strength activity of calcined clays. Improvements in SAI values of calcined clays by LS addition can be attributed to combined effects of enhanced particle packing (filler effect) due to finer particle size distribution of LS (Table 3), formation of carboaluminates as additional hydration products filling the capillary pores [44] and improved pozzolanic reactivity of calcined clay in presence of LS (Fig. 6 and Fig. 7).

SAI values of calcined clay-limestone systems are comparable to pozzolans such as fly ash, zeolite, and metakaolin reported in accordance with ASTM C311 standard test methodology [45–47]. In particular, standard water requirement and SAI values of the Cly1-700-LS sample are very competitive when compared to the fly ash, which is one of the widely used SCMs in the world [47–49].

4. Conclusions

The effect of limestone powder addition on pozzolanic reactivity of clays calcined at different temperatures was investigated. The following conclusions can be drawn based on the experimental results:

1. Calcination of raw clays at various temperatures reduced their kaolinite and/or halloysite content by dehydroxylation, and the higher the calcination temperature the lower the kaolinite/halloysite content. Kaolinite and/or halloysite content of Cly1 and Cly2 reduced from 69.7% and 45.2% to 13.9% and 11.0%, respectively, when they are calcined at 700 °C.
2. Cly1 was characterized by XRD in terms of mineralogical composition qualitatively as containing kaolinite in addition to quartz whereas Cly2 composed of kaolinite and halloysite as clay minerals as well as sanidine and glassy phase. Calcinations at 400 °C and 520 °C did not alter the XRD pattens significantly, however 700 °C resulted in almost disappeared kaolinite/halloysite peaks.
3. BET surface area of clays increased in the case of lower calcination temperature (400 °C), however decreased for higher calcination temperatures (520 °C, 700 °C) due to increased level of dehydroxylation.
4. Calcination of raw clays did not alter their morphology substantially as inspected by SEM micrographs. Cly2 was characterized with a clear tubular structure indicating the morphology of halloysite, which is confirmed by XRD analysis.
5. Limestone addition improved the pozzolanic reactivity of calcined clays, contingent on the nature of the clays and calcination temperature, as indicated by increased lime consumption and higher heat released during reactivity in lime pastes. Formation of carboaluminate phases (monocarboaluminate and hemicarboaluminate) in the case of limestone addition was demonstrated in hardened lime pastes by XRD analyses.
6. Limestone addition slightly reduced the water requirement of calcined clays and significantly improved their strength activity indices.
7. It was demonstrated that calcined clays as supplementary cementitious materials have more pozzolanic reactivity and higher strength activity when used with limestone addition. Therefore, calcined clay-limestone binary system as a hybrid supplementary cementitious material for concrete mixtures should be evaluated in further research studies.

CRediT authorship contribution statement

G. Argın: Investigation, Writing - original draft, Visualization. **B. Uzal:** Conceptualization, Methodology, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] R.M. Andrew, Global CO2 emissions from cement production, 1928–2017, Earth Syst. Sci. Data 10 (4) (2018) 2213–2239.
[2] J. Yu, H.-L. Wu, C.K.Y. Leung, Feasibility of using ultrahigh-volume limestone-calcined clay blend to develop sustainable medium-strength Engineered Cementitious Composites (ECC), J. Clean. Prod. 262 (2020) 121343.
[3] F. Avet, K. Scrivener, Influence of pH on the chloride binding capacity of Limestone Calcined Clay Cements (LC3), Cem. Concr. Res. 131 (2020) 106031.
[4] P. Suraneni, J. Weiss, Examining the pozzolanicity of supplementary cementitious materials using isothermal calorimetry and thermogravimetric analysis, Cem. Concr. Compos. 83 (2017) 273–278.
[5] S. Mindess, Developments in the Formulation and Reinforcement of Concrete, Woodhead Publishing, 2008.
[6] C. Ouellet-Plamondon, S. Scherb, M. Koberl, K.C. Thienel, Acceleration of cement blended with calcined clays, Constr. Build. Mater. 245 (2020).
[7] K. Scrivener, F. Martirena, S. Bishnoi, S. Maity, Calcined clay limestone cements (LC3), Cem. Concr. Res. 114 (2018) 49–56.
[8] S. Hollanders, R. Adriaens, J. Skibsted, O. Cizer, J. Elsen, Pozzolanic reactivity of pure calcined clays, Appl. Clay Sci. 132 (2016) 552–560.
[9] A. Parashar, S. Bishnoi, A comparison of test methods to assess the strength potential of plain and blended supplementary cementitious materials, Constr. Build. Mater. 256 (2020) 119292.
[10] F. Zunino, K. Scrivener, Increasing the kaolinite content of raw clays using particle classification techniques for use as supplementary cementitious materials, Constr. Build. Mater. 244 (2020) 118335.
[11] J. Tang, S.F. Wei, W.F. Li, S.H. Ma, P.G. Ji, X.D. Shen, Synergistic effect of metakaolin and limestone on the hydration properties of Portland cement, Constr. Build. Mater. 223 (2019) 177–184.
[12] Q.D. Nguyen, A. Castel, Reinforcement corrosion in limestone flash calcined clay cement-based concrete, Cem. Concr. Res. 132 (2020) 106051.
[13] Y. Dhandapani, T. Sakthivel, M. Santhanam, R. Gettu, R.G. Pillai, Mechanical properties and durability performance of concretes with Limestone Calcined Clay Cement (LC3), Cem. Concr. Res. 107 (2018) 136–151.
[14] C. Rodriguez, J.I. Tobon, Influence of calcined clay/limestone, sulfate and clinker proportions on cement performance, Constr. Build. Mater. 251 (2020) 119050.
[15] F. Avet, K. Scrivener, Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC3), Cem. Concr. Res. 107 (2018) 124–135.
[16] S. Ferreiro, D. Herfort, J.S. Damtoft, Effect of raw clay type, fineness, water-to-cement ratio and fly ash addition on workability and strength performance of calcined clay – Limestone Portland cements, Cem. Concr. Res. 101 (2017) 1–12.
[17] Y. Dhandapani, M. Santhanam, Assessment of pore structure evolution in the limestone calcined clay cementitious system and its implications for performance, Cem. Concr. Compos. 84 (2017) 36–47.
[18] R.E. Grim, R.A. Rowland, Differential thermal analysis of clays and shales, a control and prospecting method, J. Am. Ceram. Soc. 27 (3) (1944) 65–76.
[19] G. Qiu, T. Jiang, G. Li, X. Fan, Z. Huang, Activation and removal of silicon in kaolinite by thermochemical process, Scand. J. Metall. 33 (2) (2004) 121–128.
[20] B.B. Sabir, S. Wild, J. Bai, Metakaolin and calcined clays as pozzolans for concrete: A review, Cem. Concr. Compos. 23 (6) (2001) 441–454.
[21] P. Yuan, D. Tan, F. Annabi-Bergaya, W. Yan, M. Fan, D. Liu, H. He, Changes in structure, morphology, porosity, and surface activity of mesoporous halloysite nanotubes under heating, Clays Clay Miner 60 (6) (2012) 561–573.
[22] M. Yang, X. Liang, L. Ma, J. Huang, H. He, J. Zhu, Adsorption of REEs on kaolinite and halloysite: A link to the REE distribution on clays in the weathering crust of granite, Chem. Geol. 525 (2019) 210–217.
[23] Z. Rozynek, T. Zacher, M. Janek, M. Čaplovičová, J.O. Fossum, Electric-field-induced structuring and rheological properties of kaolinite and halloysite, Appl. Clay Sci. 77–78 (2013) 1–9.
[24] P. Thakur, A. Kool, B. Bagchi, S. Das, P. Nandy, Enhancement of β phase crystallization and dielectric behavior of kaolinite/halloysite modified poly (vinylidene fluoride) thin films, Appl. Clay Sci. 99 (2014) 149–159.
[25] L. Deng, P. Yuan, D. Liu, F. Annabi-Bergaya, J. Zhou, F. Chen, Z. Liu, Effects of microstructure of clay minerals, montmorillonite, kaolinite and halloysite, on their benzene adsorption behaviors, Appl. Clay Sci. 143 (2017) 184–191.
[26] A. Alujas, R. Fernández, R. Quintana, K.L. Scrivener, F. Martirena, Pozzolanic reactivity of low grade kaolinitic clays: Influence of calcination temperature and impact of calcination products on OPC hydration, Appl. Clay Sci. 108 (2015) 94–101.

[27] G. Kakali, T. Perraki, S. Tsivilis, E. Badogiannis, Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity, Appl. Clay Sci. 20 (1–2) (2001) 73–80.

[28] A. Tironi, F. Cravero, A.N. Scian, E.F. Irassar, Pozzolanic activity of calcined halloysite-rich kaolinitic clays, Appl. Clay Sci. 147 (2017) 11–18.

[29] D. Tan, P. Yuan, F. Annabi-Bergaya, D. Liu, L. Wang, H. Liu, H. He, Loading and in vitro release of ibuprofen in tubular halloysite, Appl. Clay Sci. 96 (2014) 50–55.

[30] W. Yu, H. Xu, D. Tan, Y. Fang, E.E. Roden, Q. Wan, Adsorption of iodate on nanosized tubular halloysite, Appl. Clay Sci. 184 (2020) 105407.

[31] Z. Giergiczny, Thehydraulic activity of high calcium fly ASH, J. Therm. Anal. Calorim. 83 (1) (2006) 227–232.

[32] J. Zelić, D. Rušić, D. Veža, R. Krstulović, The role of silica fume in the kinetics and mechanisms during the early stage of cement hydration, Cem. Concr. Res. 30 (10) (2000) 1655–1662.

[33] M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Cement substitution by a combination of metakaolin and limestone, Cem. Concr. Res. 42 (12) (2012) 1579–1589.

[34] L.M.V. Andres, M.G. Antoni, A.A. Diaz, J.F.M. Hernandez, K.L. Scrivener, Effect of fineness in clinker-calcined clays-limestone cements, Adv. Cem. Res. 27 (9) (2015) 546–556.

[35] G. Mishra, A.C. Emmanuel, S. Bishnoi, Influence of temperature on hydration and microstructure properties of limestone-calcined clay blended cement, Mater. Struct. 52 (5) (2019).

[36] J. Rocha, J.M. Adams, J. Klinowski, The rehydration of metakaolinite to kaolinite: Evidence from solid-state NMR and cognate techniques, J. Solid State Chem. 89 (2) (1990) 260–274.

[37] J. Rocha, J. Klinowski, The rehydration of metakaolinite to kaolinite, J. Chem. Soc. Chem. Comm. 8 (1991) 582–584.

[38] N. Ranjbar, C. Kuenzel, J. Spangenberg, M. Mehrali, Hardening evolution of geopolymers from setting to equilibrium: A review, Cem. Concr. Compos. 114 (2020) 103729.

[39] S.E. Schulze, J. Rickert, Suitability of natural calcined clays as supplementary cementitious material, Cem. Concr. Compos. 95 (2019) 92–97.

[40] Y. Knop, A. Peled, Packing density modeling of blended cement with limestone having different particle sizes, Constr. Build. Mater. 102 (2016) 44–50.

[41] J.I. Tobón, O. Mendoza, O.J. Restrepo, M.V. Borrachero, J. Payá, Effect of different high surface area silicas on the rheology of cement paste, Mater. Constr. 70 (340) (2020) e231.

[42] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, Cem. Concr. Compos. 37 (2013) 319–327.

[43] S. Ferreiro, M.M.C. Canut, J. Lund, D. Herfort, Influence of fineness of raw clay and calcination temperature on the performance of calcined clay-limestone blended cements, Appl. Clay Sci. 169 (2019) 81–90.

[44] A.M. Ramezanianpour, R.D. Hooton, A study on hydration, compressive strength, and porosity of Portland-limestone cement mixes containing SCMs, Cem. Concr. Compos. 51 (2014) 1–13.

[45] J. Tangpagasit, R. Cheerarot, C. Jaturapitakkul, K. Kiattikomol, Packing effect and pozzolanic reaction of fly ash in mortar, Cem. Concr. Res. 35 (6) (2005) 1145–1151.

[46] M. Rose-Lam, E. Villar-Cocina, M. Frias, Study on the pozzolanic properties of a natural Cuban zeolitic rock by conductometric method: Kinetic parameters, Constr. Build. Mater. 25 (2) (2011) 644–650.

[47] A. Mardani-Aghabaglou, G.I. Sezer, K. Ramyar, Comparison of fly ash, silica fume and metakaolin from mechanical properties and durability performance of mortar mixtures view point, Constr. Build. Mater. 70 (2014) 17–25.

[48] H. Myadraboina, S. Setunge, I. Patnaikuni, Pozzolanic Index and lime requirement of low calcium fly ashes in high volume fly ash mortar, Constr. Build. Mater. 131 (2017) 690–695.

[49] T.B.T. Nguyen, W. Saengsoy, S. Tangtermsirikul, Effect of initial moisture of wet fly ash on the workability and compressive strength of mortar and concrete, Constr. Build. Mater. 183 (2018) 408–416.