Waste Egg Shell – Cement Paste Composites For Sustainable Construction Applications

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Abstract — Utilization of waste materials as construction material is necessary to achieve sustainable construction, and reduce CO₂ emissions. This paper examined the effect of egg shell as cement replacement on properties of cement paste composites for sustainable construction. To this end, granulated egg shell (GES), egg shell dust (ESD), and egg shell dust-marble powder (MP) substited composites were produced. Fresh mixtures subjected to flow table test, while hardened composite samples subjected to compressive strength, permeable voids, and porosity tests. The results further show that addition of MP along with ESD is beneficial for performance of cement paste composites.

Keywords — *egg shell dust*, *graulated egg shel*, *marble powder*, *cement paste composites*, *compressive strength*

I. INTRODUCTION

A. Preliminary remarks

Ordinary Portland cement (OPC) is widely used construction material in worldwide [1]. The main raw materials used in the production of OPC are (CaCO₃), sand (SiO₂), clay (SiO₂, Al₂O₃, and Fe₂O₃), iron ore (Fe₂O₃), and gypsum (CaSO₄) [3, 4]. OPC contains between 93-97% clinker which is obtained by burning limestone with high heat treatment [2]. In the burning process called calcination (about 3.2-6.3 GJ energy is required), the calcium carbonate (CaCO₃) decomposes, causing CaO formation and CO₂ release (CaCO₃ \rightarrow $CaO + CO_2 \uparrow$ [5–8]. It is known that the amount of CO_2 released to the atmosphere during burning process is more than 50% of the total amount of CO₂ released during the cement production process [9, 10]. Previous studies have reported that 1.5 tonnes of raw material, 0.3 tonnes of air is needed for one tonne of cement production, 0.74–0.90 tonnes of CO₂ is released into the atmosphere during production, even so is causing global CO₂ emissions in large quantities [11–14]. For this reason, the sustainability of the cement and concrete industries is necessary to the livable environment and to human life cycyle [15]. Sustainability term was defined by World Commission on Environment and Development as "meeting the

needs of the present without compromising the capability of the future generations to meet their own needs" [16, 17]. In order to avoid to environmental problems due to cement production (such as CO_2 and NO_x emissions, use of natural reources, need more energy, etc.) researchers have investigated byproducts or waste materials that can be used as an alternative to cement for civil engineering applications [18–21].

According to the March 2017 report of the Statistical Institute of Turkey, the number of eggs were produced in 2017 is 1.6 billion [22]. Egg shell with high amounts of CaCO₃ in their chemical structure has been commonly used for various purposes like animal feeds, cosmetics and medicine as a raw material [23, 24]. It is known that CaCO₃ in egg shell reacts with C₃A, the main constituent of the cement, to form the binding carboaluminate [25–27].

Marble powder is an industrial non-biodegradable waste with generated during marble cutting at mines [28]. Due to the high amount of CaCO₃ present in the chemical structure and the relatively low amount of SiO₂, some researchers have described it as pozzolan [29, 30]. Turkey has nearly $3.872 \times 106 \text{ m}^3$ of marble mine reserves, of which approximately to 125×103 t/year are generated in Afyon City [31]. Globally, the storing or abandonment to nature of these marble wastes is a serious environmental problem. However, there were many studies reported that the waste marble (dust, powder, slurry, coarse or fine particles) can be improve some properties of concrete [32–36].

B. Research significance

Egg shell's chemical composition nearly same as that of limestone. In literature, there are limited number of studies examining the availability of egg shells for concrete production. Nevertheless within the scope of sustainability there is a need to understand effect of egg shell dust on fresh and hardening properties of cement based materials. In addition the usage of waste marble (dust, powder, particles, etc.) in civil engineering applications may be an important step toward sustainable development. Aim of this study was substitution of egg shell dust by cement which is a major constituent in cement paste composites, from which concrete is made.

C. State of art

Bandhavya et al. [37] reported that the egg shell dust at a cement replacement ratio of 5-10% increased the 28-day compressive strength by 7.8% and 9% compared to reference sample. Binici et al reported that the compressive strength decreased at ratios of 10.6%, 16.4%, 21.3%, 28%, 34% and 40.6% when egg shell dust used as replacement by fine aggregate at ratios of 5-50%. However, but, Kumar et al. [38] reported that the compressive strenth of concrete specimens produced with 5% and 10% egg shell dust subsitution higher than reference sample by 11% and 9.3%. Hama et al. [39] replaced cement with 5, 10, 15 and 20% egg shell dust. They reported that the 28-day compressive strength decreased by 2.6%, 4.4%, 7.43% and 11.5%. Similarly, Parthasarathi et al. [40] argued that egg shell powder increased the compressive strength up to a 10% substitution ratio and decreased compressive strength by 15% substitution. Rana et al. [41] determined that decreased the 28 day compressive strength by 5.8% with 10% marble powder substitution with cement. Shirule et al. [42] reported that marble powder at a cement-replacement ratio of 10% increased the 28-day compressive strength by 17%.

II. MATERIALS AND METHADOLOGY

A. Materials

In the experimental study, Ordinary Portland cement (OPC) 42.5 R was used in accordance with ASTM C150 [43]. The blaine fineness and specific gravity of cement was 310 m²/kg and 3.15, respectively. The chemical properties of cement is given in Table 1.

The marble slurry was provided from a dumping ground near a marble processing plant. Slurry was dried at room temperature for 72 h and marble slurry return to marble powder (MP). The specific gravity was 2.49 and the fineness of the powder was $335 \text{ m}^2/\text{kg}$. Its chemical composition is presented in Table 1.

Table 1. Chemical properties of cement and marble powder

Chemical components (%)	OPC	Marble powder _		
C ₃ S	59.7			
C_2S	7.1	-		
C ₃ A	2.53	-		
C ₄ AF	8.33	-		
MgO	2.4	3.8		
SiO ₂	21.10	14.4		
CaO	62.2	52.5		
Al ₂ O ₃	3.7	4.23		
Fe ₂ O ₃	2.97	1.57		
K ₂ O	0.33	0.16		
SO ₃	2.4	0.13		
Na ₂ O	0.11	-		
L.O.I.	2.46	41.26		

Egg shells were provided from integrated egg facility in Nicosia/Cyprus and grinding process was carried out in laboratory. The chemical properties of egg shells were specified by the facility. Before use, egg shells were washed with tap water to purify albumin. The chemical compisition of egg shells are given in Table 2.

Table 2. Chemical properties of egg shell

Chemical components	(%)
CaCO ₃	92–98
Mg	0.2-1.0
$Ca_3(PO_4)_2$	0.2-0.9
Organic materials	2–3
Na	≤ 0.1
K	≤0.1
Fe	≤0.1
Mn	≤0.1

B. Methadology

Prior to grinding, the egg shells were dried for 24 h in an oven at a temperature of 105 °C. After 24 h, the temperature was reduced by 20 °C per minute. After that, egg shells were cooled at room temperature which is 22 °C for 12 h (see Figure 1). Grinding process carried out was 2 steps: 1) The egg shells was grinded until to particle size range of 2–2.36 mm (see Figure 2– a, b), thus granulated egg shell (GES) was obtained. 2) GES was grinded until to particle size range of 0–1 mm (see Figure 3), thus egg shell dust (ESD) was obtained.



Fig1. Egg shells at room temperature



Fig. 2-a Minning apparatus Fig. 2-b Granulated egg shell (GES)



Fig. 3 Egg shell dust (ESD)

Cement paste composites were mixed in mini–mixer having 2.5–liter capacity. Egg shell wastes (GES and ESD), marble powder (MP) and cement were mixed for 30 s in mixer. After that tap water was added to mixture and mixed for 30 s more. The mixtures was vibrated by vibration table for 45 s and casted to 50–mm cubic molds. ESD samples were demolded after 1 day and subjected to standard curing according to ASTM C31 [44] standard. GES samples were demolded after 1 day and kept in laboratuary conditions at 18 ± 2 °C and 70% relative humidity according to Binici et al. [45] methods until testing. Same method have been selected for benchmarking to experimental results.

The prepared 50–mm cubic samples were subjected to compressive strength on days 7, 14 and 28 in accordance with ASTM C109 [46] standard. A total of 168 samples were produced, 126 for compressive strength test and 42 for permeable voids and porosity tests. Flow values of mixtures were measured on the flow table test according to ASTM C230 [47] standard. Porosities of composites were measured using a vacuum saturation apparatus. While the porosity values of the samples are calculated, the formula used given by Xu et al [48]. The formula used is shown below in Equation (1):

 $P(\%) = (Ws - Wd) / (Ws - Wb) \times 100$ (1)

Where *P* is porosity, *Ws* is water saturated sample weight, *Wb* is weight of the sample in water, *Wd* is oven dry weight of the sample.

Permeable voids in cement paste composites were calculated using the following Equation (2):

Permeable voids = $(A - B) / V^*100$

Where A is the weight of surface dried saturated sample after 28 days immersion period, B is the weight of oven dried cement paste composites in air, V is the volume of composite [24].

C. Mixture proportions

There were 3 type mixtures prepared for experimental work: 1) cement was replacement by granulated egg shell ranging from 5 to 15%, 2) cement was replacement by egg shell dust ranging from 5 to 10%, 3) cement was replacement by combination of egg shell dust (2.5%) and marble powder (7.5%). The water–to–binder (w/b) ratio were kept constant at 0.4 in all mixtures. Design of mixtures were chosen based on the w/b ratio of the cement composites. Samples were encoded the form of X–Y. Where X is substitution ratio, Y is type of waste. Mixture ratios are presented in Table 3.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Flow table

Flow table results of egg shell dust–marble powder– cement paste composites are shown in Figure 4, while granulated egg shell–cement paste composites are shown in Figure 5.



Samples	Content (kg)						
	Cement	GES	ESD	MP	Water	w/b	
Reference	1.2	1	I	I	0.48	0.4	
5–GES	1.14	0.06		Ι	0.48	0.4	
10-GES	1.08	0.12	-	-	0.48	0.4	
15–GES	1.02	0.18	-	-	0.48	0.4	
5–ESD	1.14	-	0.06	-	0.48	0.4	
10-ESD	1.08	-	0.12	-	0.48	0.4	
2.5–ESD7.5– MP	1.08	-	0.03	0.09	0.48	0.4	



Fig. 4 Flow spread results of egg shell dust-marble powder-cement paste mixtures



Fig. 5 Flow spread results of granulated egg shell-cement paste mixtures

The flow spread of the cement paste mixtures increased as the both egg shell dust and granulated egg shell replacement increased (see Figure 4 and 5). However, as seen in Figure 4, egg shell dust-marble powder combination was decreases cement paste mixtures. The flow spread value decreased by 57% compared to reference sample. Similarly, Rana et al. [41] reported that the slump values at 5 and 10% substitution rates of marble powder in concrete mixtures prepared by keeping the w/b ratio decreased by 3.57% and 7.1%, respectively. In addition flow spread vaues were increased at ratios of 6.8%, 11.3% and 15.9% for 5, 10 and 15% egg shell dust replacement, respectively. The granulated egg shell was showed increasing effect to flow values in all replacement ratios compared to egg shell dust. For example, compared to reference sample, the 10-GES mxiture showed 6.8% higher while 10-ESD mixture had 4.5% higher value. There are three possible reason of this situation: 1) the granulated egg shell, which is composed of very large particles compared to the cement and egg shell dust, was not exhibit any frictional

force due to heterogeneous distribution in the mixture (although the geometric structure is irregular), 2) the viscosity of the cement paste was reduced, 3) despite the decreasing amount of cement, it's thought that the amount of unchanged water was released in the mixture because the ratio of w/b is constant. Sivakumar and Mahendan [21] reported, however, that the slump values of mixtures containing egg shell powder tendency to decreased. The main reason for this distinction is thought to be the addition of egg shell powder as a mineral additive. The slump spread values were determined to be lower in composite mixture produced with combination of egg shell dust and marble powder substitution compared to mixtures produced with granulated egg shell substitution, and reference mixture. Similarly Rodrigues et al. [49] and Hebhoub et al. [35] reported that the slump values were decreased with increasing marble powder substitution.

B. Permeable voids

The determined permeable voids values are presented in Figures 6 and 7



Fig. 6 Permeable voids of granulated egg shell-cement paste composites



Fig. 7 Permeable voids of egg shell dust-marble powder-cement paste composites

The data in Figures 6 and 7 show that the permeable voids values increased in all composites compared to reference sample. Considering the 5–GES, 10–GES, 15–GES, 5–ESD, 10–ESD, 2.5–ESD7.5–MP samples permeable voids were, 97%, 189%, 268%, 13.1%, 21%, and 14.5% greater than reference sample, respectively. However, it was observed that the permeable voids values of the composites produced with ESD and MP substitution were relatively low compared to the samples produced with GES

substitution. For example, This situation can be explained by two ways: 1) The CaCO₃ in the chemical structure of ESD and MP showed the nucleation effect for the formation of C–S–H gel. Thus, a relatively non– empty internal structure is formed. 2) ESD and MP wastes showed an uniform distribution than GES waste. Similarly, Hama et al. [39] and Yerramalla et al. [24] reported that the permeable voids increased with increasing egg shell powder substitution.

C. Porosity

Figure 8 and 9 shows porosity values of composites. Figure 10 shows relationship between

permeable voids, porosity (P) and dry unit mass (DUW).



Fig. 8 Porosity results of granulated egg shell-cement paste composites



Fig. 9 Porosity results of egg shell dust-marble powder-cement paste composites



Fig. 10 Relationship between porosity, permeable voids and dry unit mass of composites

When Figure 8 is examined, it is seen that porosity values increase with increasing the substitution ratio of granulated egg shell waste; however, the increasing ratio slowed down between 5-10% substitution ratios. Composites produced with 5, 10 and 15% granulated egg shell substitution, showed high porosity values compared to reference sample by 15.2%, 18.4%, 31.7%, respectively. However, porosity of composites produced with egg shell dust was linearly increased at all substitution ratios, except combination of egg shell dust and marble powder (see Figure 9). This could be explained by uniform distribution of marble powder than other wastes. Thus, it causes a realatively regular internal structure. Similarly Demirel [33] reported that porosity was reduced through to filler effect of marble powder. Figure 9 shows that the porosity values of composites increased by 5, 12 and 11% for composites produced with 5, 10% egg shell dust and 7.5%-2.5%

egg shell dust-marble powder combination, compared to reference sample. Similarly, Rana et al. [41] reported that total porosity reduced by 6.9% and 21.5% with 5% and 10% marble powder substitution. It was also determined that the increase of permeable voids were caused to increased porosity and reduced of 28th days DUW values (see Figure 10).

D. Compressive strength

Compressive strength test results and the relationship compressive strength and porosity (P) are presented in Figure 11-13.



Fig. 11 Compressive strength results of granulated egg shell-cement paste composites



Fig. 12 Compressive strength results of egg shell dust-marble powder-cement paste composites



Fig. 13 Relationship between porosity and compressive strength of cement paste composites

Figures 11 and 12 are indicated that all samples continue to gain compressive strength during curing days, but the compressive strengths for all substitution ratios is lower than the reference sample. When Figure 11 were examined, the highest compressive strength was observed on reference sample with 18 MPa, while the lowest compressive strength was observed on the composite produced with 5% granulated egg shell substitution. The composites produced with 5, 10 and 15-GES substitution were showed low compressite strength by 48.3%, 38.9%, 41.6% compared to reference sample. Moreover, composites produced with egg shell dust substitution presented in Figure 12, showed similar results to granulated egg shell. Compressive strength of 5-ESD, 10-ESD, 2.5-ESD7.5-MP composites lower by 37%, 28%, 16.6%, compared to reference sampl at 28 days. The loss of compressive strength was observed at least on composites produced with combination of egg shell dust and marble powder substitution. This could be explained by two way: 1) Firstly, hydration of alite (C_3S) and belite (C_2S) with water (H_2O) generates formations calcium silicate hydrates (C-S-H) and calcium hydroxide (Ca(OH)₂). After that, the SiO₂ in chmeical structure of marble powder gives reaction with Ca(OH)₂ and produces secondary C-S-H gel. Thus, a relatively smooth internal matrix was formed [50]. It was observed that the compressive strength was increased with decrease of total porosity (see Figure 13).

IV. CONCLUSION AND RECOMMENDATION

The conclusions of this study are summarized as follows:

- Flow spread was increased with increased substitution ratio of granulated egg shell and egg shell dust. Highest flow spread values were observed with composites produced with granulated egg shell substitution. However, combination of egg shell dust and marble powder caused major reduction on flow spread values.
- The permeable voids were trend to increased with egg shell powder and egg shell dust substitution. In addition combination of egg shell dust and marble powder caused to minor reduction on permeable voids.
- Porosity values were increased by increasing granulated egg shell and egg shell dust substitution. However, a minor reduction was observed with combination of egg shell dust and marble powder.
- Compressive strength of composites showed highest reduction with increasing granulated egg shell subsitution. In addition, compressive

strength could be developed by egg shell dust and combination of egg shell dust.

Use of silica fume or novel bottom ash with egg shell dust-high C_3A cement may be developed physical properties of cement paste composites. Future work should use scanning electron microscopy to understand the hydration process in these composites. Also more fine-grained egg shell dust should use than used this study. XRD and thermal conductivity investigations may also facilitate understanding of hardened state of such cement paste composites.

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