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# Strength and Durability Performance of Mortars Incorporating Calcined Clay as Pozzolan in Comparison with silica fume

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## ABSTRACT

The use of low-grade calcined clays is the only potential material available in large quantities to meet the requirements of eco-efficient supplementary cementitious materials by decreasing the clinker content in blended types of cement or cement content in concrete. In the present paper, six mortar mixtures with a constant w/b ratio were used to investigate the mechanical and durability properties of mixtures substituted with low-grade calcined clays with/without limestone compared to PC and silica fume mixtures. The results show that using calcined clays with low or intermediate purity (i.e., kaolinite content) leads to enhanced durability besides the comparable strength development characteristics compared to PC mortar. In this regard, the addition of 30% calcined clay with/without limestone led to a marked decrease (about 80 and 40%) in chloride ion diffusion coefficient ( $D_a$ ) and an increase in surface chloride content ( $C_s$ ) compared to the reference mixture. In addition, the utilization of calcined clay with a kaolinite content of 56.7% led to a reduction of 52% in  $D_a$  and an increase of 140% in electrical resistivity compared to silica fume binder. The primary reason for the better performance is attributed to the refined pore structure and dense microstructure of the cement paste with the calcined clay pozzolan compared to PC and silica fume.

**Keywords:** Calcined clay; durability; Kaolinite; Limestone; chloride diffusion.

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## 1. INTRODUCTION

The use of supplementary cementitious materials (SCMs) has a high potential to enhance strength characteristics, improve durability issues, reduce carbon emissions, and intact resource utilization in cement and concrete production, especially for developing countries. However, it should be noted that the dilution effect could negatively influence the mechanical properties, particularly at early ages. Additionally, it was reported that the cement industry is responsible for approximately 5–8% of the world's CO<sub>2</sub> emissions [1, 2]. A forward-looking solution and strategy for decreasing CO<sub>2</sub> emissions during the cement manufacturing stage

are reducing the clinker-to-cement ratio by substitution a percentage of supplementary cementitious material as clinker. However, the most replacement value for pozzolans is about 35% and proved to be insufficient to drastically reduce the worldwide carbon emissions from cement production [3]. Today, in cement manufacturing, more than 80% of the supplementary cementitious materials for replacement of cement clinker are: limestone, fly ash, or slag [4]. It was also reported that the substitution of slag and fly ash, regardless of their quality, has particular problems [4]. Regarding limestone, it has been reported that adding more than 10% limestone to

cement leads to increased porosity and reduced durability [5]. In the case of natural reserves of pozzolans as an alternative choice, it can be stated that reserves of natural pozzolans (i.e. volcanic ash or zeolite tuffs) are not widely distributed everywhere, and they are only available in certain regions of the earth [6]. Therefore, their transportation for use in the cement and concrete industry, especially for long distances, creates a great economic and environmental burden. Therefore the development of new cement-based materials with the evaluation of pozzolanic activity is always of interest. In addition, there is also a shift and tendency to seek alternative SCM sources due to supply-and-demand concerns in the future. In this context, one of the most promising alternative sources for cement substitution is calcined clays since they have not yet reached their full potential. The clay reserves with poor or medium purity in the world are abundant and widespread. Therefore transportation costs for the production of cement are often reduced considerably no matter other benefits like energy saving [3]. The use of supplementary cementitious materials (SCMs) has a high potential to enhance strength characteristics, improve durability issues, reduce carbon emissions, and intact resource utilization in cement and concrete production, especially for developing countries. However, it should be noted that the dilution effect could negatively influence the mechanical properties, particularly at early ages. Additionally, it was reported that the cement industry is responsible for approximately 5–8% of the world's CO2 emissions [1, 2]. A forward-looking solution and strategy for decreasing CO2 emissions during the cement manufacturing stage are reducing the clinker-to-cement ratio by substitution a percentage of supplementary cementitious material as clinker. However, the most replacement value for pozzolans is about 35% and proved to be insufficient to drastically reduce the worldwide carbon emissions from cement production [3]. Today, in cement manufacturing, more than 80% of the supplementary cementitious materials for replacement of cement clinker are: limestone, fly ash, or slag [4]. It was also reported that the substitution of slag and fly ash, regardless of their quality, has particular problems [4]. Regarding limestone, it has been reported that adding more than 10% limestone to cement leads to increased porosity and reduced durability [5]. In the case of natural reserves of pozzolans as an alternative choice, it can be stated that reserves of natural pozzolans (i.e. volcanic ash or zeolite tuffs) are not widely distributed everywhere, and they are only available in certain regions of the earth [6]. Therefore, their transportation for use in the cement and concrete industry, especially for long distances, creates a great economic and environmental burden. Therefore the development of new cement-based materials with the evaluation of pozzolanic activity is always of interest. In addition, there is also a shift and tendency to seek alternative SCM sources due to supply-

and-demand concerns in the future. In this context, one of the most promising alternative sources for cement substitution is calcined clays since they have not yet reached their full potential. The clay reserves with poor or medium purity in the world are abundant and widespread. Therefore transportation costs for the production of cement are often reduced considerably no matter other benefits like energy saving [3]. Based on data available in the literature, calcined clays from different locations in the world have been largely studied [4, 10, 26-29]. It was demonstrated that even calcined clay with kaolinite content of less than 50% is suitable for usage in ternary systems, including calcined clay with limestone (LC3) [12,30], and possesses 16% to 30% less CO2 footprint [31]. It was reported that the addition of calcined clay results in an increased hydration degree of clinker at early ages. However, the ultimate hydration degree of the clinker would be the same or lower than that of the PC mixture [8,32-34]. Clay deposits are usually composed of a mixture of different clay minerals (kaolinite, illite, montmorillonite, etc.) and a large proportion of impurities of non-clay materials such as quartz, mica, feldspars, calcite, anatase, and sulfides. The pozzolanic reactivity of calcined clays depends mainly on the type and amount of clay minerals (especially kaolinite content) in the raw material (which is also directly related to the SiO2 and Al2O3 content) and the degree of structural disorder resulting from thermal activation, the amount of thermal activation temperature and conditions governing the heating and cooling process [19]. The chemical reactions involved when calcined clays are used as a replacement for cement in concrete have been discussed in the previous study [15]. The preliminary reaction is between the AS2 and the CH produced from cement hydration. As a result of this reaction, cementitious aluminum-containing CSH gel, accompanied by crystalline products, which include calcium aluminate hydrates and aluminosilicate hydrates (i.e. C4AH13, C2ASH8, and C3AH6) is formed. Besides, the utilization of SCMs with high alumina content leads to an increase in the chemical chloride binding capacity of binders [15, 35-36], reduced permeability [18, 37], and lower chloride ions diffusion [37-38]. The results of different experimental studies showed that concrete made with LC3 binder has a lower chloride ions diffusion coefficient than Portland cement mixtures, leading to excellent resistance to chloride ingress [11-12,23,39-40]. This study reports a detailed investigation of the influence of four low and intermediate available calcined clays with or without limestone as a replacement for cement on mortar mixtures' mechanical and durability properties. The level of four grades of calcined clay and limestone in cement replacement was fixed at 30% and 15% by weight, respectively, based on the results of previous investigations [7-8, 20]. Properties, including compressive strength, water, and chloride-ion permeability, as well as electrical resistivity and

carbonation resistance, were investigated. The results of this study might help to get more knowledge about the influence of kaolinite content on the durability of calcined

clay pozzolan in comparison with silica fume and indicate the potential of low-grade or moderate-grade calcined clays to produce durable mixtures.

## 2. MATERIALS AND METHODS

### 2.1. MATERIALS AND CHARACTERIZATION

Four natural clays were used as raw materials. X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) determined the chemical and mineralogical composition. XRD data were collected on Philips PW 1050 diffractometer using Cu-Ka graphite-monochromatized radiation ( $k = 1.5418 \text{ \AA}$ ). Measurements were carried out in the  $2\theta$  range  $5\text{--}40^\circ$ . In order to determine the kaolinite

content of calcined clays, thermo gravimetric analysis (TGA) using the tangent method [41] (Eq. 1) was used on raw and calcined materials according to Table 1.

$$\text{Kaolinite content (\%)} = \text{Mass loss due to dehydroxilation (\%)} \times \frac{258}{36} \quad (1)$$

**Table 1.** Chemical and mineralogical composition of the materials.

Oxides (wt-%)	KZ-1	KZ-2	KG-1	KG-2	Portland cement (PC)	Silica fume (SF)	Limestone (LS)
SiO <sub>2</sub>	64.0	73.0	63.0	63.5	20.7	92.1	12.4
Al <sub>2</sub> O <sub>3</sub>	25.5	14.0	24.5	12.1	4.0	0.3	1.8
Fe <sub>2</sub> O <sub>3</sub>	0.3	0.4	0.7	5.0	4.1	0.2	2.1
CaO	0.8	1.0	4.0	1.3	63.2	0.9	40.5
MgO	0.3	0.3	0.4	1.9	1.5	1.2	5.3
SO <sub>3</sub>	-	-	-	-	2.2	0.3	-
Na <sub>2</sub> O	0.3	0.3	0.3	0.2	0.5	-	-
K <sub>2</sub> O	0.4	0.4	0.4	2.6	0.4	-	-
TiO <sub>2</sub>	0.04	0.04	0.04	0.05	-	-	-
L.O.I	6.5	7.1	8.0	8.6	1.5	1.6	37.9
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>	89.8	87.4	88.2	80.6	-	-	-
<b>Mineralogical composition of raw clays (%)</b>							
Kaolinite	56.7	28.3	40	12.8	-	-	-
Quartz	24.2	42.5	28.5	28.1	-	-	-
Anatase	0.7	0.5	0	0	-	-	-
Calcite	1.2	1.5	0	0	-	-	-
Muscovite	8.4	5.0	20.7	29.4	-	-	-
Illite	0	0	3.7	21.3	-	-	-
Amorphous	8.8	21.8	7.1	8.4	-	-	-
C <sub>3</sub> S	-	-	-	-	61	-	-
C <sub>2</sub> S	-	-	-	-	13	-	-
C <sub>3</sub> A	-	-	-	-	4	-	-
<b>Physical properties of calcined clays</b>							
Specific gravity	2.7	2.7	2.8	2.8	3.1	2.2	-
BET specific surface (m <sup>2</sup> /g)	4.6	4.0	3.4	3.6	0.9	-	1.2
<b>Particle size distribution</b>							
d <sub>10</sub> (μm)	1.3	1.8	3.1	4.4	-	-	-
d <sub>50</sub> (μm)	4.3	5.8	47	62.5	-	-	-
d <sub>90</sub> (μm)	97.5	150	233	252	-	-	-

The cement used was Portland cement, equivalent to ASTM Type II. Silica fume (SF) obtained from Azna ferrosilicon alloy manufacture was used for comparison purposes with calcined clay mixtures. The results of the

chemical composition for all cementitious materials are presented in Table 1. It must be noted that the four clays used in this study before the thermal treatment meet the chemical requirements stated in ASTM C618 for Class N

pozzolan. In this study, according to kaolinite contents of clays, KG-1 (12.8%) and KZ-2 (29%) have been regarded as low-grade calcined clays, and KG-1 (40%) and KZ-1 (56.7%) classified as moderate calcined clays, respectively. Figure 1 shows the X-ray diffraction (XRD) spectra of four clays, and the mineralogical species are identified. For three clays, XRD patterns display distinct peaks of kaolinite (K) and quartz (Q), accompanied by a weak main peak of illite (I). As can be seen, the intensity of the peaks determined to kaolinite decreases from KZ to

KG-clay and agrees well according to the kaolinite content of the raw clays, according to Table 1. Additionally, there is no peak attributed to kaolinite at the KG-2 specimen. Instead, a peak located around  $2\theta=9^\circ$  is attributed to illite. TG and DTG curves for the four raw clays are presented in Figure 2. Mass loss in the range of 30–180°C can be accompanied by drying of the adsorbed water. Dehydroxylation of kaolinite, including the removal of the OH groups from kaolinite, occurs at about 400–650°C range.

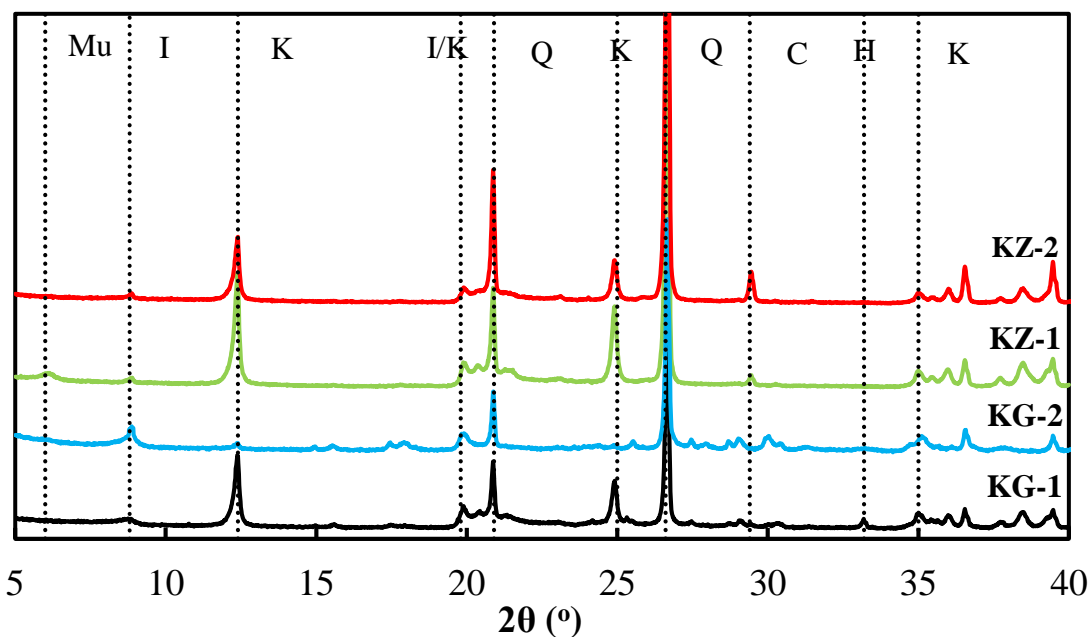


Figure 1. XRD spectra for natural raw clays used (K: Kaolinite, C: Calcite, Mu: Muscovite, I: Illite, Q: Quartz).

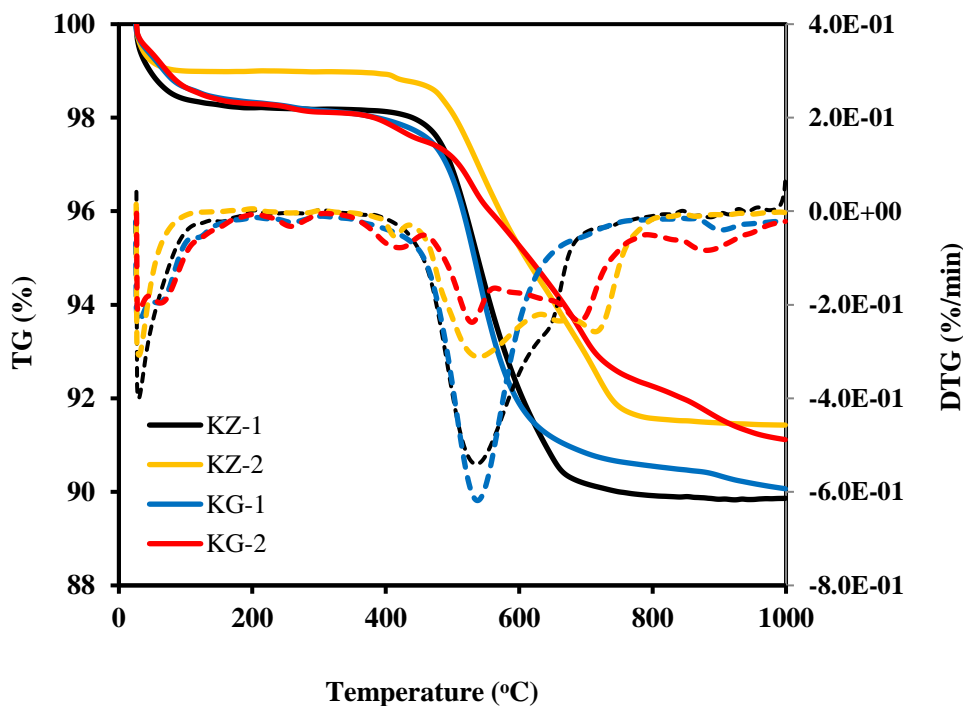
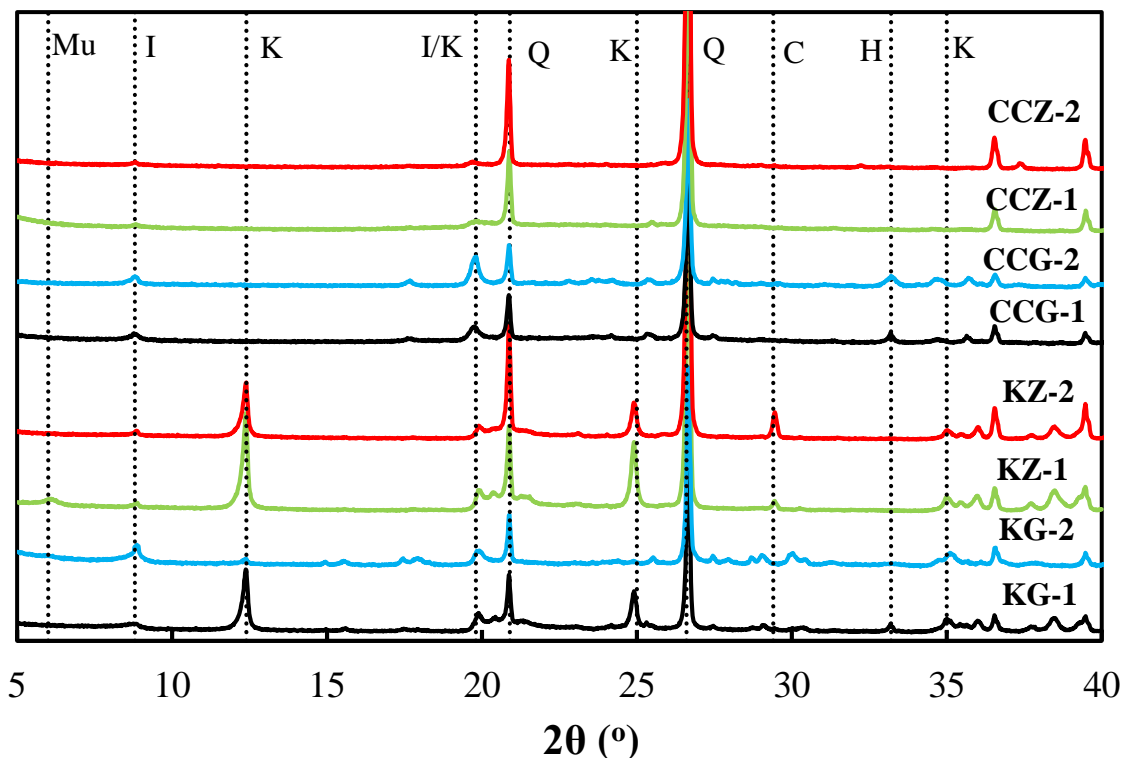


Figure 2. TG and DTG curves of raw clays.

## 2.2. THERMAL TREATMENT AND CHARACTERIZATION OF CALCINED CLAYS

The thermal treatment of clays was carried out in a programmable laboratory furnace. The four clays were heated from ambient temperature up to 800°C, a recommended temperature that transforms kaolinite into an amorphous phase [8], and then remained for 60 min at 800°C. Subsequently, specimens were cooled down rapidly by removing the crucibles from the furnace and spreading the material on a steel plate at laboratory temperature (23±2)°C. As a result, four types of KZ calcined clay (CCZ-1 and CCZ-2) and KG calcined clay (CCG-1 and CCG-2) were obtained. XRD patterns of calcined clays (Figure 3) indicate that peaks corresponding

to kaolinite disappeared completely for KZ and KG patterns, confirming that heating raw materials at the temperature of 800°C for 60 minutes is sufficient to complete the kaolin transformation to an amorphous material in these clays. It should be noted that in accordance with the KG-2 specimen with the main illite peak, the calcination temperature is not enough to decompose the crystalline structure of illite, which would be why the peaks do not disappear after the thermal treatment. Additionally, specific surface, particle size distribution, and bulk density were measured and presented in Table 1.



**Figure 3.** XRD spectra for natural raw clays (KG&KZ) and calcined clay (CCG&CCZ) used (K: Kaolinite, A: Amorphous, C: Calcite, Mu: Muscovite, I: illite, Q: Quartz).

The particle size distribution was determined by Malvern Mastersizer 2000 laser particle size analyzer, and the  $d_{90}$ ,  $d_{50}$ , and  $d_{10}$  diameters were calculated and presented in Figure 4 and Table 1. Nitrogen surface area measurements are performed on four calcined clay specimens by a BET sorptometer (model: Bellsorp-miniII) and reported in Table 1. As can be seen in Figure 4, CCG (type of KG calcined clay) used in this study included a larger amount of coarser particles than CCZ (type of KZ calcined clay). Subsequently, CCZ showed higher cumulative particle passing from 1µm to 100µm. Therefore CCZ presented

lower  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  in comparison with CCG. Based on results obtained here, it was shown that both calcined clays, although classified as coarse calcined clays [42], still meet the fineness requirement according to ASTM C618, which is less than 34 wt.% of particle retained on 45µm sieve for use as SCM in concrete. It should also be noted that compressive strength, especially at an early age, will considerably improve with finer calcined clay PSD in comparison with the coarser PSD. It was also revealed that finer PSD leads to higher pore refinement and a lower total porosity in comparison with coarse PSD [42].

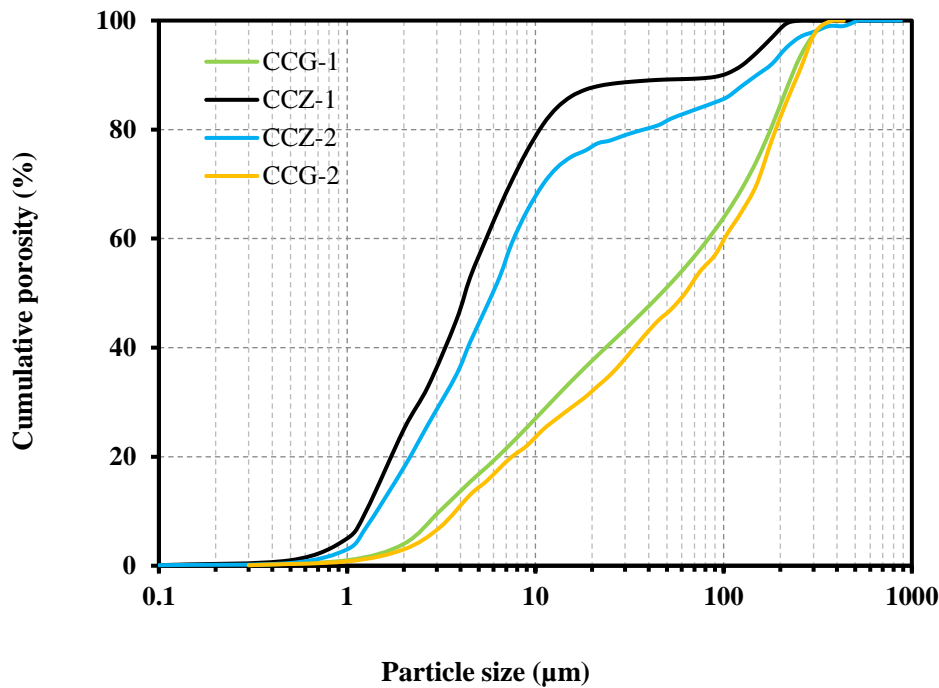


Figure 4. Particle size distribution of calcined products.

### 2.3. POZZOLANIC ACTIVITY

The pozzolanic activity of calcined clays depends on different parameters, including the type and amount of clay minerals (i.e. kaolinite, illite, or montmorillonite), the nature and amount of impurities, the thermal treatment (temperature and the time of heating used for its activation) and the specific surface. In the present study, the

pozzolanic activity of calcined clay was determined with two different methods: 1) Compressive strength in mortars made with a blend of PC–pozzolan according to ASTM C311 and 2) The measurement of pozzolanic activity, lime binding capacity, correspond to thermo-gravimetric analysis.

#### 2.3.1. STRENGTH ACTIVITY INDEX (SAI)

In the strength activity index method according to ASTM C618 and ASTM C311, for the assessment of pozzolanic reactivity by compressive strength in mortars cubes (50×50×50 mm<sup>3</sup>) including pozzolan, two types of mortars were used. In this regard, the strength index is specified as the ratio of compressive strength for mortar with 20% pozzolan substitution to the compressive strength of PC mortar. Reference mortar (PC mortars) cubes were prepared using a normal Portland cement (PC) with a chemical composition presented in [Table 1](#). It should be noticed that for the control mortar, w/b is 0.485, whereas, for the mortar with pozzolan replacement, the water content is adjusted to result in the same consistency

(flow) as the reference mortar. The cube specimens were demolded after 24 h and immersed in saturated lime water at 20 ± 1°C until test time. At 7, 28, and 90 days, the compressive strength was determined. The strength activity index (SAI = (A/B)×100) was calculated as the ratio of the compressive strength of PC-pozzolan mortar (A) to the strength of the reference mortar (B) at the same age as a percentage. According to ASTM C618, the intended pozzolan is active when SAI is greater than 75% at 28 days. The results of the compressive strength index related to mortar specimens incorporating four intended calcined clays are shown in [Table 2](#).

Table 2. Strength Activity Index of standard mortar with KZ and KG calcined clays according to the ASTM C618.

Type of clays	w/b	Strength Activity Index (%), 7days	Strength Activity Index (%), 28days	Strength Activity Index (%), 90days
KZ-1 (56.7%)	0.51	80	84	106
KZ-2 (28.3%)	0.50	74	76	80
KG-1 (40.0%)	0.49	76	78	85
KG-2 (12.8%)	0.49	65	70	72

Based on results obtained from [Table 2](#), at the early age of 7 days, replacing PC with 20% calcined clays was found to reduce the compressive strength in comparison to the reference mortar. This could be attributed to the dilution effect and delayed onset of the pozzolanic reaction of calcined clays with Ca(OH)<sub>2</sub>. It was shown that values for the strength activity index of four intended calcined clay were lower than 1.0 after 28 days of curing. It means that the compressive strengths at 7 and 28 days for all four calcined clays are still lower than for the PC. Irrespective of coarse PSD for both calcined clays, it is likely the number of hydration products formed through the

pozzolanic reaction did not yet compensate for the dilution effect. The results of this test confirm that higher kaolinite content led to higher pozzolanic activity. After 90 days, KZ-1 calcined clay is the only one that has an SAI greater than 1, while the other calcined clays presented an SAI lower than 1.0, indicating that the contribution of pozzolanic reaction cannot compensate for the reduction of cementitious materials. Regarding low kaolinite content and low activity index obtained for KZ-2 and KG-2 calcined clays, these two clays were not used for mechanical and durability assessment in follow.

### 2.3.2. THERMO-GRAVIMETRIC ANALYSIS (LIME BINDING CAPACITY)

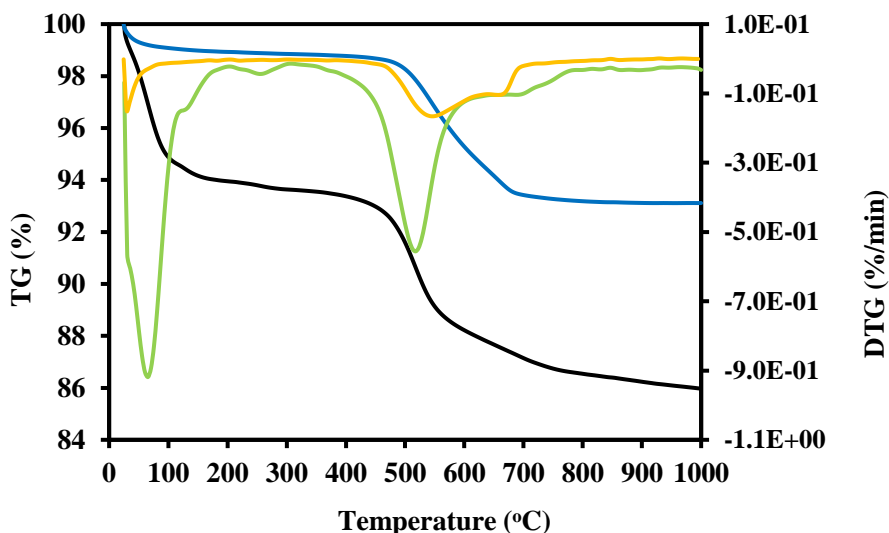
This method is based on the thermal decomposition of crystalline calcium hydroxide in a temperature range of 400–500°C to calcium oxide and water. In this study, the mixtures of calcined clay and hydrated lime were dry-mixed in a 1:1 weight ratio using a Turbula mixer for 4 h. Distilled water was added to obtain a water/solid ratio of 1:1. The mixtures were then stored in sealed containers for 7 days at the temperature of 50°C and 90% humidity [43]. The Ca(OH)<sub>2</sub> consumption over time was monitored by thermo-gravimetric analysis (TGA), using a Netzsch STA-449 C Jupiter, by calculating the mass loss in the range of 350–600°C. [Figure 5](#) indicates TG/DTG curves of lime–

pozzolan mixtures related to both calcined clays (KZ-1 and KG-1). As can be seen, the thermo-grams indicate the thermal decomposition of Ca(OH)<sub>2</sub>, which has not contributed to the pozzolanic reaction. The exothermic peaks located below 250°C are possibly attributed to the release of water adsorbed on the surface and in the interlayer region of expandable clays. Second exothermic peaks in DTG curves at about 450–550°C are attributed to the decomposition of Ca(OH)<sub>2</sub>. In order to calculate the mass loss of Ca(OH)<sub>2</sub> for two specimens, first the mass of Ca(OH)<sub>2</sub> that is converted to CaO and H<sub>2</sub>O can be calculated from TGA curves according to Eq.2.

$$Ca(OH)_{2,measured} = (Mass\ loss\ between\ 400 - 500^{\circ}C) \times \frac{74}{18} \tag{2}$$

By subtracting this amount from the initial mass of Ca(OH)<sub>2</sub>, the final amount of Ca(OH)<sub>2</sub> consumed in the pozzolanic reaction will be calculated easily. Furthermore, by this method, the pozzolanic activity number can be estimated according to [Table 3](#). It can be seen from [Figure 5](#) that the partial consumption of portlandite by the pozzolanic reaction is confirmed for two calcined clay. As

can be seen in [Figure 5](#), the higher rate of Ca(OH)<sub>2</sub> consumption is measured for KZ (56.7%), and the pozzolanic activity of clays shows a good correlation with the kaolinite content and SAI ratio. It was observed that KZ-1 (56.7%) with higher kaolinite content indicated higher pozzolanic activity rather than KG-1 (40.0%).



**Figure 5.** Time derivative of the mass loss as a function of the increasing temperature obtained by TGA analysis of calcined clays.

**Table 3.** Results of thermo-gravimetric measurements.

Type of calcined clay	Pozzolanic activity, Ca(OH) <sub>2</sub> consumption (%)
KZ-1 (56.7%)	64.3
KG-1 (40.0%)	50.0

**2.4. MIXTURE PROPORTIONS**

The experiments were performed on six mortar mixtures, including a binary blended binder consisting of 70% of Portland cement + 30% calcined clay in CCZ (56.7%) and CCG (40.0%) mixtures and 55% Portland cement + 30% calcined clay + 15% limestone powder as filler in L15CCZ30 (56.7%) and L15CCG30 (40.0%). A control mixture with no Pozzolan and a mixture including 8% silica fume as the comparison was also made. All six mixtures were proportioned to have the same cementitious materials content of 400 kg/m<sup>3</sup>, and the water-to-binder ratio (w/b) was adopted to 0.40. The total fine aggregate content was 1600-1650 kg/m<sup>3</sup>, and a polycarboxylate ether-based high-range water reducing agent (HRWRA) complied with ASTM C494 was used to adjust the flow ability of mixtures to a target flow of about 120±20 mm

according to ASTM C1437 method. The details of the mixture proportions of mortars and the flow values are presented in Table 4. To prepare the mortars, a horizontal pan mixer was used. In this regard, in the first step, whole materials, including aggregate and cement with SCMs mixed for 2 min. In the second step, water, in addition to a portion of HRWRA added to the mixer for 2 min, and in the third step adjusted, the flow ability of mixtures was by adding HRWRA. Once the fresh mortar properties were found to be acceptable, the specimens were cast in steel molds and consolidated with a vibration table. After the specimens were mixed, they were left in molds for 24 h. All mortar specimens were demolded after 24 hours and then were cured in water saturated with calcium hydroxide at (23 ±1)°C for 28 days.

**Table 4.** Mixture proportions of fresh mortars

Mixtures	Percent of Cementitious materials substitution					w/b	Sand (kg/m <sup>3</sup> )	Superplasticizer (%)	Flow of mixtures (mm)	Air content (%)
	Cement (%)	KZ (%)	KG (%)	SF (%)	LS (%)					
PC	100	0	0	0	0	0.4	1631	0.83	167	4.8
SF8	92	0	0	8	0	0.4	1623	0.75	151	4.8
CCZ30(56.7%)	70	30	0	0	0	0.4	1603	0.75	128	4.7
CCG30(40.0%)	70	0	30	0	0	0.4	1608	0.85	120	5
L15CCZ30(56)	55	30	0	0	15	0.4	1617	0.80	122	5
L15CCG30(40)	55	0	30	0	15	0.4	1622	0.80	129	5.1

**2.5. TEST METHOD**

The freshly mixed mortar was tested for air content according to ASTM C185 and flow according to ASTM C1437. The mortars were tested for compressive strength, water absorption, electrical resistivity, rapid chloride penetration, accelerated chloride penetration, and carbonation depth in the following. (1) *Compressive strength*: Three concrete cubes of 10×10×10 cm dimension of each mixture were tested for compressive strength after 28 days of curing with a loading rate of 0.5 N/mm<sup>2</sup>/s. (2) *Water absorption*: A water absorption test was carried out according to BS 1881-122 on three specimens of each mortar mixture. In this regard, the specimens were initially cured for 28 days and then oven-dried until aimed to constant weight at the temperature of 105°C. The increase in mass resulting from immersion in water for 24 hours, as a percentage of the mass of the dry specimen, is according to the percentage of water absorption. (3) *Electrical resistivity*: The electrical

resistivity of mortar mixtures was evaluated by Wenner 4-probe resistivity meter on the lateral surface of saturated cylindrical specimens of 100mm diameter and 200mm height. The cylindrical specimens were removed from the saturated lime water, and then their lateral surface, where the readings will be performed there, was wiped with a dry cloth, and then the measurements were performed immediately. (4) *Resistance to chloride ingress*: The resistance to chloride ingress was evaluated using two different tests. The rapid chloride penetration test (RCPT), according to ASTM C1202, was adopted in the first step to obtaining qualitative criteria of the mortar's resistance to chloride ingress at 28 days' age. In the second step, accelerated chloride penetration, according to NT Build 443, was also adopted to estimate the diffusion coefficient of the mortar. For the RCPT test, a specimen with 50 mm thickness is cut from 100 mm (diameter) × 200 mm cylindrical mortar specimen. After the vacuuming process,



According to the instruction proposed in the standard, the specimen is placed in the test device, and the total charge passed is determined for each mixture. For accelerated chloride penetration, a 100 mm thick specimen is cut from a 150mm (diameter) × 300mm cylindrical mortar specimen after 28 days of curing. The slices were sealed with epoxy resin coating on all sides except the top surface to simulate one-dimensional diffusion. The slices were immersed in NaCl solution with a concentration of 165 g/l. After an exposure period of 90 days, the specimens were removed from the NaCl solution, and mortar powder was obtained according to the method described elsewhere [44-45]. The powder from each ground layer was collected and analyzed separately according to ASTM C1152 and ASTM C114 for measuring acid-soluble chloride content. The resulting output of the test is a plot of chloride concentration versus depth from the exposed surface.

### 3. RESULTS AND DISCUSSION

#### 3.1. COMPRESSIVE STRENGTH

The compressive strength of different mortar mixtures is presented in Figure 6. The compressive strength of all mixtures varied between 32MPa and 65MPa after 28 days of curing. At the age of 90 days, there is a continuous improvement in the compressive strength performance of all the mixtures. As can be seen in Figure 6, at 7, 28, and

Apparent diffusion coefficient ( $D_a$ ) and surface chloride concentration ( $C_s$ ) were determined for each mixture by fitting profiles of chloride concentration versus depths according to Fick's second law of diffusion [46]. (5) *Carbonation resistance*: In order to determine the depth of carbonation, the 100mm (diameter) × 200mm cylindrical mortar specimen is used. For this purpose, five-cylinder mortar specimens, after 28 days of water curing, were dried at a temperature of 105°C for 7 days before exposure to CO<sub>2</sub>. After preconditioning, the specimens were placed in an accelerated carbonation chamber for 3 months. The accelerated carbonation environment was set with a temperature of 23±2°C, relative humidity of 70±5%, and a CO<sub>2</sub> concentration of 3.5%. After the accelerated carbonation process, the cylinders are split, and the phenolphthalein indicator is sprayed onto the split faces of the cylinders from the plain face.

90 days, the mixture containing the type of KZ-1 calcined clay (CCZ30) with kaolinite content of 56.7%, and the control mixture exhibited comparable compressive strength but lower than the mixture containing 8% silica fume.

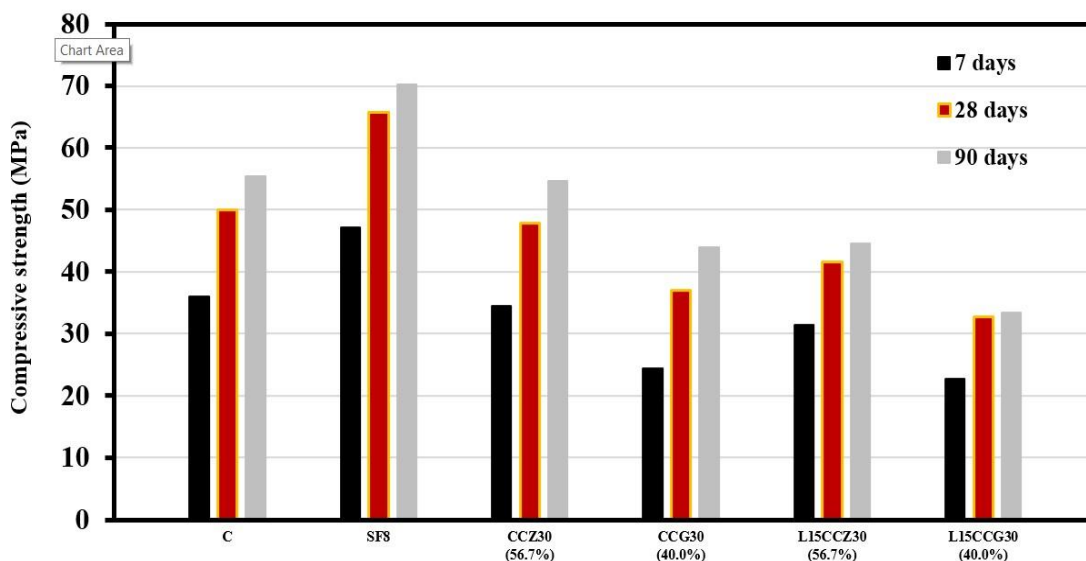


Figure 6. Compressive strength of control and calcined clay mortar specimens.

According to the normalized compressive strength results indicated in Figure 7, the relative compressive strengths of CCZ30 (56.7%) and CCG30 (40%) mixtures were 96% and 68% after 7 days of curing, while the relative compressive strength of these mixtures increased slightly to the 99% and 79% after 90 days of curing. This increase is attributed to the superiority of pore refinement and improvement of microstructure due to pozzolanic reactions of calcined clays rather than the negative dilution effect. In addition, the 7, 28, and 90-day compressive strength of CCG30 (40%), the calcined clay with lower

pozzolanic activity and greater particle size, is lower than CCZ30 (56.7%), about 20-29%. In fact, the reduction of kaolinite content and somewhat increase in particle size led to a reduction of compressive strength. Adding 15% limestone with specifications corresponding to Table 1 led to a reduction of compressive strength. In this regard, the two mixtures with 15% limestone exhibited a reduction in strength between 11% and 13% compared to those without limestone. As can be seen in Figure 7, regarding L15CCZ30 (56.7%) and L15CCG30 (40%), the relative compressive strengths were reduced by increasing curing

time from 87% to 80% and 63% to 60%, respectively. In this case, despite some documents [11-12], pore refinement due to pozzolanic reaction in addition to the reaction between alumina-containing phases with

limestone powder could not compensate negative dilution effect, and as result, relative compressive strength was reduced slightly.

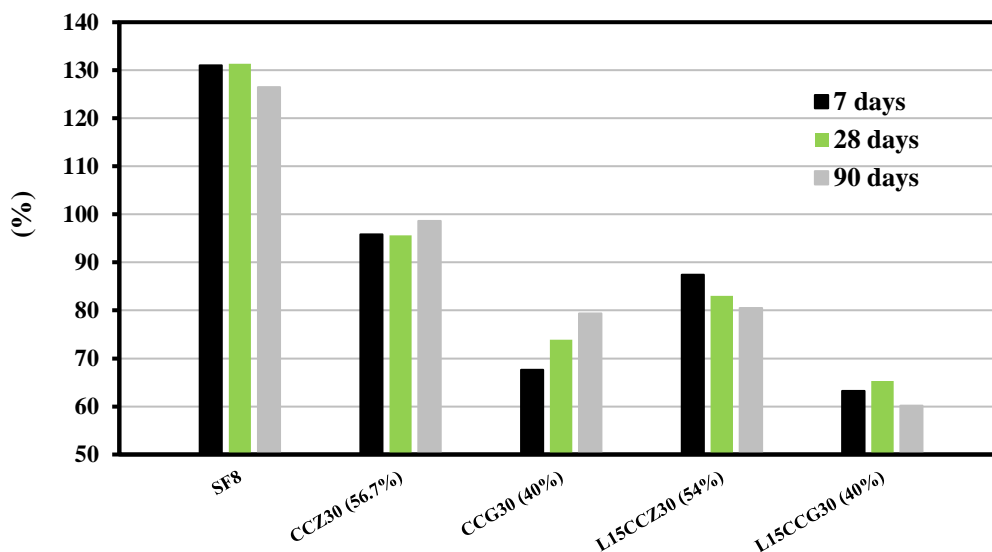


Figure 7. Compressive strength of mixtures normalized to the compressive strength of PC mixture

### 3.2. WATER ABSORPTION

The results of water absorption related to mortar specimens are presented in Figure 8. It can be seen that both the SF8 and CCZ30 (56.7%) mortar mixtures displayed a lower amount of water absorption compared to the control. This event may be attributed to the fact that the hydration products formed by the pozzolanic reaction in mixtures, including calcined clay, are deposited in the pores, and as a result, these mixtures contain fewer interconnected pores compared to the control mixture. According to Figure 8, the CCZ30 (56.7%) mixture exhibits the lowest amount of water absorption after the SF8 mixture, and the mortar containing the type of KG-1 calcined clay with and without limestone has higher water absorption values among all mixtures. The results display that substitution of 30% type of KZ-1 calcined clay, with

56.7% kaolinite content, reduces the amount of water absorption by about 34% compared to the control mixture. Additionally, due to the greater pozzolanic activity of CCZ30 (56.7%) than CCG30 (40%) (See Table 3), the water absorption values of CCZ30 (56.7%) were less than CCG30 (40%) mixture. It is worth mentioning that for both types of calcined clay, the addition of limestone has increased the amount of water absorption due to the negative dilution effect. It should be noted that drying the mixtures, including limestone, in 105°C according to the proposed method of BS 1881-122, could change the hydrated cement system with the presence and stability of formed ettringite and leads to an error in the evaluation of permeability [11].

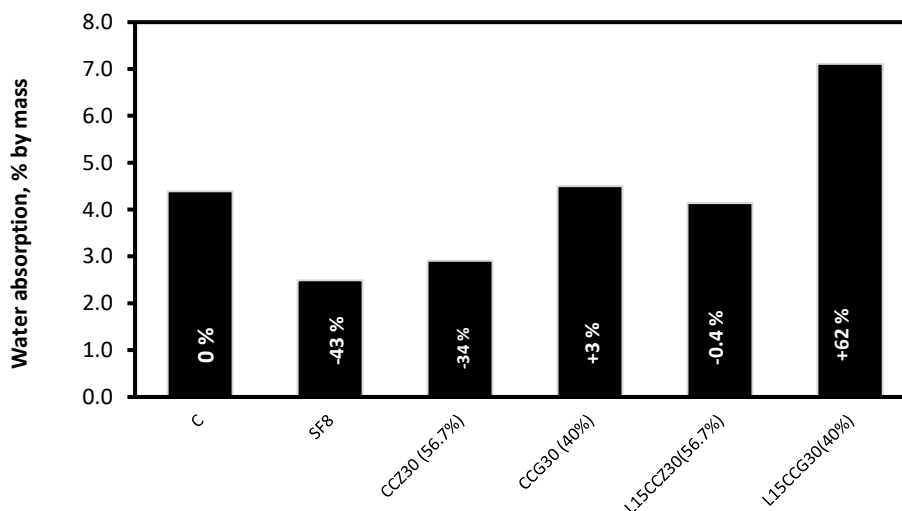


Figure 8. Water absorption of control and calcined clay mortar samples (28-day curing).

### 3.3. ELECTRICAL RESISTIVITY

Generally, electrical resistivity represents the interconnectivity of pores in the cement paste and has strong positive correlation with the resistance to ionic ingress. Given this assumption, [Figure 9](#) indicates the values of surface resistivity of all the mortar mixes studied at 7, 14, 21, and 28 days. As can be seen, in all the mixtures, the results show that the CCZ30 (56.7%) specimen indicates higher electrical resistance than other mortar mixes. As shown in this figure, all mortar mixtures

increased electrical resistivity irrespective of the type of pozzolan used in mixes. Additionally, an increase in resistivity occurred with increasing age. At all ages, it is obviously shown that the electrical resistivity of the mortar mixtures with the type of KG-1 calcined clay (with or without limestone) was lower than those recorded for the type of KZ-1 calcined clay (CCZ30 and L15CCZ30 mortars with the same replacement level.

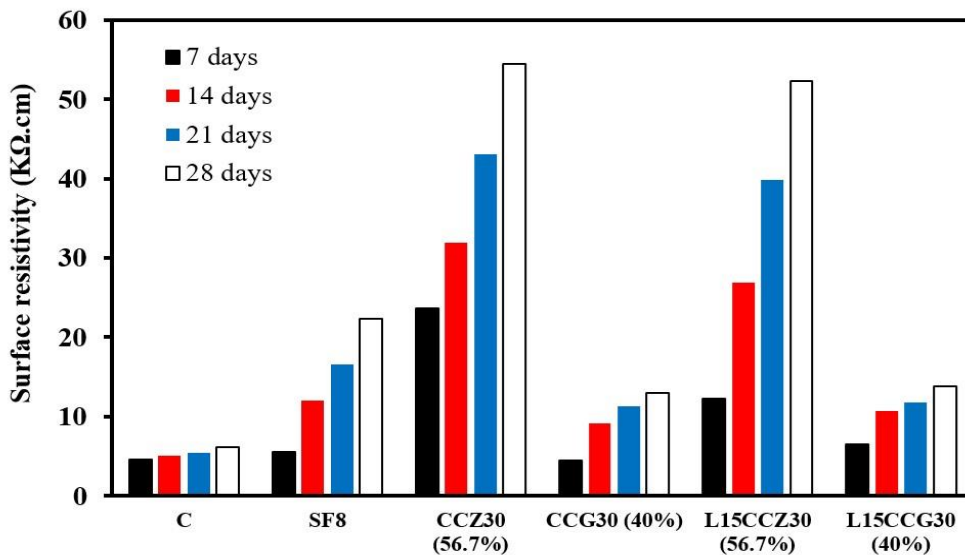


Figure 9. Surface resistivity of control and Calcined clay mortar at 7, 14, 21 and 28 days.

[Figure 10](#) illustrates the development of the electrical resistivity of mixtures with time. As can be seen, the curve of the control specimen had minimal changes beyond 7 days, while CCZ30 (56.7%) and L15CCZ30 (56.7%) show a distinct increase from 7 to 28 days. These electrical resistivity trends confirm the difference in kinetics of microstructural change in the present mixtures. As can be seen, for CCZ30 (56.7%) and L15CCZ30 (56.7%) mixtures, the slope of the electrical resistivity curve is steeper, corresponding to other mixtures. This means that, with the development of the pozzolanic reaction, the

electrical resistivity for these two mixtures has increased more than the others. This behavior is probably attributed to the previously mentioned pore refinement in the calcined clay, and calcined clay, along with limestone, leads to an increase in resistivity, especially at early ages, against other mixtures. In the case of CCG30 (40.0%) and L15CCG30 (40.0%), results are consistent with previous results obtained by compressive strength and water absorption tests and indicate that for both mixtures, pore refinement and improvement of microstructures are not as well as the type of KZ-1 calcined clay.

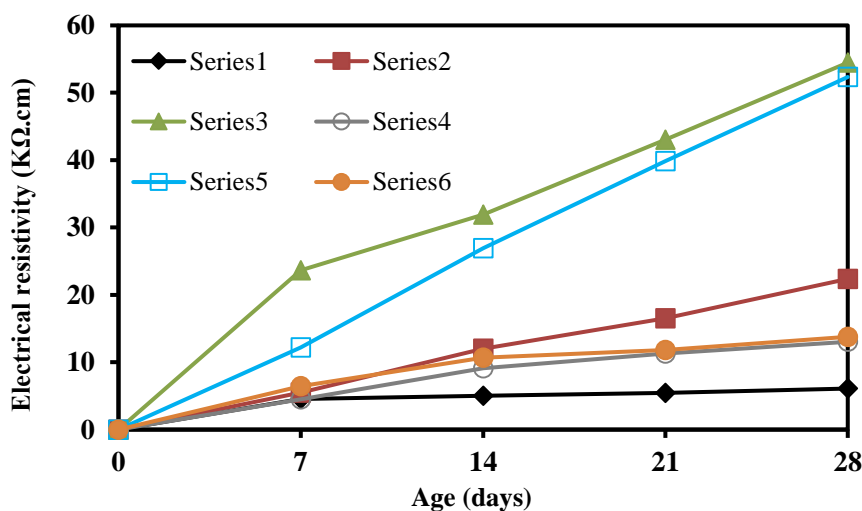
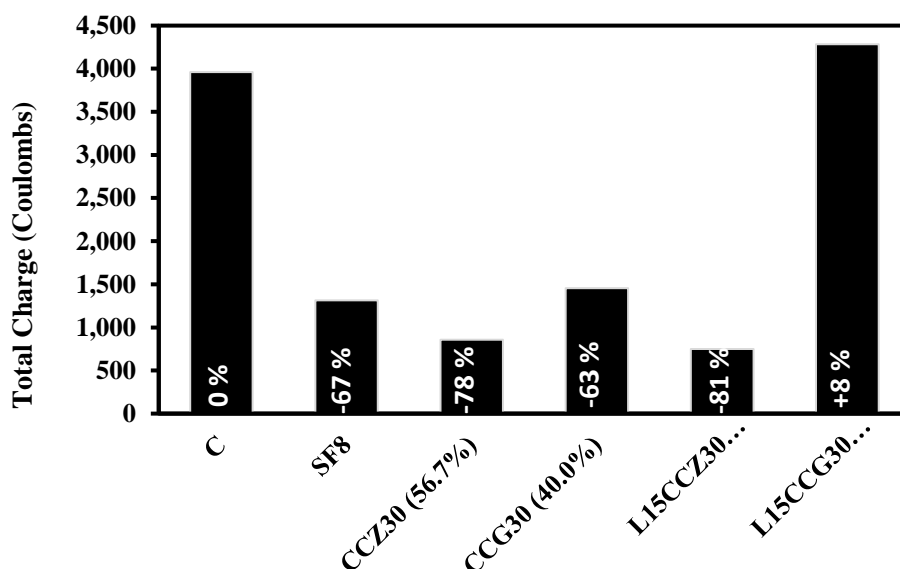


Figure 10. The development of electrical resistivity of control, calcined clays and silica fume mortar specimens with age.

### 3.4. RESISTANCE TO CHLORIDE INGRESS

Results of rapid chloride penetration resistance at 28 days measured in terms of electric charge passed through the specimens in coulombs are illustrated in [Figure 11](#). Except for the mixture of L15CCG30, other mixtures indicated lower values of the charge passed correspond to the control mixture, indicating higher resistance to chloride-ion penetration. In other words, in mixtures made with the calcined clay or calcined clay with adding 15% limestone binder, the 28-day chloride resistance has improved by nearly 60–80%, corresponding to the control mixture. This is consistent with the excellent resistance of calcined clay binder to chloride ingress at an early age, with appropriate results reported in previous sections. The improvement of the microstructure resulting from the pozzolanic reaction,

which has been correlated with the kaolinite content of calcined clay, has led to a reduction in the rapid chloride penetration. According to [Figure 11](#), the L15CCG30 mixture presented a higher charge value compared to all other mixtures - around 4280 coulombs. Based on ASTM C1202, this value indicates a high permeability. This is consistent with all other tests, including compressive strength, water absorption, and electrical resistivity. Additionally, in the present study, at 28 days, chloride-ion penetration of mixtures incorporating 15% of limestone was found to be higher than that of mixtures without limestone. For L15CCG30 (40.0%) mixture, the lower kaolinite content, in addition to the coarser particle size, could not collectively compensate negative dilution effect.



**Figure 11.** Total charge passed for calcined clay mixtures at 28 days.

The chloride concentration profiles as the results of the second method for the determination of resistance to chloride ingress are illustrated in [Figure 12](#). As can be seen, generally, the chloride contents decrease at higher depths. It can also be found that the use of SCMs remarkably enhances the resistance of mortar mixtures against chloride diffusion due to cement microstructure improvement. As it is shown in chloride profiles, the concentration of chloride ions in SF8, CCZ30 (56.7%), and L15CCZ30 (56.7%) mixtures were lower than the control mixture for interior depths below 8 mm. In this regard, the results clearly show that at 30% calcined clay, there was a marked decrease in chloride penetration depth compared to the control mixture. It was demonstrated that the number of pores with smaller size increases in mixtures including calcined clay due to the pozzolanic reaction of calcined clay helping in the refinement of the pore structure. On the other hand, the refined pore structure

increases the tortuosity of the system, thereby restricting the movement or transport of ions/fluids in the concrete or mortar. Apart from this pore refinement, chloride binding can also occur in mortars, including calcined clay, due to the higher amount of alumina hydrates. As a result, the above phenomena can collectively result in lower chloride ingress in mixtures containing calcined clay as compared to the control mixture. In this regard, it was observed that after 3 months of exposure to NaCl solution, chloride penetration depth was deeper than 25mm in the control mixture, while in the CCZ30 mixture; chloride ions reached a depth of about 15mm, in fact, something about 50% less. Adding 15% limestone to both mixtures incorporating calcined clay increased chloride penetration depth, but this increase is much greater for the type of KG-1 calcined clay. Among all the mixtures, the L15CCG30 (40.0%) mixture, as expected earlier, has the highest chloride penetration depth (more than 30mm).

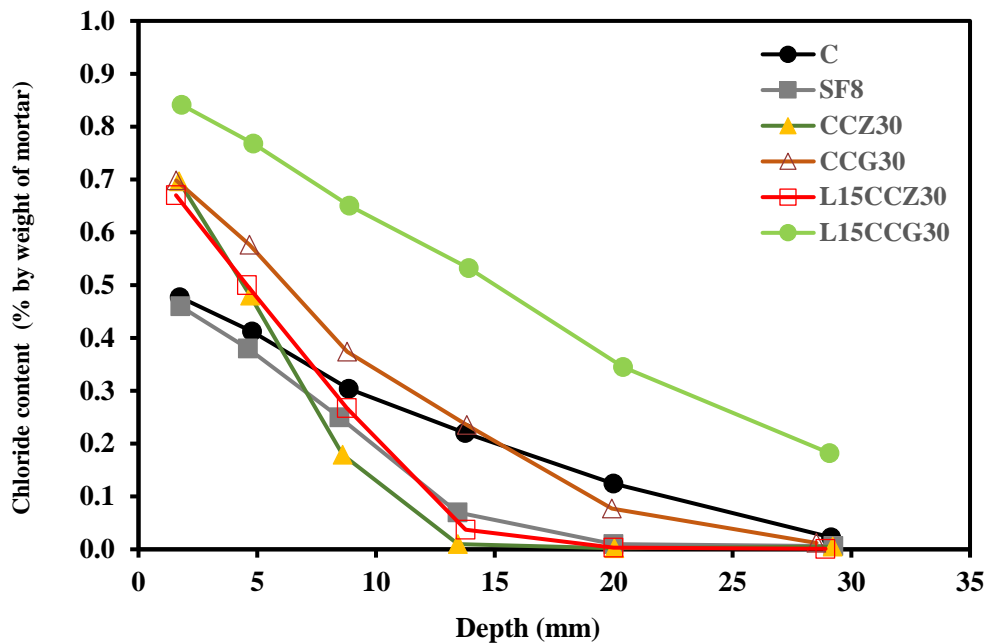


Figure 12. Chloride profiles in the mortar mixtures.

The calculated apparent diffusion coefficients ( $D_a$ ) and surface chloride concentrations ( $C_s$ ) for all mixtures after 3 months of exposure to the saline solution are presented in Table 5. As can be seen, the results agree well with those obtained earlier by the RCPT test. As shown in Table 4, regardless of the addition of limestone, the use of SF and calcined clay decreases  $D_a$  dramatically compared to the control mixture. The use of 30% type of KZ-1 and KG-1

calcined clay reduced apparent chloride diffusion of mortar by about 80 and 40%, respectively, and the use of 15% limestone and 30% type of KZ-1 calcined clay decreased  $D_a$  by 73%. As can be seen, for the L15CCG30 (40.0%) mixture, the  $D_a$  increased by about 100%. This increase in  $D_a$  was expected earlier due to poor results obtained by other durability factors.

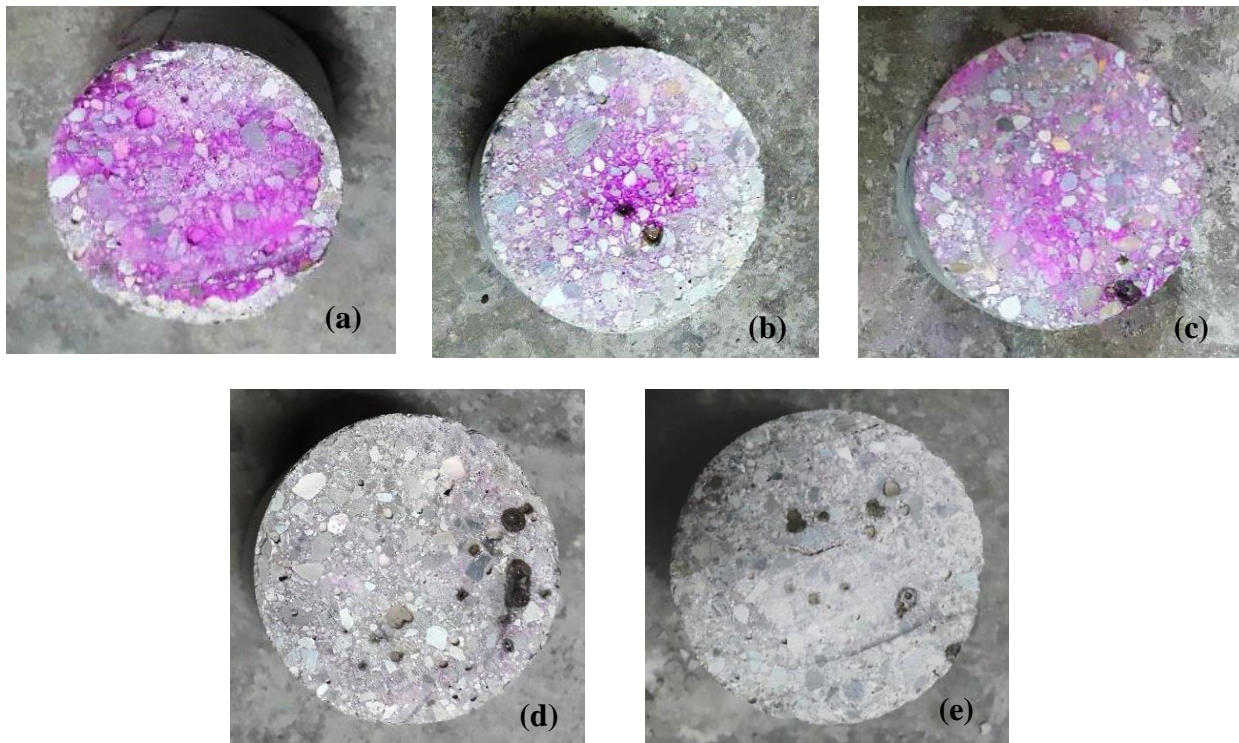
Table 5. Apparent chloride diffusion coefficients and surface chloride concentrations in the mortar mixtures.

Mixture	Apparent diffusion coefficient- $D_a$ ( $\times 10^{-12} \text{ m}^2/\text{s}$ )	Chloride surface concentration- $C_s$ (% by wt of concrete)	Correlation of determination, $r^2$
C	17.5	0.526	0.996
SF8	6.47	0.558	0.986
CCZ30 (56.7%)	3.07	0.889	0.992
CCG30 (40.0%)	10.4	0.785	0.997
L15CCZ30 (56.7%)	4.61	0.808	0.991
L15CCG30 (40.0%)	35.7	0.913	0.996

### 3.5. RESISTANCE TO CARBONATION

To determine the carbonation resistance of mortar mixtures, the carbonation depth was measured by spraying 1% phenolphthalein indicator solution on the freshly broken surface of cylinder specimens after 3 months of exposure. It can be seen from Figure 13 that on the uncarbonated surface of the specimen where the mortar is still highly alkaline, purple-red color has appeared. On the carbonated surface, no coloration occurs. Based on the results obtained, a minimum carbonation depth of 5mm was observed for the control mixture. As can be seen in Figure 13, for CCG30 and L15CCZ30 mixtures, the whole surface of the specimens was carbonated. For CCZ30 and SF8, the carbonation depth was less than 20 mm. The

results indicate that the carbonation resistance of mixtures containing SCMs is generally lower as compared to PC due to lower total alkalinity and agree with data available in the literature [47-48]. It should be noted that the lower carbonation depth obtained for the control specimen compared to SF8 and CCZ30 mortars should not be taken into account as an advantage to reinforced concrete structures. The results obtained in other studies indicate that the reinforced concrete structures with no pozzolan are more vulnerable to the combined attack of carbonation and chloride ingress due to the higher chloride ion diffusion coefficient [49-50].



**Figure 13.** Carbonation depth in the a) C, b) SF8, c) CCZ30, d) CCG30 and e) L15CCZ30 mortar mixtures.

#### 4. CONCLUSION

This study investigated the feasibility of using a new type of supplementary cementitious materials as cement replacement. The influence of cement replacement levels with two moderate-grade kaolinite clay and limestone on strength development, transport properties, and carbonation was investigated, and the following conclusion can be drawn:

- It was observed that mortars made with 30% KZ calcined clay (> 40% kaolinite content), with a similar mixture proportion, showed comparable strength development characteristics with PC mortar and lower strength development compared to SF8. The addition of 15% limestone in mortar caused a reduction of 11-13% in compressive strength regardless of the calcined clay type.
- The water absorption was found to reduce by the replacement of cement with the type of KZ calcined clay. Based on the present results, a reduction of 34% in 24 h water absorption was found for mortar with 30% calcined clay compared to control mixtures, respectively. This reduction could be primarily associated with the reduction in the total volume of capillary pores and increased tortuosity.
- Based on the results obtained, mortar made with calcined clay presents significantly higher electrical resistivity than the control mortar mixture. This also results in better resistance against ingress of chloride ions which were evaluated by RCPT and accelerated chloride penetration.
- Except for the mixture of L15CCG30, other mixtures showed lower values of the charge passed compared to the control mixture. Furthermore, the chloride resistance has improved by nearly 60–80% with respect to the control mixture by 28 days, indicating higher resistance to chloride-ion penetration.
- The results of the accelerated chloride penetration test and calculated diffusion coefficient are in agreement with the results obtained by the RCPT test. The results show that at 30% calcined clay, there was a marked decrease (about 80 and 40%) in  $D_a$  and an increase in  $C_s$  compared to the control mixture. The use of 15% limestone and 30% KZ calcined clay also decreased  $D_a$  by about 73%. However, the mixture, including the KZ calcined clay, had a better influence on improving diffusion characteristics of mortar compared to the KG calcined clay mortar at the same level of substitution.
- It was observed that the utilization of 15% limestone with 30% KZ calcined clay, unlike KG, improved all durability parameters (except carbonation resistance) and reduced compressive strength in comparison with PC mortar.
- The results indicate that the carbonation resistance of mixtures containing calcined clays and SF is lower compared to the control mixture due to lower total alkalinity.

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AUTHORS CONTRIBUTION

This work was carried out in collaboration among all authors.

CONFLICT OF INTEREST

The author (s) declared no potential conflicts of interests with respect to the authorship and/or publication of this paper.

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