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Original Article

Development and assessment of cement and concrete made of the burning of quinary by-product



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ABSTRACT

The aim of this study is to evaluate the usability of new cement (NC) made by the burning of quarry by-product to make commercial binders. Chemical analysis of the by-products and NC as well as X-ray diffraction (XRD) analysis of NC, fineness, density, consistency, and setting time of NC paste, and slump in addition to compressive strength (CS) and splitting tensile strength (STS) of NC concrete (NCC) were conducted. The results suggested that chemical composition of by-products is suitable to make NC binder. The NC contains Ca_3SiO_5 , Ca_2SiO_5 , $\text{Ca}_3\text{Al}_2\text{O}_6$, and $\text{Ca}_3\text{Al}_2\text{FeO}_{10}$. The particles passing through the 200 μm Sieve were 56% compared with 52% for Portland cement (PC). The density of the of NC was similar to that of PC. The NC needed 48% more water than PC for normal consistency. The initial and final setting-time of NC was 105 min and 225 min respectively which is much higher than that of PC (15 and 45 min). The slump, compressive strength and splitting tensile strength were slightly lower for concrete containing NC compared with that of PC concrete. Although the CS and STS of NCC are the lowest, the rate of the CS and STS gain of NCC is greater than that of PC. It was concluded that NC is a viable alternative to PC for the production of greener concrete.

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1. Introduction

In 2020, the World Bank reported that 2.01 billion tons of the municipal solid waste (MSW) are generated annually in the world, and approximately 230 million tons of it was burned. It is expected that the global municipal solid waste will grow to 3.46 billion tons by 2050 [1]. Considering the fact related to the municipal solid waste, coal bottom ash is another waste material generated by power plants. The annual production of coal bottom ash (CBA) is 25 million tons of coal bottom ash (CBA) in India [2], 14 million tons in US, 4 million tons in Europe [3] and about 1.7 million tons in Malaysia [4] which creates environmental problems for the global society. The majority of CBA is used as landfill material and there is no effort to transform it into construction material or other useful products. This situation is not different for pulverized fuel ash (PFA) where 360 million tons of PFA are generated every year and most of the waste (216 million tons) are still stored on the land. According to the United States Environmental Protection Agency (EPA), the use of PFA for landfilling and for construction materials is not harmful to ground water resources [5]. Therefore, using PFA in concrete can reduce the amount sent to landfill and generate income for the producer which is currently between US\$ 20 and 45 per ton [6]. In Europe, according to the European Union (EU) report presented in 2011, the amount of construction and demolition waste (CDW) generated annually in Europe is approximately 1

billion tons, including waste calcined clay brick remnant (WCCBR) [7]. Conventional method to overcome WCCBR is through dumping in landfills which is also expensive. The cost of recycling of one ton of CDW, concrete, brick, and masonry remnants, is about \$21/ton, whilst the cost of landfilling is about \$136/ton [8]. Mediterranean soil, and rock contain high amount of lime component which is essential for cement production.

Additionally, cement manufacturing system releases large amounts of CO_2 into the atmosphere through combustion of fossil fuels and the decomposition of calcium carbonates. This release leads to approximately 7% of total green-house gas (G-HG) emission in the world. Reduction of CO_2 emission due to cement manufacturing can be achieved through: (a) minimizing clinker quantity and increasing the supplementary cementitious materials (SCM) quantity; (b) manufacturing of innovative cement; (c) developing existing cement plants with renewable energy resources, to create new alternative fuels (e.g., bio-mass and waste materials in the burning steps) and (d) making capturing of CO_2 emission during cement manufacturing and its reuse in the production of cement and cement-based material [9].

Supplementary cementitious materials (SCM) can be used to minimize the clinker quantity. These include the use of rice husk ash, palm oil fuel ash, bagasse ash, blast furnace slag, coal fly ash, steel slag and silica fume [10–17]. Using more than one type of waste as supplementary cement materials is not very common. Kikuchi [18] used solid waste incineration

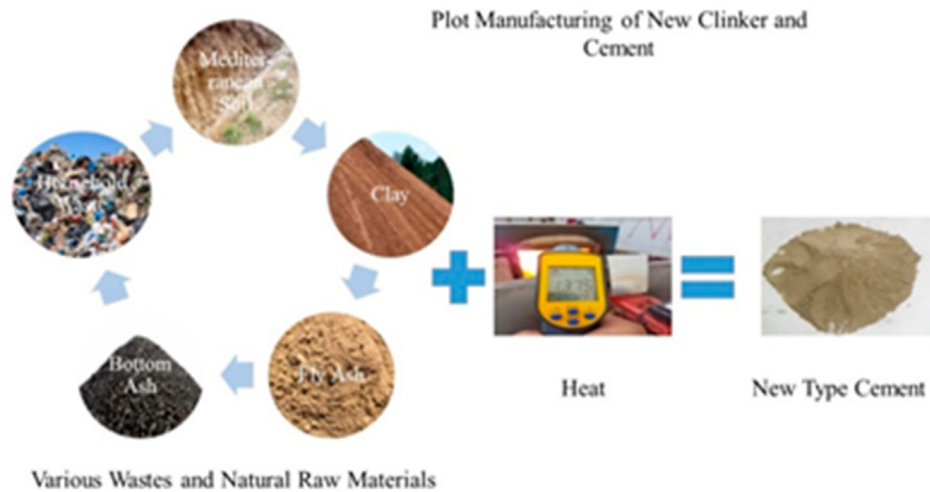


Fig. 1 – Various wastes and natural raw materials, and new clinker and cement manufactured.

ash for the production of cement and recommended the use of approximately 50% of this waste can be used as raw materials. This process of manufacturing does not lead to secondary pollution in air, earth and water. In 2018 Joseph et al. [19] reported that huge quantities of the municipal solid waste (MSW) are generated annually and most of it is sent to landfill. Therefore, using MSW in the manufacture of cement will reduce the quantity sent to landfill and the associated pollution.

In 2014, the European Cement Research Academy [20] reported that the compressive strength of grout containing cement manufactured using kaolinite clay as one of raw materials was higher than that using traditional cement. Apart from the burning process to dispose the waste, another significant study was carried out by Ferraro et al. [21] to produce lightweight aggregate with waste and to minimize risks related to disposal of waste. Analysis of cold-bonding method gave a broad outcome on the treatment and reuse of waste materials productively. Additionally, it presented an important way to decide optimization of waste usefully for both producers and researchers who would like to work on the cold-bonding method.

BS EN 197-1 standard [22] specifies limits for the oxide composition of new cements; the CaO–SiO₂ ratio (by mass) should not be lower than 2 and the magnesium oxide and the

loss on ignition should not be greater than 5%. However, there is no standard limit for heavy metal leaching for cement and cement-based materials [22].

This paper examines the properties of an innovative cement made of more than one type of by-products. The raw materials used for the production of clinker are; pulverized fuel ash, bottom ash, calcined clay waste, Mediterranean soil and household waste ash. To the authors knowledge, there is no research combining more than two waste materials mentioned above in the production of a new cement. The properties of the new cement included fineness, density, consistency, setting-time, chemical component, mineralogy of new cement, and workability, compressive strength, and splitting tensile strength.

2. Materials and methods

2.1. Research procedures

The study was planned in four stages. First stage is related to measure chemical components of by-products (coal bottom ash, coal fly ash, household waste, Mediterranean soil, calcined clay) according to ASTM C 114-18 [23]. This stage is called as description stage of by-products. Fig. 1 illustrates various wastes and natural raw materials, and new clinker and cement manufactured.

Second stage deals with manufacturing new cement with burning the farina which was prepared with quinary by-product. New cement was called as organic cement.

Third stage scope is measurement of new cement specifications, such as chemical components, water demand, fineness, density, setting-time, mineralogy with X-ray powder diffraction (XRD). The specifications were determined according to ASTM C 114-18 [23], ASTM C 187-04 [24], ASTM C 204-18e1 [25], ASTM C 188-95 [26], ASTM C 191-19 [27], ASTM C 1365-18 [28].

Fourth stage deals with manufacturing concrete specimens made of new organic cement and measurement of their slump, compressive strength, and splitting tensile strength.

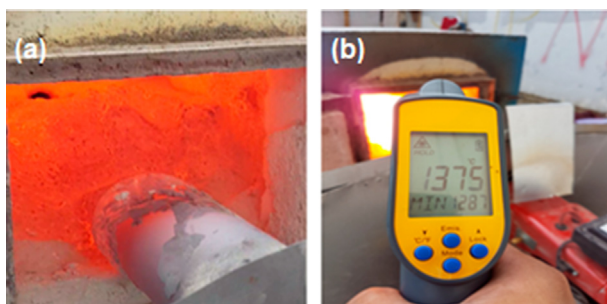


Fig. 2 – The clinkerization from the waste concentrate used in the study: (a) furnace; (b) process temperature.



Fig. 3 – The cement raw material before the combustion process to become the cement concentrate: (a) the Mediterranean soil; (b) the household waste; (c) the calcined clay; (d) the pulverized fuel ash; and (e) the bottom ash.

Table 1 – Percentage of new cement forming.

No	Material source	Main composition (Major)			Additional chemical elements (minor)
		Major chemical elements	Material source	Material used elements	
1.	Mediterranean Soil/S	CaO	60.93	54	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , MgO, SO ₃ , Na ₂ O, K ₂ O
2.	Clay/I	SiO ₂	30.63	10	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , CaO, Na ₂ O, K ₂ O, MgO, SO ₃
3.	Fly Ash/N	SiO ₂	22.14	4	Al ₂ O ₃ , CaO, Fe ₂ O ₃ , SO ₃ , Na ₂ O, K ₂ O, MnO, MgO, TiO ₂
4.	Bottom Ash/A	SiO ₂	15.20	4	CaO, Al ₂ O ₃ , Fe ₂ O ₃ , MgO, K ₂ O, Na ₂ O
5.	Household waste/R	SiO ₂	46.65	28	CaO, Al ₂ O ₃ , Fe ₂ O ₃ , MgO, K ₂ O, TiO ₂ , Na ₂ O, P ₂ O ₅

The compressive strength measurement was performed at 3, 7, 14, 21, and 28 days, and the splitting tensile strength measurement was carried out at 28 days. The properties were determined according to ASTM C 143/C 143M-20 [29], ASTM C 39/C 39M-21 [30], and ASTM C 496/C 496M-17 [31].

The empirical Eq. (1) was used with the by-products mentioned previously to obtain farina.

$$\sum R_{if} = \frac{\sum S + \sum I + \sum N + \sum A + \sum R}{100} \quad (1)$$

where $\sum R_{if}$ is the new cement concentrate (kg); $\sum S$ is the Mediterranean soil concentrate (%); $\sum I$ is the calcined clay waste concentrate (%); $\sum N$ is the household waste concentrate (%); $\sum A$ is the fly ash concentrate (%); and $\sum R$ is the bottom ash concentrate (%).

To manufacture new cement clinker, the farina (combination of Mediterranean soil, household by-product, calcined

clay by-product, fuel ash, and bottom ash) prepared by Eq. (1) was burned at 1375 °C, maintained for four hours and cooled in the laboratory. This new clinker was mixed with 2 wt% gypsum and ground to make the new cement. Fig. 2 shows the clinkerization from the waste concentrate used in the study and Fig. 3 shows the cement raw material before the combustion process to become the cement concentrate.

The percentage of the main ingredients used in the new cement forming is shown in Table 1 below.

2.2. Methods

2.2.1. Chemical component test of by-products and new cement

Chemical composition of Mediterranean soil, household by-product, calcined clay by-product, fuel ash, and bottom ash was determined according to ASTM C114-18 [31] standard,

Table 2 – Details of the concrete mixes.

Types of material	w/c	Proportion of materials (kg/m ³)				Target slump height planned (mm)
		Water	Cement	Materials		
				FA ^a	CA ^b	
New cement concrete	0.52	195	375	538	1232	120
Portland cement concrete	0.52	195	375	538	1232	120

^a Fine aggregates (FA) ≤ 2.5 mm.

^b Coarse aggregates (CA) ≤ 20 mm.

Table 3 – Chemical composition of the by-products used in the manufacturing of new cement.

Chemical compound	Chemical composition (%)				
	Mediterranean soil	Household waste	Calcined clay	Fly ash	Bottom ash
SiO ₂	60.93	46.65	30.63	22.14	15.2
Al ₂ O ₃	0.44	2.28	3.41	3.84	2.99
Fe ₂ O ₃	0.15	0.18	0.20	0.20	0.20
CaO	19.35	11.09	0.51	6.87	1.41
SO ₃	1.66	1.01	0.36	0.89	0.15
Na ₂ O	0.01	2.24	0.01	0.37	1.03
K ₂ O	0.09	11.98	0.23	0.58	0.17
MgO	0.018	0.02	0.02	0.03	0.02
P ₂ O ₅	N/A	0.47	N/A	N/A	N/A
LOI	N/A	N/A	N/A	N/A	N/A

The N/A stands for the “Not available” and the LOI stands for the “Loss on ignition” in the chemistry of cement.

which is known the wet chemical analysis method. Chemical component of the new cement was determined by using the Energy Dispersive X-Ray Fluorescence method.

2.2.2. XRD analysis

Mineralogy of new cement was conducted by XRD analysis according to ASTM C1365-18 [20]. Equations of Bogue calculation and being created of such Bogue chemical compounds as the C₃S, the C₂S, the C₃A and the C₄AF led to some discussion related to the strength gain mechanism of cement-based materials. In the light of the discussion, some comprehensive studies, which used X-ray powder diffraction (XRD), investigate mineral compound of new cement according to ASTM C1365-18 [28]. Bragg equation (Eq. (2)) was used to calculate diffraction angle of X-rays dispersed from sample.

$$n\lambda = 2d \cdot \sin \theta \quad (2)$$

where the symbol of θ is a diffraction angle of material, the symbol of n is a constant, the symbol of λ is a wavelength of the X-ray scattered from new cement, and the symbol of d is a distance between two adjacent parallel lattice planes in the inner crystal structure.

2.2.3. Fineness test

For establishing the size of cement particle firstly, sieve analysis was conducted with a 200-mesh sieve. In accordance

with ASTM C 204-18e1 standard [23], fineness of new cement was determined with the following processes: (1) get some specimen from new cement, (2) scrub the specimen to prevent lumps, (3) have a weigh of 100 g specimen and make it note as (W_1), (4) put the 100 g of specimen on the 200 mesh sieve, and make its lid covered, (5) vibrate the sieve for fifteen (min) (6) have a weigh of residue left on the 200 mesh sieve, and make it note as (W_2), (7) make the left percentage of weight of cement calculate with Eq. (3) and note as (W_t). The test was repeated the mentioned processes with three different specimens of new cement. The presented fineness result is the average quantity of new cement as descriptive statistic.

$$W_t = \frac{W_2}{W_1} \times 100 \quad (3)$$

2.2.4. Density test

Density of new cement and Portland cement was measured according to ASTM C 188-95 standard [26]. The following processes were employed in the test; (1) have a weigh of clean and dry the Le Chatelier flask and make it record as (W_1), (2) fill the new cement specimen up to half of the flask (approximately 50 mg), (3) have a weigh of the Le Chatelier flask along with the specimen and make it note as (W_2), (4) add kerosene into the flask until the flask is almost full of half, (5) make the flask blend thoroughly to remove air entrapped, (6) continue the blending of flask and add kerosene until the flask is filled

Table 4 – Chemical component of the new cement, its comparison with Portland cement, and the limits in chemical component of hydraulic binder to BS EN 197-1:2011 standard [22].

Chemical component	New cement (%)	Portland cement (%)	The limits in chemical component of hydraulic binder to BS EN 197-1:2011 (%) [14]
Alite (C ₃ S)	69.9	50–70	–
Belite (C ₂ S)	7.3	15–30	–
Tri calcium aluminat (C ₃ A)	10.3	5–10	–
Brownmillerite (C ₄ AF)	3.1	5–15	–
Silicon oxide (SiO ₂)	21.29	20.6	–
Aluminum oxide (Al ₂ O ₃)	7.86	5.07	–
Iron oxide (Fe ₂ O ₃)	4.4	2.9	–
Calcium oxide (CaO)	68.43	63.9	–
Sulfate oxide (SO ₃)	3.2	2.53	≤5
Sodium + Potassium oxide Na ₂ O + K ₂ O	1.58	0.88	≤2
Magnesium oxide (MgO)	4.8	1.53	≤5
Loss on ignition (LOI)	1.03	1.58	≤5

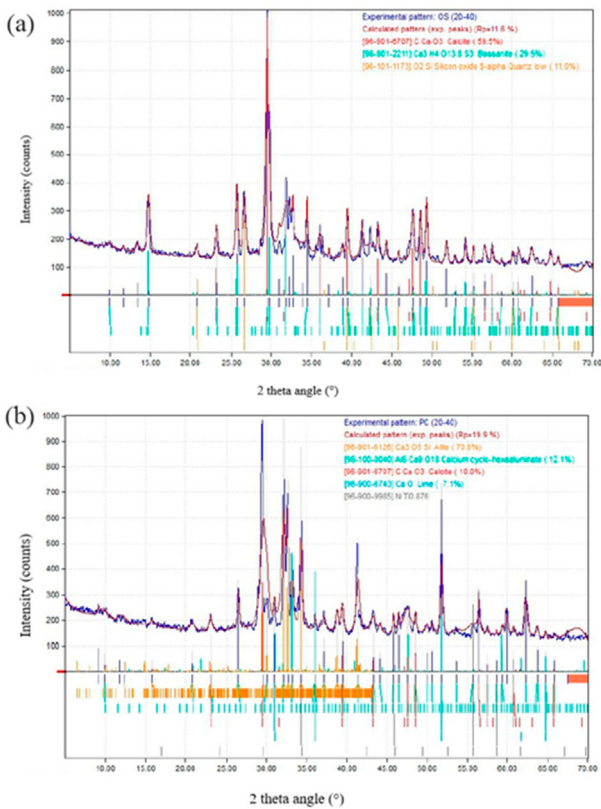


Fig. 4 – XRD diffractograms of: (a) Portland cement; and (b) new cement.

up the graduated mark, (7) make the flask outside dry and get a weigh of flask and note it as (W_3), (8) discharge the flask and make it dry, (9) fill the kerosene into the flask with the graduated mark, (10) make the flask outside dry and have a weigh of the flask with kerosene and note it as (W_4). The density of new cement and Portland cement was calculated along with the following Eq. (4) as will be seen below.

$$\gamma = \frac{(W_2 - W_1)}{[(W_2 - W_1) - (W_3 - W_4)] \times 0.79} \quad (4)$$

In Eq. (4), γ is the density of cement as g/cm^3 and the density of kerosene is 0.79 g/cm^3 was used.

2.2.5. Consistency test

Consistency test of new cement paste and Portland cement paste was conducted to establish the need of water to reach the normal consistency of cement paste. The consistency of new cement paste and Portland cement paste was performed according to ASTM C 187-04 standard [24]. Following process summarizes the test; (1) have a weigh of 400 g specimen and put it in a bowl along with lid (2) make the specimen prevented humidity, (3) put 28% of water by mass of cement specimen and blend it, (4) continue blending cement paste for 3–5 min, (5) fill up the cement paste in the Vicat mold, (6) make the plunger touched the surface of cement paste in the Vicat mold, (7) let the plunger fall to sink into the test mold, (8) make the penetration depth of the plunger from the bottom of mold record, as indicated on the scale of Vicat, (9) repeat the same test along with new paste which was made of different percentages of water until the penetration depth of plunger reaches a degree among 5–7 mm. Three different specimens of cement paste

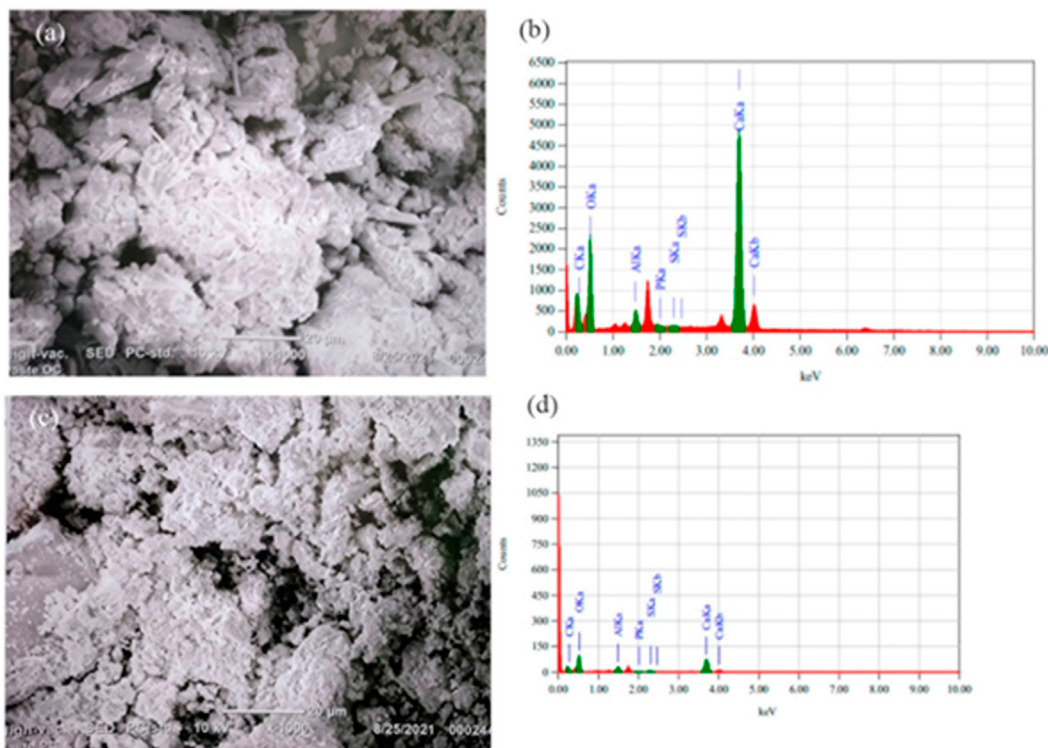


Fig. 5 – (a) New cement SEM; (b) New cement EDX; (c) Portland cement SEM; (d) Portland cement EDX.

Table 5 – EDX results of new organic cement and Portland cement pastes.

Specimen	Chemical composition (%)					
	Ca	O	Al	C	P	S
New organic cement paste	66.81	29.04	2.18	1.67	0.17	0.13
Portland cement paste	58.07	32.05	6.97	1.11	0.08	1.72

were used to repeat the processes of consistency mentioned above, to make it recorded as an average result of consistency.

2.2.6. Setting-time test

According to ASTM C 191-19 standard [27], the setting-time of new cement paste and Portland cement paste was performed as follows: (1) have a weigh of 400 g of specimen from cement (2) make the specimen placed in a bowl along with lid to prevent humidity, (3) put three fifths milliliters of water by mass of cement in the bowl, (4) blend the water and cement specimen, (5) fill the cement paste up Vicat mold, (6) make the plunger of Vicat touched on the surface of cement paste, (7) let the plunger drop to sink into the test mold, (8) make the penetration depth of the plunger from the bottom of mold recorded, as indicated on the scale of Vicat, (9) do again the dropping of plunger at different places on the surface of cement paste until the plunger ceases penetrating 25 ± 2 mm from the bottom of the Vicat mold. At 5 ± 2 mm penetration depth, it is the time for the initial time of setting of the cement paste, (10) record the time for the final setting-time once the plunger is not sinking 0 ± 2 mm from the upper surface of cement paste in the Vicat mold.

2.2.7. Slump test

Slump of concrete was determined according to ASTM C 143/C 143M-20 standard [29]. To obtain the required workability, a mix design was made as shown in Table 2.

2.2.8. Compressive strength test

Compressive strength of concrete was determined according to ASTM C39/C39M-21 standard [30]. The compressive strength of cylinder concrete was calculated according to Eq. (5).

$$\sigma = \frac{P}{A} \quad (5)$$

where the σ is the compressive strength of concrete (MPa), P is the compressive force in failure (N), and A is the cross-sectional field of concrete used (mm^2).

2.2.9. Splitting tensile strength test

Splitting tensile strength of concrete was determined according to ASTM C496/C496M-17 standard [31]. The splitting tensile strength was calculated according to Eq. (6).

$$f_{ct} = \frac{2 \times P}{L \times D} \quad (6)$$

where the f_{ct} is the splitting tensile strength (MPa), P is the maximum force in failure (N), L is the length of concrete specimen (mm), and D is the diameter of concrete specimen (mm).

3. Results and discussions

3.1. Chemical composition of by-products

The wet analysis method was used to determine the chemical composition of the binder. This includes the by-product materials such as Mediterranean soil, house hold waste, calcined clay, fly ash and bottom ash. Table 3 shows the chemical composition results of various by-products used in the manufacturing of new cement.

If it is necessary, the technique which includes separation and isolation is applied to the specimen. The methods of stoichiometric, such as the gravimetric method and the volumetric method, are used in the wet chemical analysis to get the quantitative elements and chemical compounds of the specimen. There are two wet chemical analysis types. The first is the qualitative analysis that establishes which elements are in the specimen, and the second is the quantitative analysis which gives the quantity of elements in the specimen. Almalkawi et al. in 2019 [32] recommended that the use of industrial by-product in geopolymers binder as a green construction material is beneficial and used the wet analysis method for the determination of the chemical components. The study's results proved that ternary blend of by-products could be used to make hydraulic geopolymers binder along with the strength and the upcycling targeted.

Another study on by-product packing glass by bottle, which is similar to Almalkawi et al. was conducted by Ibrahim and Meawad in 2018 [33] and the authors also used the wet chemistry method for the chemical composition of the by-products. Their results revealed that the powder of by-product which was obtained from uncolored glass, green glass, and brown glass is available to make supplementary cementitious materials, and their ions are responsible for their color do not have an effect on the binder properties negatively. ASTM C618-19 standard [34] identified that fly ash pozzolan used has to include more than 70 wt% of silicon oxide (SiO_2) + aluminum oxide (Al_2O_3) + iron oxide (Fe_2O_3) in total. In the current study, the content of SiO_2 , Al_2O_3 , Fe_2O_3 and calcium oxide (CaO) suggests valuable chemical component and potential for new hydraulic binder, and will let the new cement develop strength gain slowly.

There are other studies that show the necessity of the chemical component identification for new material and

Table 6 – The fineness of new cement and Portland cement determined in the experimental study.

Type of fineness measure	Types of material	
	New cement	Portland cement
200 mesh sieve passing (%)	56	52
Specific surface area (m^2/kg)	1200	1250

conventional binder. One of them is an important study reported by Ruiz-Sánchez et al. in 2019 [35], entitled “Waste marble dust: An interesting residue to produce cement”. This study made six clinker types through by-product of marble powder. In order to better examine the chemistry of new binder, they performed the wet chemical analysis on the binder. The results revealed that the chemical component of by-product of marble powder consists of the major presence of CaO, and its physico-chemical analysis confirmed its feasibility, pureness, and cleanness. Additionally, another work conducted by Kirgiz [36] also demonstrated that chemical component of cement manufacturing with burning marble powder and brick powder is essential to decide on this method's usefulness. The works mentioned above support the current work in term of chemical component necessity once new hydraulic cement is manufactured.

3.2. Chemical component

Table 4 shows chemical component of new cement, its comparison with Portland cement, and the limits in chemical component of hydraulic binder according to BS EN 197-1:2011 standard [22]. Chemical component performed by XRF was identified and enumerated with the X-ray radiation reflecting from the material with photoelectric way. The way of photoelectric catches the gamma radiation of X-ray because the electrons are spread from atoms in the specimen through high-energy collisions.

ASTM C 114-18 standard [23] was known as the guideline for this test because the reference is a normative reference which is considerably relevant to the process of chemical component testing of cement. In Table 3, new cement shows that all the limits presented by BS EN 197-1:2011 standard [22] are satisfied. The major ingredient of new cement consists of, as shown in Table 3, the calcium and silicon oxides (greater than 89.7% in total). This quantity of such oxides makes new cement get hydraulic binder properties. Moreover, because of surplus of C_3S , new hydraulic cement can be sorted as an alite along with minor content of belite, tri calcium aluminate, and brownmillerite.

3.3. Microstructural analyses

Fig. 4 shows the comparison of XRD results between the new cement and Portland cement. The X-ray diffraction test result

of the new cement is, then, analyzed by searching and matching, like being in references [37–40].

Additionally, to the result of the searching and matching, it has been concluded that the chemical component of new cement shows similar components as Portland cement. Of all the chemical component presents in the Portland cement, the most important chemical components are alite (Ca_3SiO_5 : C_3S stands for tri-calcium silicate), belite (Ca_2SiO_5 : C_2S stands for di-calcium silicate), aluminate ($Ca_3Al_2O_6$: C_3A stands for tri-calcium aluminate, and ferrite ($Ca_3Al_2FeO_{10}$: C_4AF stands for tetra-calcium alumina ferrite). The four chemical components were obtained for the new cement after its combustion at high and controlled temperature at 1375 °C.

SEM/EDX analyses of new cement paste made of the burning of pulverized fuel ash, pulverized bottom ash, household waste, Mediterranean soil, and calcined clay waste are shown in Fig. 5.

The SEM micrographs in Fig. 5 which were taken from paste specimen containing new cement shows the ettringite crystals which were spread into calcium hydroxide. Ettringite is formed in the early age of paste to reduce the flash setting of cement, nevertheless; its meaning is that the hydration of the paste mixing had not been completed, which will lead to an expansion. Therefore, it weakens the interfacial transition zone in cement-based materials. It was observed in hydration of new cement paste, angular cement grains were surrounded by radiating amorphous of calcium hydroxide (CH) which resemble the pattern of CH in ordinary cement paste. Randomly oriented portlandite (CH) crystals and prismatic ettringite crystals were widely dispersed throughout the paste. Table 5 shows the chemical elements of new cement paste and ordinary cement paste which were observed in SEM/EDX machine.

However, in the new cement paste, SEM found out that the ettringite prisms were covered with amorphous layered CH hydration products. Matrix phase is mainly composed of short radicular outgrowths of CHs around cement grains and needle-shaped ettringite crystals (Fig. 5(a)). Microstructure of hydrated new cement paste was presented by amorphous gel filling spaces between hydrated particles. Moreover, the new cement pastes layered accumulations of the CH crystals which are approximately 10–12 μm in width are intermingled throughout the paste (Fig. 5(a)). There is a visible densification around new cement grain, leading to formation of additional

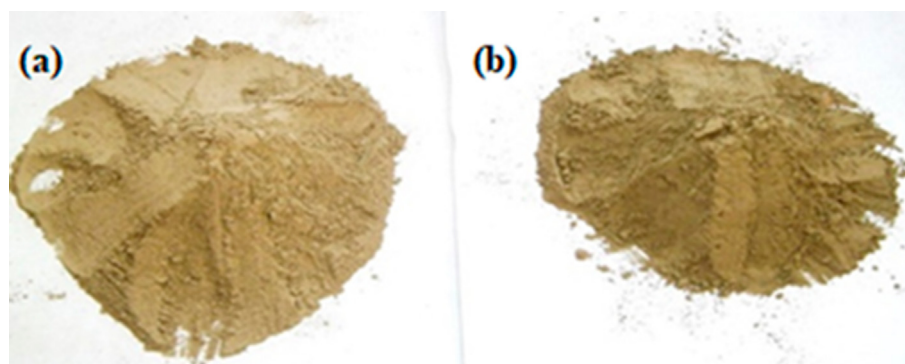


Fig. 6 – A process of measuring the fineness and the density of cement: (a) new cement; and (b) the Portland cement that is used as a comparator in testing the physical properties.

Table 7 – Normal consistency results of new cement paste and Portland cement paste.

Type of binder and mixing material quantity		Test of consistency			Average results of consistency (%)
		Specimen I	Specimen II	Specimen III	
Portland cement	Cement (g)	500	500	500	25
	Water (ml)	128	125	122	
New cement	Cement (g)	500	500	500	37
	Water (ml)	175	180	200	

C–S–H for later age. Observation of new cement paste demonstrated that the CH phase is found to be richer than C–S–H gel.

Fig. 5(c) and (d) shows SEM and EDX analysis of ordinary Portland cement paste respectively. The ordinary cement paste contains calcium hydroxide (CH), ettringite needles, CSH gel and calcium alumina hydrate (C–A–H).

Table 5 presents EDX results of both new organic cement and Portland cement pastes. From the comparison of chemical elements of new organic cement paste and ordinary Portland cement paste, it can be deduced that their results are similar. This means that both SEM/EDX; wet chemical; and XRD results support the properties of new organic cement and Portland cement pastes.

3.4. Fineness

The more fineness is the more cement particles participate in hydration since cement starts hydration process from surface to inside in the cement-based materials. Thus, hydration performance is related to the fineness of cement, and for a rapid gain of strength, the more fineness is a necessity. On the other hand, the greater fineness is the more cost of grinding process is for cement. Moreover, the effect of more fineness on such other properties as slump of fresh concrete, gain of strength and need of gypsum have to be taken into account. Fineness is an important property of binder, and it is necessary to make the fineness be determined with sieve method and specific surface method in m^2/kg according to the rules of BS and ASTM standards. The air permeability method, which makes the pressure drop once dry air flows at a constant velocity through a bed of cement known porosity and thickness determines the specific surface of cement. In 2020, Kumar and Nath [41] suggested that the finer cement, the better are its properties and the better is the development of its

microstructure. Kan et al. in 2019 [42], explained the importance of fineness property for cement-based binders. The fineness of new cement and Portland cement determined was given in Table 6.

The quantity of fineness of new cement is 56% for the 200-mesh sieve passing and $1200 m^2/kg$ for specific surface area while the quantity of fineness of Portland cement is 52% for the 200-mesh sieve passing and $1250 m^2/kg$ for specific surface area. The smoother cement is the greater specific surface area is for cement particle. An increase in fineness will accelerate the hydration process with more water demand than that of normal hydration process of Portland cement. Image of new cement and Portland cement is presented in Fig. 6.

In concrete mixing, water-to-cement ratio is calculated with water mass/cement mass and usually shorten as w/c. The water-to-cement ratio has a strong effect on the strength gain of concrete. For instance, in a concrete mixture which strength gain was targeted, increase in w/c will decrease the gain of strength at all ages, and decrease in w/c will increase the gain of strength at all ages [43]. In 2019 Ghasemi et al. recommended a relationship between the specific surface area of mortar constituent and its flow [44]. Its results revealed that the demand of water in cement-based material is related to the specific surface area of mixture constituents. Estimation of the specific surface area depends on accounting of angularity of particle while content of water and thickness of paste film are essential for estimating the fluidity [44].

3.5. Density

The adaptation of density of cement in connection with vibration and plasticizer could enable more workability for concrete [43]. Comprehensive works, which are taken into account to reach out the targeted final properties of concrete, were conducted on the bulk density of cement as plenty of many theoretical models recommended to estimate the bulk density of cement [45–48]. The bulk density of Portland cement is $3.15 g/ml$ while the density of new cement is $3.05 g/ml$ as will be observed at the current research work. In this case, the ASTM C 188-95 [26] standard formulated the bulk density of cement, and it is valid. Apparent density of fresh concrete with new cement is $2081 kg/m^3$ and its dry density is $2032 kg/m^3$. The both are lower than that of Portland cement concrete ($2525 kg/m^3$).

Additionally, these estimation models are depended on the bulk density curve optimization, vibration of cement-based material, and the quantity of ingredient calculation. Firstly, choosing of concrete and cement-based material has to consider the void of side edge in formwork for construction element, such as column, beam, and floor, so that the void of

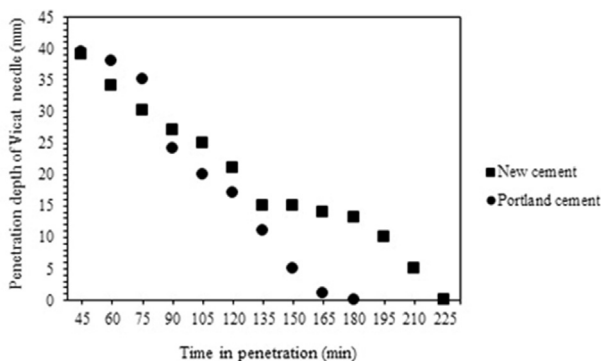


Fig. 7 – Initial and final setting time of new cement and Portland cement determined.

rust ratio could be filled concrete up. Secondly, the bulk density of materials used in the mixture needs to be known. Lastly, the modeling of bulk density relates to the theoretical density of concrete and cement-based material mixture because this theoretical density could be computed mathematically by determining the bulk density of cement which has different mean size of particle as well [46,49].

3.6. Consistency

Table 7 shows the result of normal consistency test for the new cement paste and Portland cement paste. The test of normal consistency is referred to ASTM C 187-04 [24].

The importance of consistency test stems from the fact that when water is mixed with cement, its hydration process starts. Surplus addition of water in cement leads up to an increase in water-to-cement ratio, and the increased water reduces the strength of cement paste after it hardens. If less water is added than required, the cement paste composite is not properly hydrated, and the insufficient water content leads up to the loss on the strength, especially the compressive strength. Water has an influence on the workability, strength, shrinkage, and durability of concrete. Normal consistency formed in new cement is a need of 37% water by mass of cement while the need is of 30% water by mass of Portland cement.

3.7. Setting-time

Fig. 7 shows initial and final setting time of new cement and Portland cement. As new cement contains 2% gypsum and 98% new clinker, which was prepared by burning compound of Mediterranean soil, calcined clay, bottom ash, fuel ash, and household waste. The new cement hardens slower than Portland cement, as shown in both initial set and final set test results. That setting process of new cement indicates that if it is necessary to harden rapidly, the gypsum percent within the new cement has to be increased.

The ASTM C 191-19 [27] defines the required setting-time that it starts when water contacts with cement and continues before chemical reactions cease, even if cement is placed under the water. According to ASTM C 191-19 standard [27], initial setting-time of cement should not start before

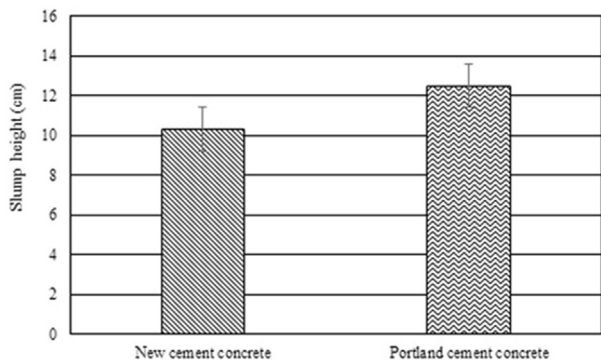


Fig. 8 – Slump heights of new cement concrete and Portland cement concrete with water-to-cement ratio 0.52 and their standard errors.

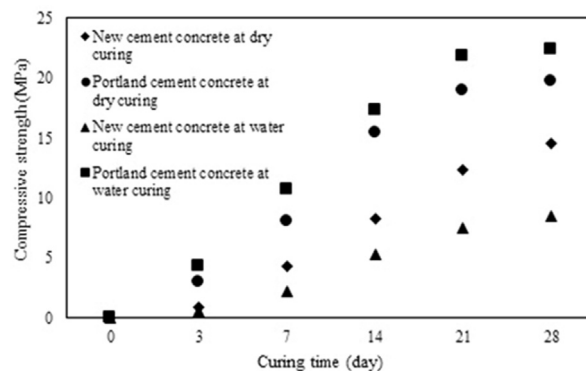


Fig. 9 – The lines of the test result of compressive strength of cylinder concretes of new cement concrete and of Portland cement concrete using dry curing and water curing methods.

75 min. Since the new cement started initial setting-time at 105 min and Portland cement started initial setting-time at 90 min, both new cement and Portland cement obtains the standard rule on initial setting-time according to ASTM C 191-19 standard [27].

At initial setting-time, new cement includes 37% water content while Portland cement contains 25% water content. The more water is the lower consistency is for the new cement and Portland cement. The final setting time of Portland cement is at 180 min, while final setting time of the new cement is at 225 min. Both final setting-time of new cement and of Portland cement enable to obtain standard rule for final setting-time of concrete that it should not be greater than ten hours. As known from literature, C₃A and C₃S starts the setting-time of Portland cement. After that, C₂S hardens the Portland cement gradually. Lastly, C₄AF participates in the setting-time of Portland cement.

As seen in Table 4, new cement has 55% greater aluminum oxide, 51% greater iron oxide, 3% greater silicon oxide, 7% greater calcium oxide, 24% greater sulfate oxide, and 313% greater magnesium oxide than that of Portland cement. Gypsum content varies between 3% and 5% in the Portland cement. New cement contained 2% gypsum, instead. The difference in chemical component and gypsum content

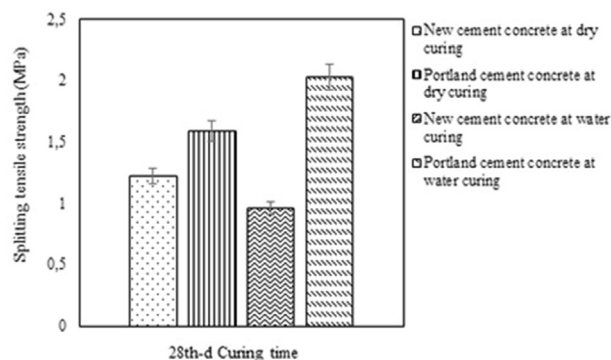


Fig. 10 – Splitting tensile strengths of concrete made of new cement and of Portland cement.

among new cement and Portland cement led to a difference in their setting-times. Apart from rapid and false setting-time and crystalline structure of cement paste, formation of film layer in the surface of cement particles and coagulation of chemical component of cement are two important factors which develop the setting-time. It is clear that the more aluminum oxide component is the more retarding of the setting time of new cement is because it leads to an increase in heat during stiffness process of the new cement. Its setting-time could be accelerated with an increase in gypsum content in new cement. Nevertheless, the initial and final setting-time is suitable for the new cement because it obtains the limit of setting-time which was specified by the BS EN 197-1:2011 standard [22].

3.8. Workability

Slump test of concrete was measured according to the rules of ASTM C 143/C 143M-20 standard method [29]. Slump is the oldest and the most widely known property for monitoring the workability of concrete. Workability of fresh concrete is related to the flow and w/c at microstructure field between cement paste and aggregate during preparing, transport, vibrating, and putting concrete into formwork. Considering the concrete mix, three different types of slump can happen: true slump, shear slump, and collapse slump. True slump depends on leveling of the concrete mass with keeping integrity.

The lack of cohesion in concrete constituent points the shear slump which leads to segregation. The collapse slump is the most dangerous one among the all. It usually points a lean, harsh, and a very wet mix. For example, many modern high-performance concrete buildings were designed for a slump of about 200 mm, which displays collapse slump effect. In situ and laboratory, the slump measurements start immediately after water and concrete ingredients contact with each other. In the work, since concrete was prepared at a room temperature of 23 ± 5 °C and of 53% humidity maintained constantly, the determined slump did not affect factors mentioned previously.

Fig. 8 shows slump heights of new cement concrete and Portland cement concrete with water-to-cement ratio 0.52 and their standard errors.

Additionally, the planned target slump height is 12 cm for both cement concretes. The Portland cement concrete exceeded the target height of slump with only 0.5 cm, while new cement concrete did not reach out to the target, its slump height was 10.3. It is clear that the greater water-to-cement ratio causes a higher slump height in concrete. This is attributed to the fact that water makes cement transform into dye, not binding material. In other words, water breaks up binder property of cement and leads to degrading of the strength of concrete, especially compressive strength.

For that reason, the chosen water-to-cement ratio in the study is enough for both new cement concrete and Portland cement concrete. Since the more water-to-cement ratio will lead to a lower mechanical strength is in concrete at all curing ages and different curing conditions, the ratio of w/c 0.52 would be constant for following sections and the CS and the STS are determined within the given w/c ratio. This will

provide standard strength development for new cement concrete, like Portland cement concrete has. Lastly, the workability of concrete is very non-objective.

The workability of concrete was sorted into three classes: qualitative, quantitative empirical and quantitative fundamental. Class I is qualitative method which is based on observation of workability, flowability, compactibility, stability, finishability, pumpability, consistency. Class II is quantitative empirical way which uses simple quantitative tests of slump, compacting factor and Ve-be, instead. Class III is a quantitative method uses viscosity and yield stress. Since slump was determined with quantitative empirical way, workability of new cement concrete is Class II.

3.9. Compressive strength

Mechanical properties depend on many factors in concrete. Major factors are the sample type, size, w/c, and test condition. A number of research measure the property through various sizes of hardened concrete and different water-to-cement (w/c) ratio. This is like comparison of apple with pear because of the fact that the preparation and w/c of concrete are not the same in the mechanical test. In order to prevent compressive strength results from any errors, all conditions regarding on the preparation, size, and w/c, and so on were kept constant in the work. The lines of the test result of compressive strength of cylinder concretes of the new cement concrete and of Portland cement concrete on which dry curing and water curing methods were applied can be seen in Fig. 9. The compressive strength of new cement concrete and of Portland cement concrete produced were calculated with the ASTM C-39/39M-21 standard [30] in the reference method that all laboratory uses. For that reason, the results could be repeated in a laboratory that can be found in any part of the world.

The compressive strength test of the cylinder concrete made of Portland cement by using water curing method results in 22.37 MPa, and it results in 19.71 MPa when the dry curing method is used. The compressive strength test for the cylinder concrete made of new cement using maintaining method of water curing results in 8.52 MPa, and it results in 14.52 MPa when the dry method is used. Although the compressive strength of new cement concrete is the lowest,

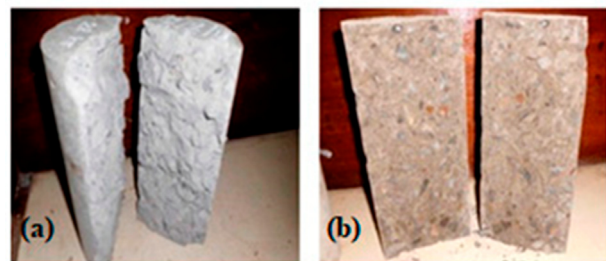


Fig. 11 – (a) Failure form of splitting tensile force at concrete cylinder made of new cement; and (b) failure form of splitting tensile force at concrete cylinder made of Portland cement.

the rate of compressive strength gain of new cement concrete is greater than that of Portland cement concrete.

Because the results of the new cement concrete and Portland cement concrete are very close to each other, it is concluded that the new cement and the new cement concrete could provide the demand of green binder and of green binder material for construction technology.

Moreover, it is necessary to review the chemical component of new cement on the compressive strength gain of new cement concrete. Since it contains much more oxides of calcium, silicon, iron, aluminum, magnesium, sodium, potassium, and sulfate, and lower gypsum content than that of Portland cement, new cement concrete demonstrates the slow compressive strength gain. This could be attributed to the lack of gypsum content in new cement concrete.

3.10. Splitting tensile strength

Fig. 10 shows the graph comparisons of graphs between splitting tensile strengths of cylinder concrete made of new cement and of Portland cement. Results indicate that the test of material enables to endurance against force of splitting tensile. Additionally, the ratio of the splitting tensile strength of concrete shows to the compressive strength of concrete approximately 0.05–0.1.

Concrete made with Portland cement and cured in water has the highest splitting tensile strength. Water curing method results in 2.03 MPa splitting tensile strength for Portland cement concrete, while dry curing method leads to 1.59 MPa splitting tensile strength for Portland cement concrete.

Concrete made with new cement and dry cured shows a higher splitting tensile strength than those treated at water curing. The water curing method results in 0.96 MPa splitting tensile strength, while dry curing method leads to 1.22 MPa splitting tensile strength in concretes made of new cement. Fig. 11 shows the failure patterns of concrete made with ordinary cement and the new cement at 28 days of curing. The failure pattern is similar for both types of cement.

Finally, despite the fact that the new cement is finer than the Portland cement, this is not a factor to affect the splitting tensile strength of new cement concrete positively. Curing conditions, wet curing and dry curing, are the most important contributing factors for the splitting tensile strength of new cement concrete. Because the splitting tensile strength results of new cement concrete and Portland cement concrete are very close to each other, it could be inferred that the new cement concrete could be a promising new green binder.

4. Conclusions

From the results of examination of fineness, density, consistency, setting-time, mineralogy, and chemical properties of new cement, there are similarities with the properties of Portland cement. This can be referred to the physical test results, XRF analysis, and XRD analysis of new cement.

The new cement is finer than Portland cement with a solid weight of 1200 m²/kg, lighter than Portland cement which reaches 1250 m²/kg. The specific gravity of Portland cement is 3.15 g/ml while the density of new cement is 3.05 g/ml. The initial setting time of Portland cement was carried out 90 min where the Vicat needle penetrated into the cement paste for 24 mm. The initial setting time of the new cement was also tested by the same method by penetrating 25 mm of cement for 105 min after the needle was removed. The final setting time of Portland cement is 180 min while the new cement reaches 225 min. Based on the results of slump, compressive strength, and splitting tensile strength, it can be concluded that new cement manufactured can be used for structural and non-structural work as well as for the installation of brick walls and for covering the walls with stucco. This demonstrated the ability of new cement to undergo chemical setting and binding of aggregate as a support material in a key process of construction work.

Additionally, the problem of waste and the effort of saving the environment from the accumulation of waste can be overcome wisely through this approach of experimental study, as this work has achieved to make new cement be an alternative binder material for construction industry, especially at dry curing condition.

Availability of data and materials

The “Experimental and Numerical Research” data used to support the findings of this study are available from the corresponding author upon request.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jmrt.2021.09.140>.

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