



Research article

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Iraqi bentonite as natural pozzolan

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Abstract. In this study, Iraqi high-calcium bentonite was used for the first time to prepare natural pozzolan for concrete by the thermal activation method (calcination). Raw bentonite was calcined at 700, 750, 800, 850, 900, and 950°C for 30, 60, 90, and 120 minutes at each temperature. X-ray diffraction and quantitative X-ray diffraction techniques identified the optimal calcination program at 800°C for 90 minutes. In this program, calcination destroyed the crystal structure of bentonite-forming clay minerals, thus converting silicon, aluminium, and iron oxides into chemically reactive amorphous phases. The prepared natural pozzolan achieves a strength activity index of 108.3% at 28 days; additionally, it meets the requirements of the Iraqi specification of pozzolanic materials. The effects of Portland cement replacement with calcined bentonite at 5, 10, 15, 20, 25, and 30% were studied on selected properties of the cementitious binder and concrete. The results indicate that replacement percentage is positively associated with initial and final setting times and negatively correlated with the concrete slump. At seven days, calcined bentonite causes the decline of the compressive strength of concrete, while at 28 days, concretes containing 5, 10, and 15% develop higher compressive strength than the control mix. However, the compressive strength of concretes containing calcined bentonite differs from the control mix by not more than $\pm 9\%$ at 90 days. Calcined bentonite reduces the concrete splitting strength and density properties, and the absorption at 25% substitution or less.

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1. Introduction

The sustainability of concrete can improve by utilizing pozzolanic materials as a partial replacement for Portland cement [1]. Natural pozzolan is one of the types of pozzolanic materials; when used as a part of the cementitious binder, it develops some of the fresh properties, mechanical properties, and/or durability of concrete [2, 3]. This research aims to prepare natural pozzolan from Iraqi high-calcium bentonite by the thermal activation method.

Bentonite is clay that consists dominantly of smectite minerals [4]. In addition to smectite minerals, bentonite may contain multiple species of clay minerals such as palygorskite, kaolinite, illite, or others. It may contain non-clay minerals such as quartz, gypsum, feldspar, or others [4, 5]. The unique property of smectite minerals is the potential to swell due to water absorption [6]. In most cases, bentonite contains a high percentage of montmorillonite mineral, a member of the smectite group. Therefore, bentonite may define as clay consisting mainly of montmorillonite mineral [7].

There are numerous allegations about the pozzolanicity of raw bentonite [8–14]. However, these allegations are not supported by conclusive evidence of the occurrence of the pozzolanic reaction between bentonite components and calcium hydroxide resulting from Portland cement hydration [15]. On the

contrary, precise examinations have shown that only minor changes in montmorillonite structure occur in highly alkaline environments [16], and a small fraction of montmorillonite may contribute to pozzolanic reaction [17]. On the other hand, the pozzolanicity of both calcined montmorillonite (CM) and calcined bentonite (CB) has been confirmed in several studies [17–23].

CB modifies the concrete properties in plastic and hardened states due to both pozzolanic and physical actions. In the plastic state, CB incorporation causes a linearly increase in water demand to achieve standard consistency of the paste [23, 24], extends both initial and final setting time [23–25], reduces the workability of concrete [26], and increases the dosage of superplasticizer required for self-compacted mortar [27] and self-compacted concrete [28]. In the hardened state, CB reduces the rate of strength gain due to the low pozzolanic reactivity of CM [21, 29–31]. Therefore, CB incorporation leads to a reduction in compressive strength of concrete at early ages, i.e., 21 days or less [8, 9, 25, 26], but the reductions in concrete strength tend to disappear at later ages, i.e., 28-90 days [25, 26, 28]. The most important effect of CB is enhancing the durability of concrete against alkalis-silica reaction [25], sulfates attack [32], acids attack [26], and chlorides penetration [25, 28]. No previous studies were related to Iraqi bentonite, which differs in chemical and mineralogical compositions.

Given the absence of naturally formed pozzolans in Iraq and the rarity in industries producing pozzolanic materials as waste, the available alternative is to utilize mineral resources in obtaining natural pozzolan. Iraqi bentonite represents a promising source for natural pozzolan production; its validity for this purpose has not previously been investigated.

In Iraq, the petroleum industries are the largest consumer of bentonite. These industries require high swelling bentonite, i.e., sodium bentonite, while the bentonite deposits in Iraq contain only low swelling bentonite, i.e., calcium bentonite [33, 34]. Therefore, Iraqi calcium bentonite shall be processed to convert it to high swelling bentonite before using it to extract the crude oil. Calcium content is the criterion in determining the validity of calcium bentonite to process and thus convert to high swelling bentonite [35]. On this basis, Iraqi bentonite is classified into two classes [33–37]: high grade or low-calcium bentonite in which $\text{CaO} \leq 5\%$, and low grade or high-calcium bentonite in which $\text{CaO} > 5\%$. High-calcium bentonite requires complex processes to be converted into high swelling bentonite [33, 36, 37]. Because of this, the production of the high swelling bentonite from the high-calcium bentonite is not economically feasible, and the utilization of Iraqi bentonite is limited to the low-calcium bentonite only. In contrast, high-calcium bentonite is considered a useless material. The main objective of this research is to determine the optimum calcination program for producing natural pozzolan from high-calcium Iraqi bentonite, and then study some properties of the cementitious binder and concrete when Portland cement is partially substituted with the prepared pozzolan.

2. Materials and Methods

2.1. Materials

Bentonite stones were obtained from the Wadi Bashira region in the Western Desert of Iraq. The coordinates of this region are $32^{\circ}59'48.2''\text{N}$, and $39^{\circ}44'53.3''\text{E}$. Wadi Bashira deposit represents the most important montmorillonitic smectites deposits in Iraq as it contains reverse of more than 300×10^6 tons [38]. This deposit contains both high-calcium and low-calcium bentonite. The chemical composition of RB is recorded in Table 1. Fig. 1 shows the status of RB as received.

Ordinary Portland cement (OPC) conforms to IQS 5/2019 type IQS 5-CEMI 32.5R. The chemical composition of OPC is listed in Table 1, and its physical and mechanical properties are listed in Table 2.

Standard sand meets the requirements of the Iraqi code of practice No. 1/198/2012 was used for making mortar for the strength activity index test. For concrete production, round graded gravel 14–5 mm, and natural sand in zone IV according to IQS. 45/1984 were used.



Figure 1. Bentonite stones as received.

Table 1. Chemical composition of materials.

	Oxide percentage		
	OPC	RB	CB (80090)
CaO	63.4	7.4	8.3
SiO ₂	21.0	57.6	60.3
Al ₂ O ₃	5.0	13.6	14.9
Fe ₂ O ₃	3.8	6.3	7.2
MgO	2.3	3.2	3.6
Na ₂ O	0.2	1.1	1.1
SO ₃	2.5	1.3	1.5
K ₂ O	0.5	0.5	0.6
P ₂ O ₅	-	0.9	0.9
TiO ₂	-	1.1	1.3
Cl	-	0.33	0.13
LOI	1.6	-	-
IR	0.3	-	-

Table 2. Physical and mechanical properties of OPC.

Property	Result	IQS 5/2019 limit
Compressive strength @ 2 days	19 MPa	10 MPa lower limit.
Compressive strength @ 28 days	34.1 MPa	32.5 MPa lower limit.
Initial setting time	70 min.	45 min. lower limit.
Final setting time	235 min.	600 min. upper limit.
Soundness	0.04%	0.8% upper limit.
Fineness	317 m ² /kg	250 m ² /kg lower limit.

2.2. Methods

The experimental program included the following sequential steps:

1. The bentonite stones were soaked in water for 24 hours as they absorbed water and turned into a soft paste, then spreading outdoors in direct sunlight for 5 to 10 days to dry. This process aims to facilitate the grinding process and increase its efficiency, as it has been observed that the process of grinding bentonite stones takes longer than the process of grinding dry bentonite paste to achieve the desired result fineness. Fig. 2 shows the drying process of bentonite paste. After drying, the bentonite was ground using a 300 g laboratory grinder for 90 seconds, then sieving the ground bentonite on a 300 μ m sieve to exclude coarse grinding products. The ground raw bentonite was kept in airtight plastic containers.

**Figure 2. Drying bentonite paste.**

2. Identify the mineral composition of the RB by the XRD technique.

3. Calcination of RB at 700, 750, 800, 850, 900, and 950 °C for 30, 60, 90, and 120 minutes for each calcination temperature. The nomenclature of each experiment shows in Table 3. Each sample was heated at the rate of 30–40 °C/min. until it reached the calcination temperature; it was kept at this temperature \pm 10 °C for the calcination period; then, it was removed from the furnace immediately after the calcination was completing. After that, it was left to cool down at ambient temperature. The purpose of fast cooling is to prevent phase transformations that may occur during slow cooling [39].

Table 3. Calcination programs.

		Calcination temperature					
		700°C	750°C	800°C	850°C	900°C	950°C
Calcination period	30 min.	70030	75030	80030	85030	90030	95030
	60 min.	70060	75060	80060	85060	90060	95060
	90 min.	70090	75090	80090	85090	90090	95090
	120 min.	700120	750120	800120	850120	900120	950120

4. Recognize the modifications on crystal phases due to each calcination experiment by XRD technique.

5. Select the probable experiments that disappear the peaks of clay minerals without the formation of new crystal phases.

6. Analyze the results of XRD of the probable examinations by quantitative XRD (QXRD) to determine the residuals of clay minerals.

7. Decide the optimum calcination program that confirms the maximum strength activity index at 28 days.

8. Verification of conformity of CB prepared by the optimum calcination program to the mandatory requirements of IQS 1748/1992 (Pozzolanic materials for use as a mineral admixture in Portland cement concrete).

9. Examine the effects of partial replacement of OPC by CB at 5, 10, 15, 20, 25, and 30 % replacement levels on the properties of the cementitious binder: water requirement, initial and final setting times, and combined water.

10. Study the effects of partial replacement of OPC by CB at 5, 10, 15, 20, 25, and 30 % replacement levels on the properties of concrete: slump, density, absorption, compressive strengths, and splitting tensile strength. The details of concrete mixtures are shown in Table 4.

Table 4. Details of concrete mixtures.

Mixture	Material content kg/m ³				
	OPC	CB	Sand	Gravel	Water
C100B0	450.0	0	650	1000	210
C95B5	427.5	22.5	650	1000	210
C90B10	405.0	45	650	1000	210
C85B15	382.5	67.5	650	1000	210
C80B20	360.0	90	650	1000	210
C75B25	337.5	112.5	650	1000	210
C70B30	315.0	135	650	1000	210

XRD patterns for RB and CB were performed using ADX-2700 diffractometer (manufactured by Angstrom Advanced Inc., Boston, USA), the range of 2θ is 3–80°, the rate of scanning is 0.05°/sec., the type of radiation is $\text{CuK}\alpha_1$, i.e., $\lambda = 1.54056\text{\AA}$, the voltage is 40kV, and the current is 30 mA.

The QXRD of probable experiments were carried out using DIFFRAC.DQUANT software from Bruker UK Limited.

Particle size analyses for CB and OPC were implemented with the NanoBrook 90Plus particle size analyzer (Brookhaven Instruments Corporation, NY, USA). The size range of the device is 0.3 nm – 6 μm , the scattering angle is 90°, the laser type is a temperature-controlled red semiconductor laser, the laser wavelength is 660 nm, the liquid of the test solution is ethanol, and the test precision is $\pm 1\%$. This device determines the equivalent diameter of the specimen's particles suspended in ethanol and subjected to the laws of Brownian motion using the dynamic scattered light technique.

Tests of water required to achieve standard consistency, initial setting time, and final setting time were carried out according to the Iraqi code of practice 1/198/2012.

Specimens of cementitious paste were prepared by mixing 200 g of the cementitious binder with 80 g of water (0.4 w/cm); the hardened pastes were cured in saturated lime water for 90 days. Five grams were taken from each specimen, dried at 40 °C for a constant mass, and weighted. A dried paste was ignited for 30 minutes at 1000 °C and then weighted. The combined water is determined as the following:

$$\% W_c = \left[\frac{(m_{40} - m_{1000})}{m_{40}} \right] \times 100,$$

where W_c , m_{40} and m_{1000} are the combined water, the mass of dried specimens, and the mass of the ignited specimen, respectively.

The tests and requirements of the CB as a pozzolanic material were carried out according to IQS 1748/1992.

Concrete mixtures were prepared according to the Iraqi code of practice 248/1991. Slump test was carried out according to Iraqi code of practice 354/1992, density test according to BS EN 12390-7:2009 (water saturated mass and actual measurements volume), absorption test according to BS 1881-122:2011, compressive strength test according to Iraqi code of practice 348/1992, and splitting tensile strength according to BS EN 12390-6:2009. All concrete specimens are 100mm cubes.

3. Results and Discussions

3.1. Physical effects of calcination

The calcination process turns the powder of RB from yellow colour to red colour. The colour of CB gets darker with the increase in the calcination temperature. Fig. 3 illustrates the changes in bentonite colour due to different calcination programs. The red colour is attributed to the formation of hematite Fe_2O_3 , and the dark colour is attributed to the formation of magnetite Fe_3O_4 [40]. The formation of hematite and/or magnetite indicates a partial or complete dissociation of the crystal structure of clay minerals that make up bentonite, as the iron cation represents the central part of some tetrahedrons in the tetrahedral sheet and the central part of some octahedrons in the octahedral sheet. The calcination process causes the iron cation to be released from the crystal structure and forms iron oxides Fe_2O_3 and Fe_3O_4 .

The bentonite powder tends to agglomerate with an increase in calcination temperature, and the formed lumps harden at higher temperatures. Table 5 elucidates the status of CB after calcination, and Figure 4 shows the statuses of some experiments. The formation of lumps is an indication to start the sintering process and formation of new crystalline phases. The formation of lumps makes it necessary to re-grind CB before using it as pozzolanic material.

Table 5. Status of CB after calcination.

experiment	status
70030, 70060, 70090, 700120, 75030, 75060, 75090, 750120, and 80030. 80060, 80090, and 85030.	Powder A mixture of friable lumps and powder
800120, 85060, 85090, 850120, 90030, 90060, 90090, 900120, 95030, 95060, 95090, and 950120.	Hard lumps

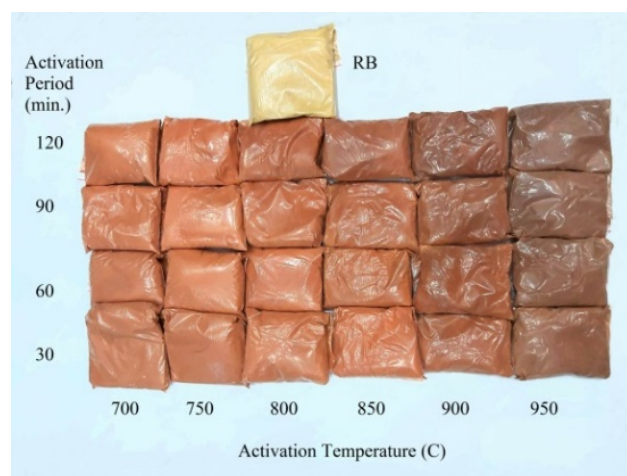


Figure 3. Colour of bentonite at different activation temperatures.

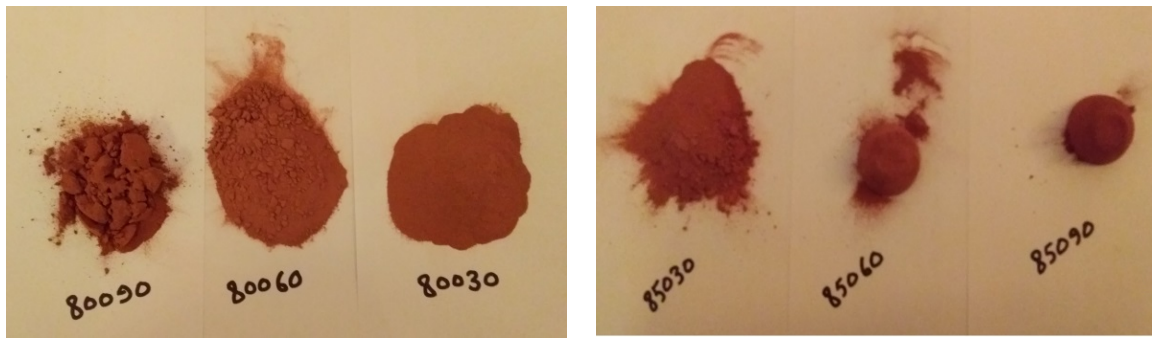


Figure 4. Status of some experiments.

The calcination process leads to a weight loss of RB by about 18–22 %. The major weight loss is ascribed to the free water release, the adsorbed water molecules from the surfaces of clay minerals, and the hydroxyl groups from the structure of clay minerals. The minor weight loss is attributed to the decarbonisation of dolomite and removing water molecules from the gypsum.

3.2. XRD and QXRD

The result of the XRD test of RB is shown in Fig. 5; Fig. 6–11 show the XRD pattern of each experiment compared to the XRD pattern of RB.

RB consists of Ca-montmorillonite as a major clay mineral, kaolinite, and palygorskite as minor clay minerals, and quartz, dolomite, and gypsum as minor non-clay minerals; Table 6 shows the crystal properties of clay minerals in RB.

Table 6. Clay minerals in RB.

Mineral	hkl	d (Å)	2 θ
Ca-montmorillonite	001	15	5.8
	005	3	29.3
	100	4.5	19.8
	300	1.5	62.1
Palygorskite	040	4.5	19.8
	101	4.3	20.8
	231	3.3	26.5
Kaolinite	020	4.5	19.8
	111	3.4	26.5
	-223	1.8	50.1
	203	1.5	60.1
	-3-31	1.5	62.1

The calcination process causes structural changes in the montmorillonite mineral. The peak of 001 plane (at 5.8° 2 θ) has shifted to the right by (4–5° 2 θ) in all experiments at 700 °C and 750 °C, and in 80030 and 85030 experiments which mean the reduction in basal spacing from 15 Å to 9–10 Å due to removing water molecules layers. The maximum shifting to 14.8° 2 θ occurred in the 80060 experiment in which the basal spacing has shrunk to 6 Å; the shifting of 001 peak associates with reductions in the intensity, indicating that the strains in the montmorillonite crystal are non-uniform [41], i.e., degrade the crystallinity. For the same experiments, the peak of 100 plane (at 19.8° 2 θ) preserves its location and intensity, which elucidates that the structural changes in the c-axis do not mean the destruction of the montmorillonite crystal [19]. In experiments 80090, 800120, and 85060, the peaks of the montmorillonite and other clay minerals disappear. That is strong evidence of transforming the crystalline phases of the clay minerals into amorphous and/or cryptocrystalline phases. This conclusion is confirmed by QXRD, which shows the absence of clay minerals in experiments 80090, 800120, and 85060, as shown in Fig. 12–14.

Despite the absence of the peaks of the clay minerals in the 85090 and 850120 experiments and all experiments at 900 °C and 950 °C but this absence is associated with the appearance of new peaks. The new peaks indicate the formation of highly crystalline inert phases such as cristobalite, spinel, and/or magnesium aluminium silicate (MgAl₂Si₄O₁₂) [19]. The results obtained are compatible with previous studies, which showed that the amorphization temperature of montmorillonite mineral lies in the range of 800–900 °C [42].

Based on XRD and QXRD results, experiments 80090, 800120, and 85060 are the probable experiment for adoption as an optimum calcination program.

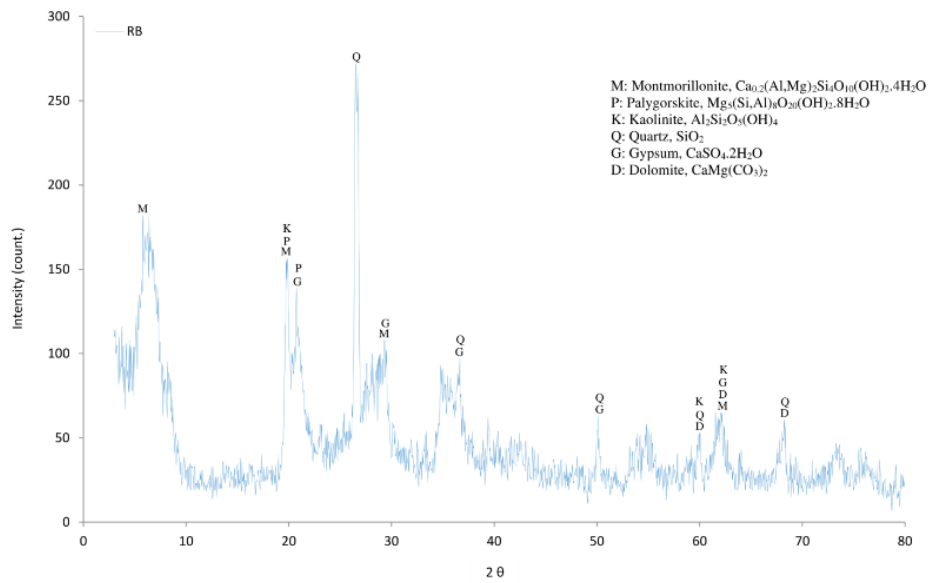


Figure 5. XRD pattern of raw bentonite.

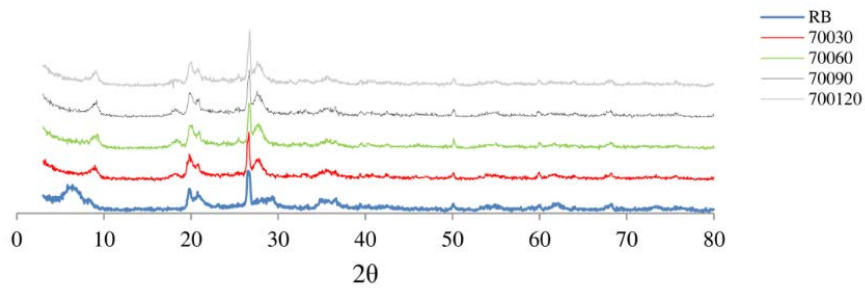


Figure 6. XRD pattern of RB and CB at 700 °C.

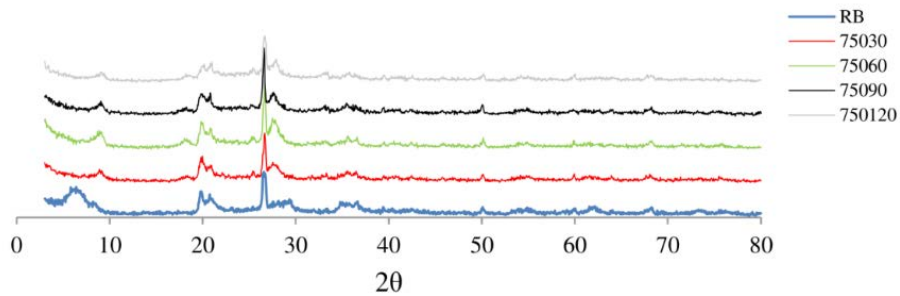


Figure 7. XRD pattern of RB and CB at 750 °C.

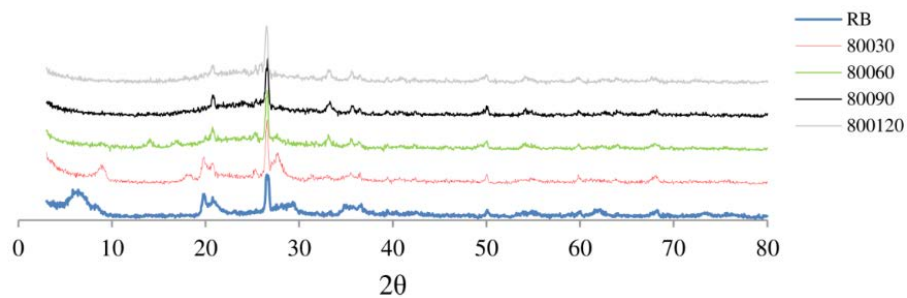


Figure 8. XRD pattern of RB and CB at 800 °C.

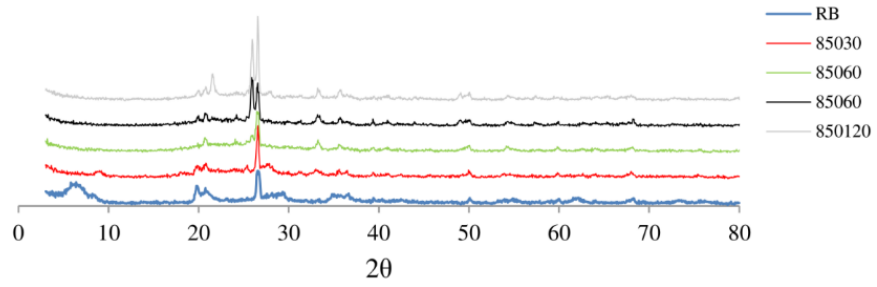


Figure 9. XRD pattern of RB and CB at 850°C.

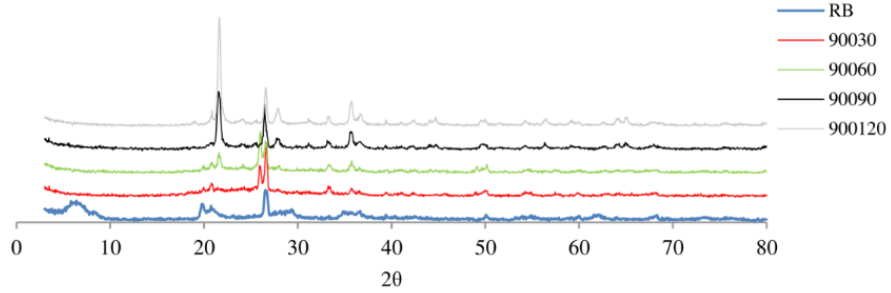


Figure 10. XRD pattern of RB and CB at 900°C.

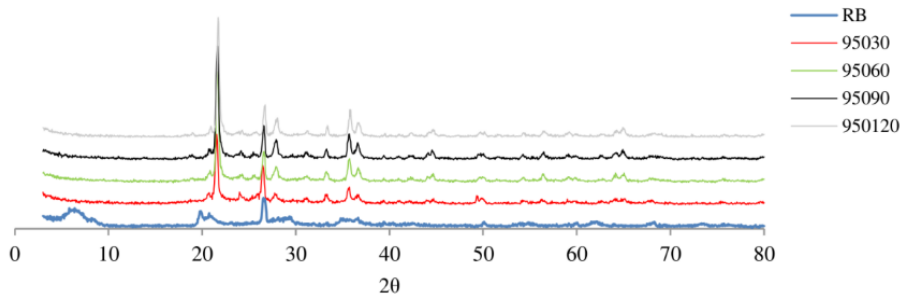


Figure 11. XRD pattern of RB and CB at 950°C.

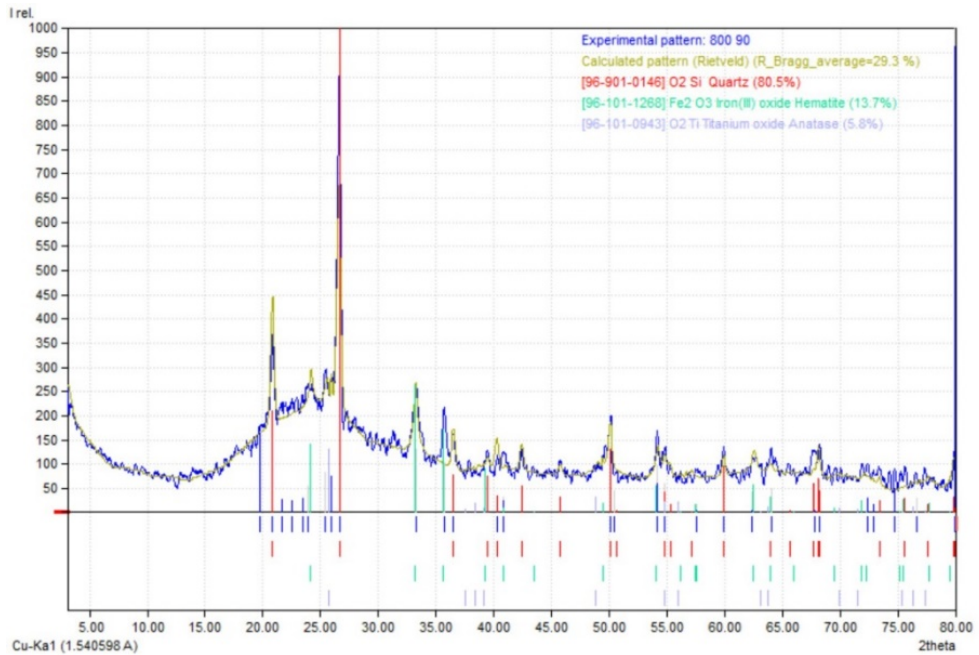


Figure 12. QXRD for 80090 experiment.

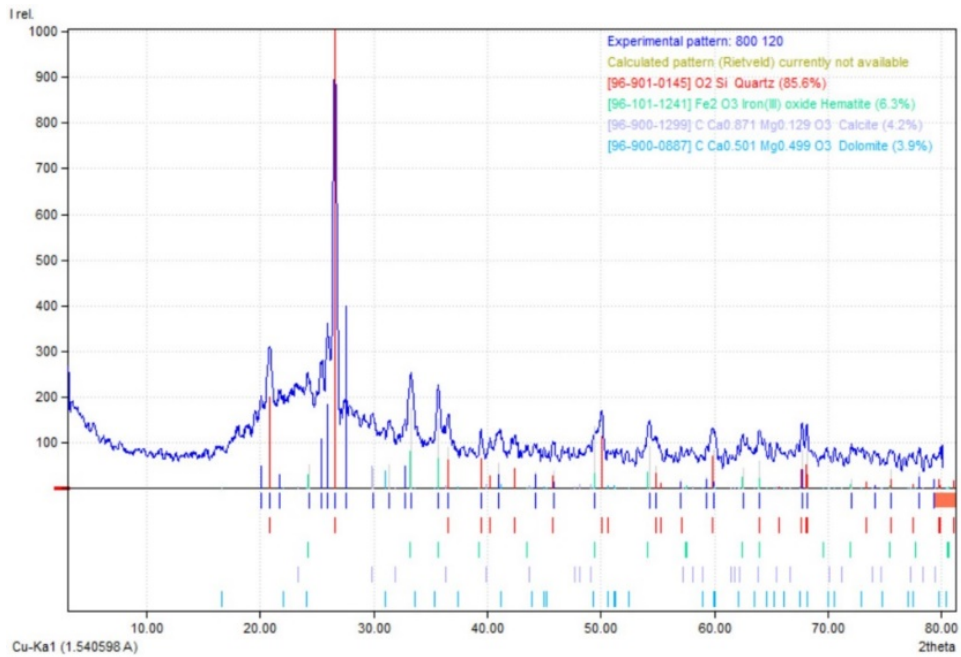


Figure 13. QXRD for 800120 experiment.

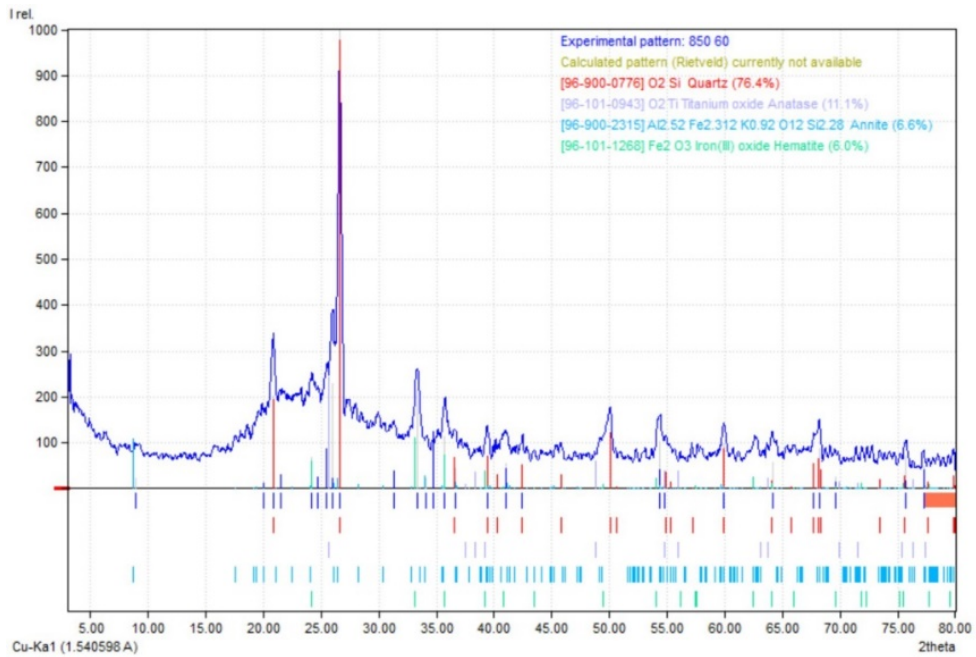


Figure 14. QXRD for 85060 experiment.

3.3. Strength activity index

The SAIs of probable experiments at both 7 and 28 days are listed in Table 7. At the age of 7 days, all SAIs were less than 100%, indicating the low reactivity of CB. At 28 days, all probable experiments developed SAI equal to or more than 100%. The highest 28 days SAI (108.3%) is that of the 80090 experiment. Therefore, the 80090 experiment was adopted as the optimum calcination program.

Table 7. SAI for probable experiments.

	f_{7d}	SAI_{7d}	f_{28d}	SAI_{28d}
Control	34.3	100%	36	100%
80090	26.6	77.6%	39	108.3%
800120	31.3	91.3%	35.8	99.4%
85060	26	75.8%	38.3	106.4%

3.4. Properties of pozzolanic materials

CB prepared according to the optimum calcination program (80090) meets the mandatory requirements of IQS 1748/1992. The results of the tests are reported in Table 8.

The particles size distribution of both CB and OPC are shown in Figure 15. The equivalent diameters of OPC and CB are listed in Table 9.

Table 8. Properties of CB.

Chemical properties		
Property	Result	IQS 1748/1992 limits
Σ (SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃)	82.4%	70.0% min.
SO ₃	1.5%	4.0% max.
Moisture content	0.4%	3.0% max.
Loss on ignition	0.4%	10.0% max
Physical properties		
Property	Result	IQS 1748/1992 limits
Amount retained on 45 μ m	0%	34% max.
Strength activity index @ 28 days	108.3%	75% min.
Water requirement	99%	115% max.
Soundness	0.05%	0.8% max.
Specific gravity	2.57	–

Table 9. Equivalent diameters (in nanometers) of CB and OPC particles.

	D ₅	D ₂₅	D ₅₀	D ₇₅	D ₉₅
CB	340.6	588.7	860.6	1258.2	2174.6
OPC	601.8	855.8	1092.8	1395.4	1984.4

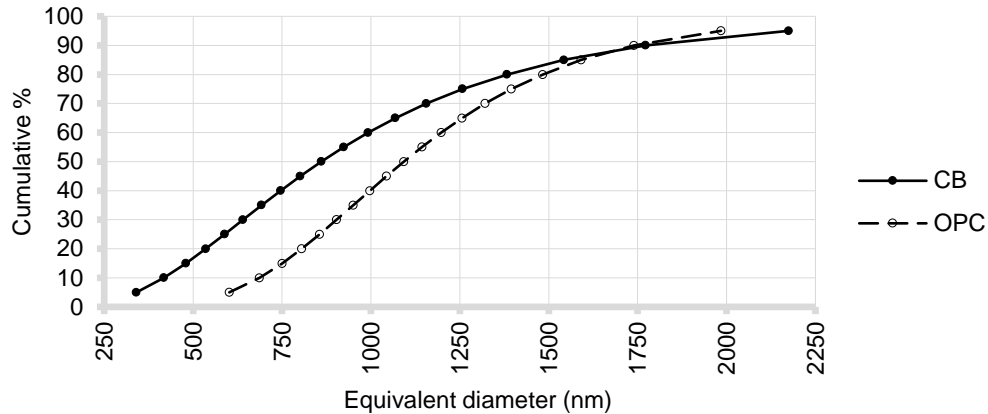


Figure 15. Particle size distribution of CB and OPC.

3.5. Properties of cementitious binder

OPC replacement by CB causes increases in water required to achieve the standard consistency of cementitious binder. Fig. 16 shows the linear relation between w/cm and the percentage of OPC replacement.

According to Feng et al. [43], the ultrafine powder, which has average particles diameter smaller than the average of cement particles diameter, influence the fluidity of the cementitious binder by two opposed effects: filling effect, which leads to reduce fluidity due to increase water demand, and dispersing effect which leads to increase fluidity due to release trapped water between cement flocks. The amorphous nature of CB, the platy shape of CB particles, and the relatively low specific CB gravity are the reasons why the filling effect dominates the dispersing effect.

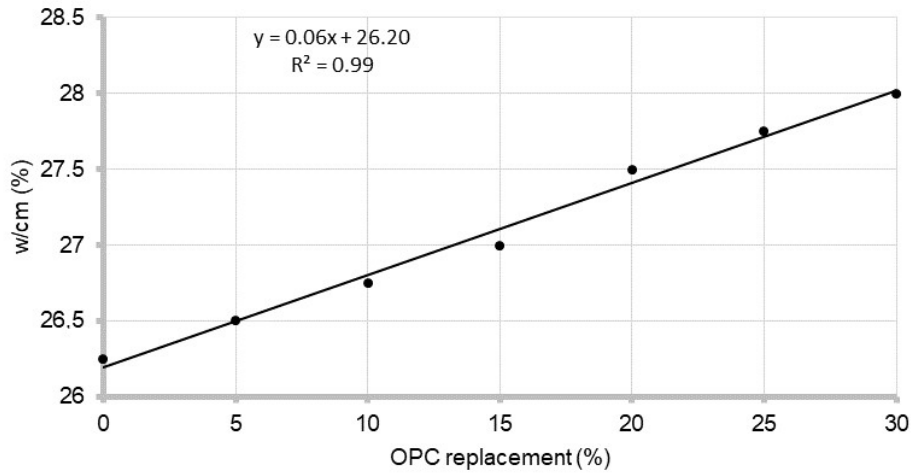


Figure 16. Effect of OPC replacement by CB on water required to achieve standard consistency.

Both initial and final setting times extend linearly with the percentage of cement substitution, as shown in Figure 17. The reductions in C₃A and C₃S contents due to OPC substitution, the low reactivity of CB components, phosphates in CB, and higher water content are the reasons for the delay in both initial and final setting time.

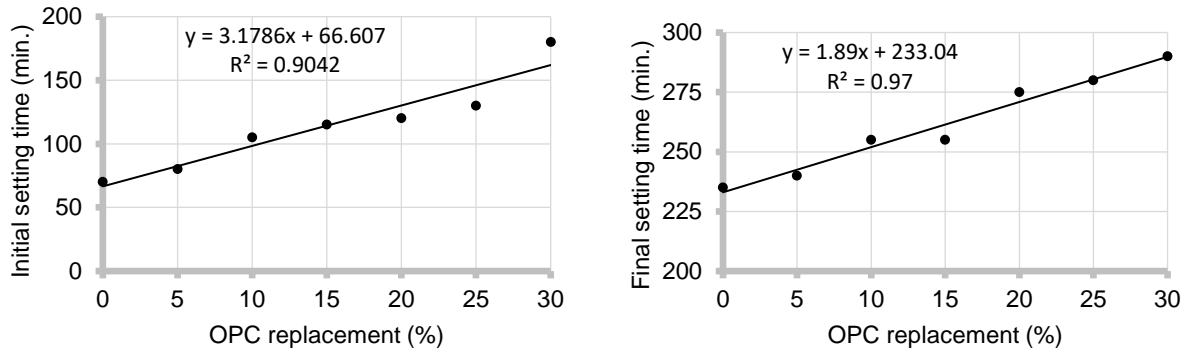


Figure 17. Effect of OPC replacement by CB on the setting time of cementitious binder.

CB incorporation causes a slight increase in combined water at 5 % replacement, while at 10 % replacement, a significant increase in combined water was observed. Accordingly, the cementitious binder containing CB at levels of 5 and 10 % produces more hydration products than products resulting from OPC’s hydration alone, as all the hydration products contain chemically combined water. The increase in the hydration products is attributed to the pozzolanic reaction. At 15–30 % replacement, the percentage of combined water reduces gradually as the OPC substitution increase due to the increase of unreacted CB. The combined water percentage is higher than the percentage calculated based on replacing OPC with an inert material, which indicates the contribution of the pozzolanic reaction to the structure of the hardening paste at any replacement level within the range of 5–30 %, as shown in Fig. 18.

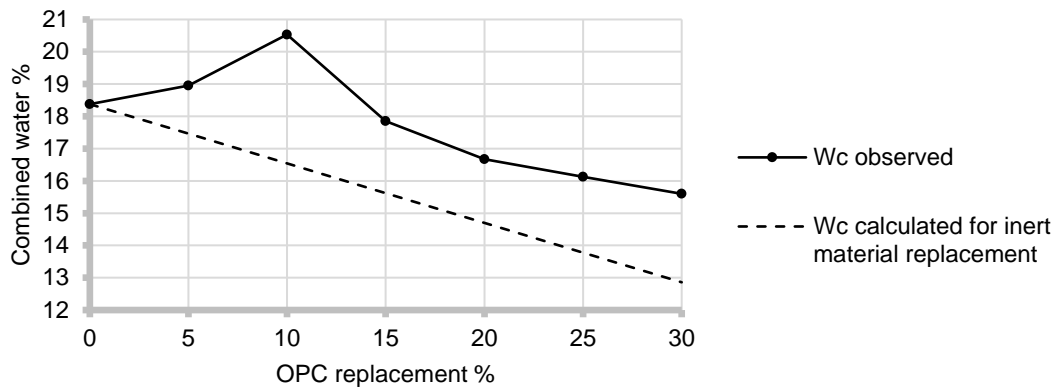


Figure 18. Effect of OPC replacement by CB on the combined water.

Similar observations of the effects of calcined bentonite on the properties of the cementitious binder were reported by Darweesh and Nagieb [23].

3.6. Workability

Its lower specific gravity characterizes CB than OPC, so the volume of CB required to replace a specific weight of OPC is greater than the volume of the substituted OPC. This increase in the volume of cementitious binder, and its relatively higher surface area due to CB finesse, require an increase in the mixing water to maintain the same workability. In the case of fixation the amount of mixing water, an increase in the volume and surface area of the cementitious binder leads to a decrease in concrete workability. Fig. 19 shows the effect of CB on the slump of concrete. It is noticeable that the slump value decreases as the CB content increases. The effect of CB in reducing the slump has previously been reported by Ahmad et al. [9].

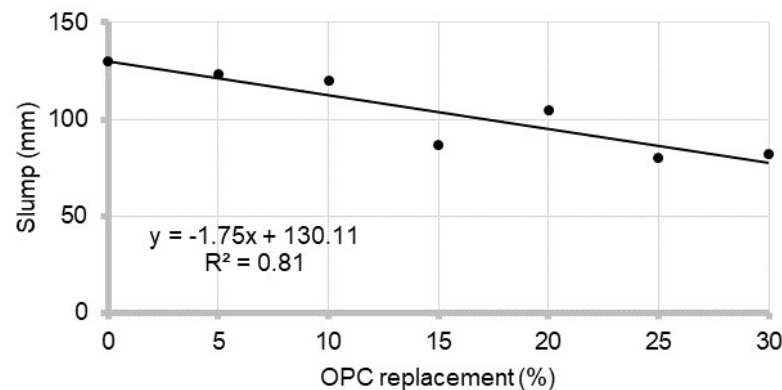


Figure 19. Effect of OPC replacement by CB on the slump of concrete.

3.7. Concrete density

Concrete density decreases slightly due to the replacement of OPC by CB. The amount of decrease in density is proportional to the replacement percentage, as shown in Fig. 20. The density reduction is attributed to the lower specific gravity of CB compared to the specific gravity of OPC. It is also observed that the density increases with age due to the progression of the hydration process and thus reducing the total porosity.

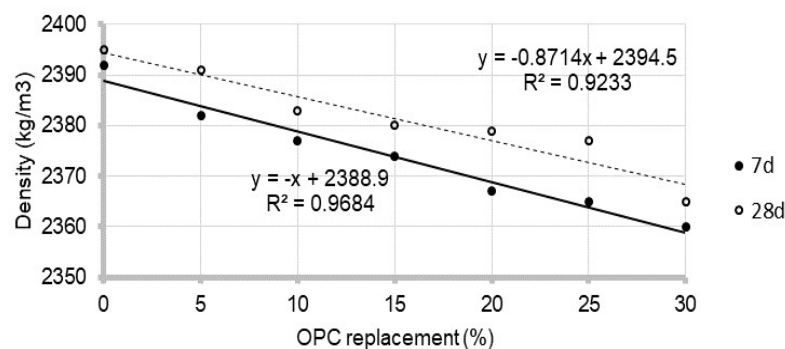


Figure 20. Effect of OPC replacement by CB on concrete density.

3.8. Concrete absorption

The partial replacement of OPC with CB results in two opposing effects on concrete absorption, one of which is positive and reduces absorption because of a modification of the pore structure caused by pozzolanic reaction and the physical effect of unreacted bentonite fine particles filling the pores. The second is negative, resulting in higher absorption resulting from the reduction of cement content and, therefore, a reduction in hydration products. At substitution levels of 5 and 10 %, the interaction between these two opposing effects causes a slight decline in absorption due to their comparative equivalence. In contrast, at substitution levels 15–25 %, the positive effect prevails due to the pozzolanic reaction and the physical effect overriding the adverse consequences of reducing cement. However, at the high replacement level, 30 %, the negative effect prevails because the lack of cement is irreplaceable. The influence of CB in reducing concrete absorption was also reported by Ur Rehman et al. [44]. Fig. 21 elucidates the effect of CB on concrete absorption.

3.9. Compressive strength

The results of the compressive strength test are illustrated in Fig. 22. At seven days age, OPC replacement by CB causes a decline in compressive strength at any replacement level and the reduction magnitude proportion to substitution percentage. The reduction in strength is attributed to the slow hydration of the cementitious mixture of OPC and CB compared with OPC. There are many reasons for the relatively slow hydration due to the incorporation of CB as part of the cementitious binder. First, CB contains a fraction of inert minerals such as quartz; second, the slow dissolution of CM in the alkaline environment [17, 21, 30, 31], and third, the reduction in C_3A and C_3S due to OPC substitution. At 28 days of age, the mixtures containing 5, 10, and 15 % CB develop compressive strength more than the control mixture. At 90 days of age, compressive strength differences tend to decrease by no more than $\pm 9\%$ from the control mixture.

Partial replacement of OPC by CB leads to numerous factors that have opposite effects on the compressive strength of concrete. The intensity of the impact of each factor varies according to the percentage of replacement and the age of the concrete. The factors divide into two categories: positive factors, which increase compressive strength, and negative factors, which decrease compressive strength.

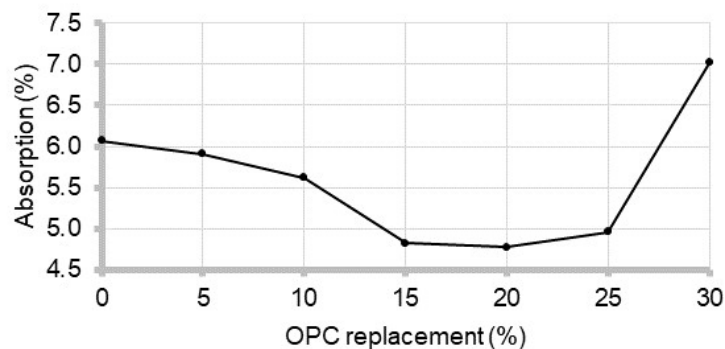


Figure 21. Effect of OPC replacement by CB on concrete absorption.

The positive factors are the pozzolanic reaction which leads to replacing $Ca(OH)_2$ with C-S-(A)-H in both matrix and interfacial transition zone, the modification of pore structure by reducing the fraction of large pores, which have an adverse effect on the concrete strength, the decrement in free water content which leads to reduce disjoining pressure subsequently increase the compressive strength, the addition of new nucleation sites by ultrafine particles of CB, the increment of the cementitious paste fraction due to variance between the specific gravity of CB and OPC, and the retardation effect due to low reactivity of CB which leads to reduce the early age deformations and more uniformity in the distribution of the hydration products.

The negative factors are the reduction in OPC content which causes the reduction in hydration products, the decrease in the rate of strength gain due to CB's low reactivity, and the increment in an unreacted fraction of cementitious binder due to the consumption of $Ca(OH)_2$ by the pozzolanic reaction.

The negative factors are dominant at early ages for any replacement level, while at 28 days, the positive factors are major at 5, 10, and 15 % replacement, and minor at 20, 25, and 30 %. At later ages, the factors are comparable approximately. The optimum replacement level is 5 %, which causes a strength gain of 12 and 9 % from the control mixture strength at 28 and 90 days, respectively.

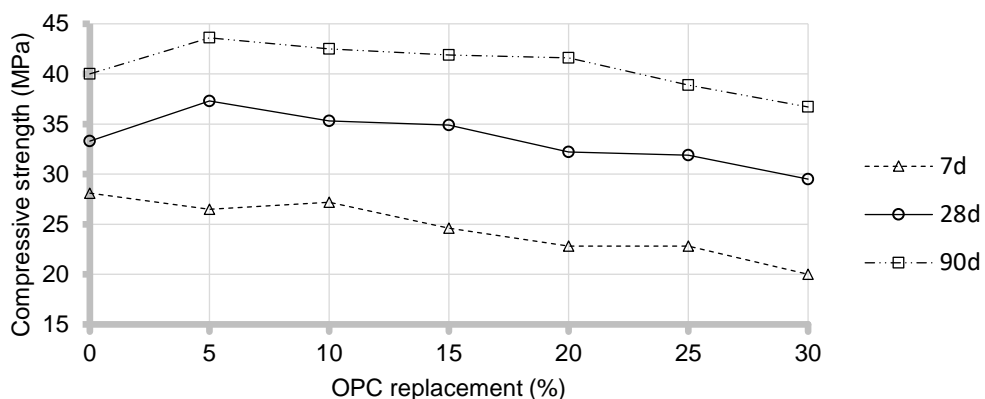


Figure 22. Effect of OPC replacement by CB on compressive strength.

The compressive strength results are consistent with those reported in the previous literature [9, 25, 44].

3.10. Splitting tensile strength

OPC replacement by CB causes decreases in the splitting tensile strength at all replacement levels at 28 and 90 days age, as shown in Fig. 23.

Despite the strong positive correlation between tensile and compressive strengths to the degree of expression of tensile strength as a function of compressive strength, inverse relations were recorded in some experiments when adding pozzolanic materials. In some cases, an increase in the compressive strength was observed as a result of replacing a percentage of Portland cement with pozzolan, at the same time, a decrease in the splitting strength was observed [45–49]; In other cases, a decrease in the compressive strength was recorded with an increase in tensile strength [50, 51].

Martin [52] observed rising in splitting tensile strength associated with the decline in compressive strength due to absorption increase in some types of rocks. The similar observation was recorded by Chen et al. [53] in concrete specimens due to increased moisture content from 80 to 100 %; in addition, it is well known that the flexural strength of saturated concrete is more than the flexural strength of dry concrete [54]. Therefore, free water may positively influence tensile strength due to Stefan's adhesion force (SAF) instead of disjointing pressure in compression. SAF proposed to explain the increase in concrete tensile strength with increasing relative humidity [55] and strain rate [56].

According to the absorption test results, CB incorporation causes reductions in free water content, consequently reducing SAF and thus reducing splitting tensile strength.

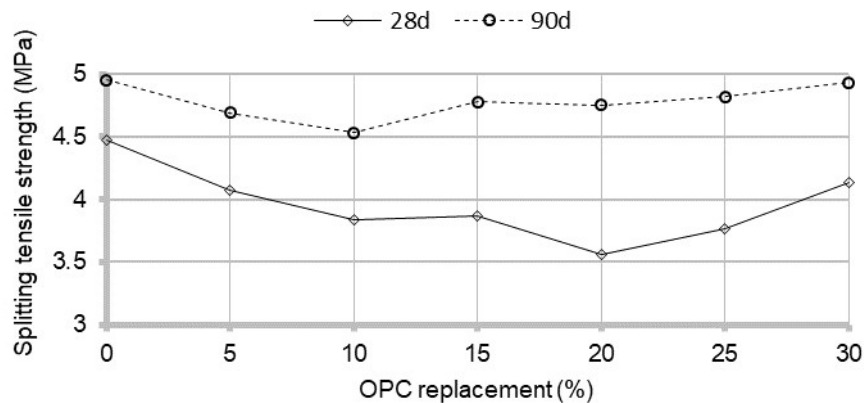


Figure 23. Effect of OPC replacement by CB on splitting tensile strength.

4. Conclusions

According to the results acquired in this study, the following conclusions can be drawn:

1. Iraqi high-calcium bentonite is suitable for preparing natural pozzolan by the method of calcination (thermal activation).
2. The optimum calcination program is 800 °C for 90 min.
3. Its slow reactivity characterizes pozzolan prepared from Iraqi bentonite; that is, it has a retarder effect on the initial and final setting time, reducing the strength gain rate.
4. CB has a reducing effect on concrete workability, and the amount of reduction is proportional to the replacement level.
5. Significant reductions in concrete absorption were observed at 15–25 % replacement levels.
6. CB reduces the compressive strength at 7 days in proportion to CB content. At 28 days, a low replacement level (5 %) leads to optimum strength gain of 12 %, moderate levels (10–20 %) does not cause a significant change in strength, and high levels (20–30 %) reduces strength by about 10 %. At 90 days, the maximum strength gain is 9 % at 5 % replacement, the maximum strength loss is 9 % at 30 % replacement, and no significant change in strength at 10–25 % replacement levels.
7. CB reduces the splitting tensile strength at any replacement level at all ages.

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