Article

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Global Eggshell Properties: Characterizing Variability for Sustainable Partial Cement Replacement in Hong Kong's Concrete

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Abstract: This study aims at the sustainable valorization of eggshells (ES) from different countries of origin in cement concrete as a cement replacement for Hong Kong. For this purpose, sixteen different eggs from different regions across the world were selected from the local market. Firstly, the extent of uniformity in the weight and mineral content of sampled eggshells were assessed by a specific gravity test and thermogravimetric analysis (TGA), respectively. It was found that specific gravity varies between 2.02 and 2.39, with an average value of 2.20 ± 0.01, whereas $CaCO_3$ varies between 94.65% and 97.23%, with an average value of 96.33%. These values were a bit lower than those of extra-pure limestone (LS) because of the organic part and the porous structure of eggshells. Secondly, three different eggshells were selected for cement replacement in cement concrete, both in the uncalcined and calcined states, based on having the highest, medium, and lowest $CaCO_3$ content, respectively. To get the calcined eggshells, the eggshells were calcined at 800°C for three hours. It was found that the strength of eggshells varies with $CaCO_3$, but the variation was acceptable. The calcined eggshells showed comparatively more compressive strength and were close to the LS because of the free CaO and the absence of an organic part. In general, the variation in the basic properties of eggshells from different regions across the world is negligible and suitable to use as a cement replacement with acceptable variation in strength in Hong Kong.

Keywords: calcined eggshells; calcium carbonate; compressive strength; eggshells; free calcium oxide; specific gravity; thermogravimetric analysis

1. Introduction

The modern urban areas have become a concrete jungle, and concrete has become the second most consuming material after water on the planet. Cement is no doubt the major ingredient of concrete, and its production is responsible for huge carbon footprints, which makes the cement industry the third most CO_2 emitter in the world [1]. The cement industry contributes a maximum of 8% of the global emission [1]. There are two ways to reduce the CO_2 emission from cement manufacturing plants; the first is to optimize process technology by using alternative fuel or raw material, and the second is the use of Supplementary Cementitious Materials (SCM) as a replacement for cement [2]. The supplementary cementitious materials are inorganic waste materials that possess hydraulic activity, pozzolanic activity, or sometimes dual nature [3]. Among them, limestone is one

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of the most commonly used SCM, and it has been used up to 10% replacement without sacrificing the compressive strength [4]. As a partial replacement for cement, limestone fillers can improve hydration in a low water-to-cement ratio [5]. Therefore, it is recommended by the ASTM to use limestone effectively up to 5% [6], whereas the BS recommends a 6% - 35% replacement level [7]. Generally, limestone can be used both as a binder replacement and as an aggregate to improve the properties of concrete [8,9]. Overall, using limestone as a replacement for cement for up to 20% can enhance the strength, workability, and durability of concrete and mortars [10,11].

The use of Eggshells (ES) has been recommended through several research studies as a potential bio-filler in cementitious materials during the past decade. The eggshells fulfill the requirements of a standard limestone for calcium silicate products as per ASTM standard specifications for limestone [12]. Incorporating eggshells as a partial replacement of cement improves the strength and other properties of cementitious materials, e.g., reduction in the setting time [13–15], good radiation shielding properties [16,17], and can be used up to 20% replacement level under the elevated temperature condition [18]. Several studies have been carried out on the optimal replacement of eggshells with cement considering strength as a deciding parameter, as shown in Table 1. It can be seen that 9 out of 25 studies recommend 5% replacement, 7 studies recommend 10% replacement, and the rest recommend different other replacements. Most of the studies recommends 5% replacement because limestone has complete reactivity up to 5% replacement level [2]. Likewise, eggshells have also been effectively blended in cement along with silica fume (SF) [19–21], fly ash (FA) [22–24], rice husk ash (RHA) [25], rice straw ash (RSA) [26], glass powder [27], palm oil fuel ash (POFA) [28–31], and bagasse ash [32]. In addition, eggshells have been used in special concrete as well, both in uncalcined and calcined forms like Foamed concrete [33,34], self-compacting concrete [35–39], and geopolymer concrete [40]. In general, using eggshells either in an uncalcined or calcined state has a positive impact on the hydration kinetics of cementitious materials [41–43]. Apart from using eggshells in the cementitious matrix, they can also be used as fine aggregates up to 40% without affecting the compressive strength [44].

Table 1. A review on the optimal replacement of ES with cement.

Ref.	Type of ES	Composite Type	Optimal Replacement	Cement Type	w/b	28th Day Strength
[45]	ES	Ordinary concrete	5%	IS grade 43	0.39 – 0.50	Compressive, flexural
[46]	ES	Ordinary concrete	5%	ASTM type I	0.6	Compressive, split tensile
[47]	ES	Ordinary concrete	5%	IS grade 53	0.5	Compressive
[48]	CES[1] (500°C)	Ordinary concrete	10%	OPC	0.6	Compressive
[49]	ES	Ordinary concrete	10% (comp.),20% (flexural)	CEM II/B-M	0.4	Compressive, flexural
[50]	ES (Brown)	Ordinary mortar	5%	CEM I 52.5 N	0.5	Compressive, flexural
[51]	ES	Ordinary mortar	5%	ASTM Type I	0.4	Compressive, flexural

[52]	ES	Ordinary concrete	15%	OPC	0.45	Compressive
[20]	ES	Ordinary concrete	5%	OPC	0.5	Compressive
[53]	ES	Ordinary concrete	12%	IS grade 43	0.4	Compressive, split tensile
[54]	ES	Ordinary concrete	20%	ASTM Type I	0.6	Compressive
[55]	Eggshell Ash (ESA)	Ordinary concrete	5%	OPC	0.55	Compressive
[56]	ES	Ordinary concrete	12% (comp.) 6% (tensile)	IS grade 43	0.4	Compressive, split tensile
[57]	ES	Concrete (waste as aggregates)	10%	IS grade 53	0.47	Compressive
[58]	ES	Ordinary concrete	15%	OPC	0.45	Compressive, flexural
[59]	ES	Ordinary concrete	7.5%	OPC	0.52	Compressive, split tensile, flexural
[60]	CES[1] (750°C for one hour)	Ordinary concrete	15%	Iraqi OPC	0.5	Compressive
[61]	ES	Ordinary concrete	10%	ASTM Type I	0.5	Compressive
[43]	CES1 (900°C for 2 hours)	Ordinary concrete	10%	ASTM Type II	0.5	Compressive, flexural
[62]	CES1 (100°C for 12 hours)	Seawater concrete	5%	OPC	0.5	Compressive
[63]	ES	High Strength Concrete (HSC)	10%	ASTM Type I	0.32	Compressive
[64]	ES	Fiber Reinforced Concrete (FRC)	5%	ASTM Type I	0.5	Compressive, flexural
[65]	ES	Ordinary mortar	10%	IS grade 53	0.5	Compressive

[66]	ES	Ordinary concrete	10%	CEM I 52.5N	0.5	Compressive, flexural
[21]	ES	Ordinary concrete	11%	OPC	0.5	Compressive, split tensile, flexural

[1] CES = Calcined eggshells.

Several SCMs and fillers have been proposed in the past few decades, while the search for new SCMs is still in progress. The chemical composition of SCMs may vary depending upon several factors like production processes and regions. For example, the composition of steel slag may vary depending on the type of furnace being used in the process of conversion from iron to steel [67]. Similarly, the Australian Fly Ash (FA) contains more SiO_2 content than the Indonesian FA and accordingly imparts more strength due to its more pozzolanic activity [68]. Therefore, it is essential to analyze the variation in the chemical compositions of different hydraulic and pozzolanic materials before proposing them for large-scale commercial application. Limestone is a less reactive hydraulic material [69], and biological limestone like eggshells have similar properties containing an overwhelmingly high content of $CaCO_3$. A study reports 94% - 97% $CaCO_3$ as an average value depending on mineral nutrition, housing system for hens, age, and animal genotype [70]. A study also reports higher content of 98.2% $CaCO_3$ [71], whereas another study reports low as 86.75% in eggshells of white silky chicken [72]. The quality of eggshells is defined as its resistance against breakage during handling of eggs [73]. This resistance varies from case to case and depends upon the breed and age of eggs [74], weight grade [75], color [76], and housing system [77,78]. However, this resistance majorly depends on the weight of an eggshell [79–83]. Therefore, a good quality egg must have a heavier eggshell, while the weight of the eggshell also varies with its size, but an average value is about 10% of the total weight of the eggshell [82]. Local weather is a significant factor affecting not only egg production but eggshell quality as well. For example, the high air temperature and the relative humidity cause heat stress, and that affects the egg's production and eggshell quality [84–86]. Hens in hot and humid environments cannot consume sufficient calcium and produce softer eggshells [86,87]. Likewise, it is quite possible that eggs and eggshells from different countries could have different properties depending on their mineral contents. However, a diversity of weather conditions is possible across big countries like the USA. A brief review on the specific gravity as shown in Table 2 depicts that specific gravity is different in different regions probably due to the local weather conditions and some other factors. Hence, it is important to analyze the eggshells from different countries before proposing them for large-scale industrial applications in cementitious materials.

Table 2. A review on specific gravity of eggshells from different regions.

Reference	Region	Specific Gravity
[88]	Malaysia	2.14
[89]	India	1.95
[40]	India	2.37
[50]	France	2.5
[90]	India	2.01
[91]	India	2.14
[92]	NA	2.13
[93]	NA	2.20

[94]	Pakistan	2.27
[95]	USA	2.09 - 2.18
[96]	NA	2.37
[46]	India	2.37
[97]	Bangladesh	2.66
[98]	Ghana	2.58
[99]	India	2.33
Average		2.29 ± 0.21

Hong Kong is the biggest consumer of eggs in the world. Notably, the consumption per capita per year has been increasing drastically during the last decade. The domestic supply of eggs in Hong Kong was 196,000 tons in 2021. At the same time, the average consumption per capita was 26.09 kg/capita/year in 2020, as reported by the Food and Agriculture Organization (FAO) [100]. According to the Observatory of Economic Complexity (OEC), eggs were the 175th most imported product in Hong Kong in 2021, having a total import value of 284 million USD, which ranks Hong Kong fourth in the list of most egg-importing countries [101]. Hong Kong's market has diverse kinds of eggs from different countries of origin. Also, the import quantity of eggs was 200,000 tons, whereas the export quantity was only 4000 tons in the year 2021 [100]. Therefore, Hong Kong is an ideal place to study the characteristics of eggshells from different countries of origin and for their sustainable utilization in cementitious materials. Not only this, but the public, and specifically the restaurants, have a positive attitude towards the recycling of waste eggshells for meaningful purposes [102].

Many studies have been carried out on the viability of eggshells in cementitious materials as a cement replacement but the effect of different eggshells from different regions on the mechanical properties of cementitious material considering the quality has not been studied yet. The proposed study aims to assess the feasibility of using eggshells from different countries of origin as a cement replacement in cementitious material. For this purpose, the extent of variation in the basic properties (e.g., specific gravity and mineral content) of different eggshells and their effect on the end cementitious products were analyzed. This study will facilitate the stakeholders to develop environmentally friendly concrete containing eggshells as a cement replacement for commercial applications.

2. Materials and Methods

2.1. Market Survey and Collection of Samples

A market survey was conducted in five different supermarkets to select the eggshells from different countries of origin for detailed investigation. Out of them, three supermarkets were selected based on having the highest number of stores, one was selected based on having a variety of egg brands, and one was selling through online mode. It was found that a total of 50 different egg brands from eleven different countries are imported into these five supermarkets. Japan has the highest number of brands, followed by Thailand, the USA, and China, as shown in Figure 1(a). Whereas import share of different countries in Hong Kong as per data from OEC for 2021 is shown in Figure 1(b). For detailed characterization, eggshells from sixteen different egg brands or countries of origin were collected. These eggshells were selected based on their popularity. Among them, twelve were collected from the supermarket, whereas the rest four were collected from restaurants. The details of these samples are listed below in Table 3. These sampled eggshells were later prepared for the measurement of specific gravity, thermogravimetric analysis (TGA), and for cement replacement. For this purpose, each sampled eggshell was cleaned with tap water and dried in air. It must be noted

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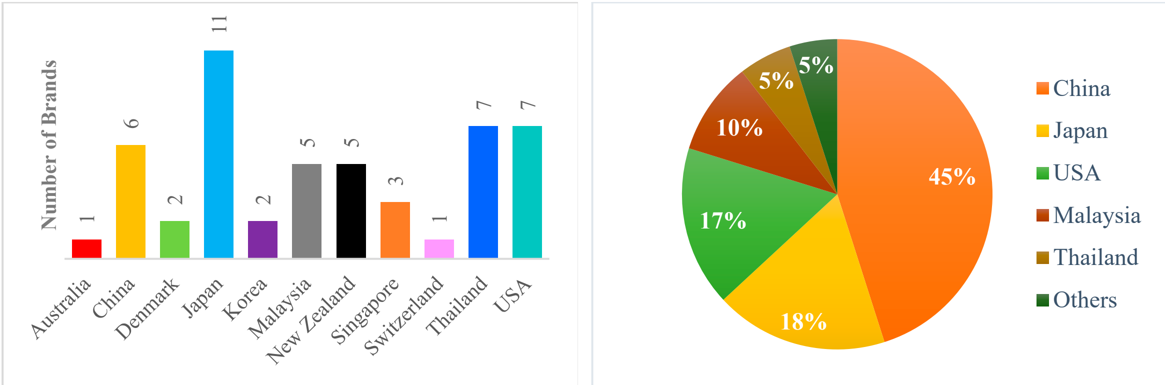
here that no commercial method is available right now to separate the eggshell membrane on a large-scale [103]. Therefore, it was not tried to remove the eggshell membrane through any dedicated method so that to meet the practical requirements. However, the process of removal of the membrane is based on cracking and grinding [104]. Therefore, it can be presumed that a part of the organic membrane drained off due to crushing during the cleaning of eggshells.



(a) (b)

Figure 1. Eggs available in Hong Kong markets (a) Number of egg brands by country of origin (b) Share of different countries in the import of eggs [101].

Table 3. Details of sample eggshells for experimentation.

Designation	Country	Color	Source
ES1	China	Dark Brown	Market
ES2	China	Light Brown	
ES3	Thailand	Dark Brown	
ES4	Japan	White	
ES5	Japan	Dark Brown	
ES6	USA	White	
ES7	USA	Dark Brown	
ES8	Singapore	Dark Brown	
ES9	Singapore	White	
ES10	Malaysia	Dark Brown	
ES11	New Zealand	Dark Brown	
ES12	South Korea	Dark Brown	
ES13	China	Dark Brown	Restaurant
ES14	China	Light Brown	
ES15	Japan	Dark Brown	
ES16	Japan	White	

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2.2. Measurement of Specific Gravity

The specific gravity of the waste eggshell is necessary to determine because it is an important factor in the mix design of concrete. It was done using the specific gravity bottle and the ethanol as a solvent on ground sampled eggshells passed through ASTM No. 200 sieve. The density bottle was half-filled with a dried powder sample while the rest was filled with solvent and was kept in for three days to let the trapped air escape.

2.3. Thermogravimetric Analysis TGA

Thermogravimetric Analysis (TGA) was performed on each sampled eggshell to find its phase composition and compare it with the extra pure limestone (LS), which contains more than 99% $CaCO_3$. For this purpose, the dried eggshells were ground and passed through ASTM No. 200 sieve. The prepared eggshells having a mass of less than 10mg were put in a 20mg sample holder, and Al_2O_3 powder was used as reference material. Each sample was heated at the rate of 10°C/min up to 1000°C in an argon environment. Later, the results were presented in the form of the Thermogravimetric (TG) curve and Differential Thermogravimetric (DTG) curve to detect the components and their quantity. The tangential method was used to determine the mass loss corresponding to each phase change. Furthermore, the results from TGA analysis were also verified by stoichiometric analysis.

2.4. Use of Eggshells as a Cement Replacement

2.4.1. Selection of Eggshells

To replace the eggshells with cement, three different eggshells from the three different countries of origin were selected based on their popularity and mineral contents. To make the selection based on mineral contents, eggshells with low calcium carbonate, medium calcium carbonate, and high calcium carbonate were selected.

2.4.2. Properties of OPC, LS, and Selected ES

Before incorporating the eggshells in the concrete mix, each type of eggshell was ground in a ball mill under a constant weight of 12kg for 6 hours and later was sieved through ASTM No. 200 sieve. The Particle Size Distribution (PSD) for each type of eggshell, LS, and CEM I 52.5N Portland cement was carried out by laser diffraction method using ethanol as a solvent. Furthermore, the oxide composition of cement by X-Ray Fluorescence (XRF) was analyzed, and its Bogue's components were found as shown below in Table 4. Each type of eggshell was also calcined at 800°C for three hours. It was done so because calcination is the effective method to remove the organic matrix [105], and the resulting ash at this calcination condition consists of a blend of $CaCO_3$, $Ca(OH)_2$, and CaO [42,106]. Furthermore, a powder X-Ray Diffraction (XRD) was also performed to validate this phase composition after calcination.

Table 4. Composition of OPC.

Oxide Composition (%)									Bogue's Components (%)			
MgO	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**K_2O**	**CaO**	**Fe_2O_3**	**Others**	**C_3S**	**C_2S**	**C_3A**	**C_4AF**
1.12	5.45	19.10	0.13	4.51	0.67	65.50	3.00	0.43	67.66	3.74	9.37	9.13

2.4.3. Detail of Concrete Mixes and Strength Measurement

The maximum size of fine aggregates was 1.18mm, whereas coarse aggregates ranged between 4.75mm to 10mm. Eight batches of concrete were prepared with a general-purpose mix composition of 1:1:2 to assess the feasibility of ES and CES in concrete. Among them were the control mix, the mix with 5% limestone (LS), the mix with 5% ES, and the mixes with 5% CES, as listed below in Table 5. The replacement level was taken as 5% because most of the studies report this replacement level as mentioned before in Table 1. Finally, each of these specimens was tested to determine the 7th-day and the 28th-day compressive strength, and their Relative Strength (RS) was measured for each mix.

Table 5. Details of concrete mixes.

Specimen	OPC	LS/ES/CES	Fine Aggregates	Coarse Aggregates	w/b	a/b
	Kg/m³	Kg/m³	Kg/m³	Kg/m³		
Control	600	-	600	1200	0.5	3
Non-Control	570	30	600	1200	0.5	3

3. Results

3.1. Specific Gravity of Sample Eggshells

The measured specific gravity of each sample eggshell is shown below in Figure 2. The specific gravity of eggshells varies between 2.02 – 2.39 having an average value of 2.20 ± 0.01. These values of specific gravity are close to the past values as reported in the literature in Table 2. The specific gravity of eggshells is typically lower as compared to the extra pure limestone (i.e., 2.71), it is due to the porous structure of the eggshells [107]. Moreover, the specific gravity of Supplementary Cementitious Materials (SCM) is normally lower as compared to cement [108]. The presence of residual eggshell membrane also affects the specific gravity of the eggshell powder [109]. It can also be seen that eggshell with a specific gravity higher than average (i.e., 2.20) are either light brown or dark brown. In contrast, all the white eggshells (i.e., ES4, ES6, ES9, and ES16) have a specific gravity less than the average. Therefore, brown pigmentation does affect the quality of eggshells, but it needs to be investigated further in the given case. Since the specific gravity of eggshells is lower as compared to both limestone and OPC, therefore, it can also be used in the production of lightweight concrete [110,111].

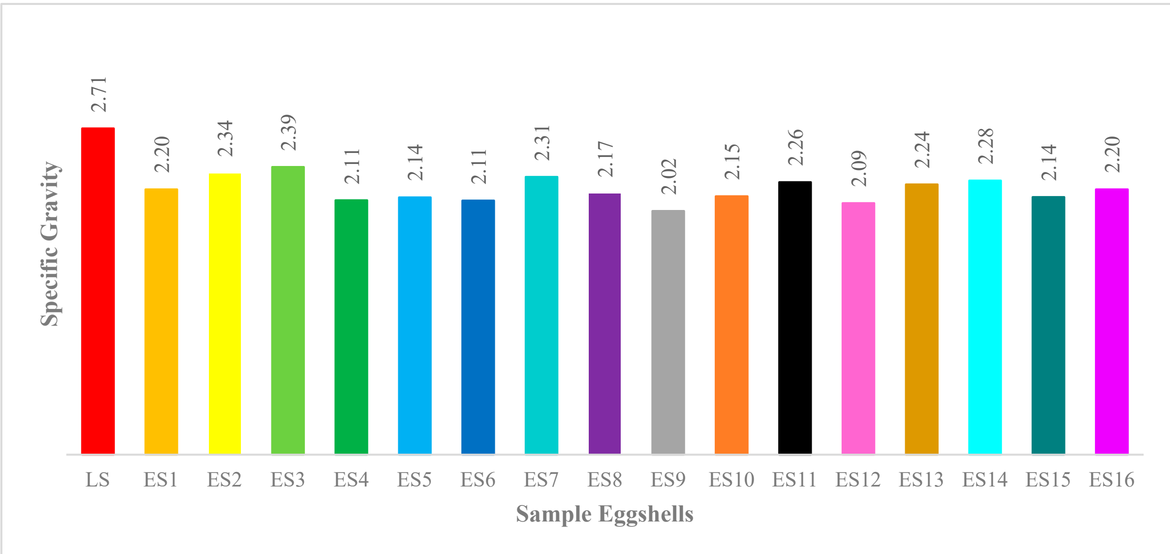
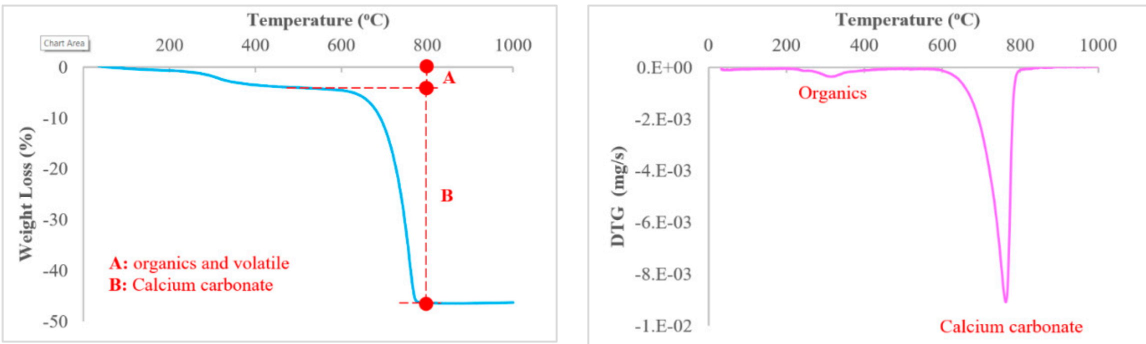


Figure 2. Measured specific gravity of sample eggshells.

3.2. Quantification of Minerals

Eggshell consists of volatile components usually water, organic components which are proteins, and the mineral part, which is $CaCO_3$ [106,112,113], whereas a typical thermogram is shown below in Figure 3. The average composition of eggshells comprised of volatile components 1.17 ± 0.16%, organic components 2.5 ± 0.63%, and the $CaCO_3$ 96.33 ± 0.67%. After complete decomposition of

$CaCO_3$ during calcination, there was on average CaO 54.24 ± 1.12%, CO_2 emission 42.09 ± 1.05% whereas the calcium content was 38.76 ± 0.80% as tabulated below in Table 6. Furthermore, the measured mineral part by TGA was correlated with the calculation by stoichiometric analysis, as shown below in Figure 4. The correlation for CO_2 is slightly lower due to the possibility of having uncertainty. CO_2 is measured by deducting the weight of volatiles and organics from the total weight loss while it is possible that some part of the organic membrane washes away with water during the cleaning of eggshells, or sometimes there is a possibility of its concentration in the given specimen. So, such a partially true quantity of organics and volatiles directly makes the calculated CO_2 uncertain. The $CaCO_3$ in all eggshells ranges from 94.65% - 97.23%, which is slightly less than the extra pure limestone, whereas the color of the eggshell does not have any effect on the composition. As far as pigmentation is concerned, pigmentation has no clear effect on the mineral content. In general, the average composition of the mineral part of eggshells from different countries is very similar to that of extra pure limestone, as tabulated below in Table 7. Therefore, it is recommendable not to discard this type of biomineral in landfills; instead, it is worthwhile to extract the pure limestone from eggshells by doing either calcination or some other treatment for further use in cementitious materials.



(a) (b)

Figure 3. Typical thermogram for eggshell (a) Weight loss (b), Differential Thermogravimetric Curve (DTG).

Table 6. Comparative composition of eggshells by thermogravimetric and stoichiometric analysis.

Sample	A[1]		B[2]								
	O[3]	V[4]	Thermogravimetric Analysis				Stoichiometric Analysis				$CaCO_3$
			CaO	ΔW	CO_2	Ca	CaO	ΔW	CO_2	Ca	
	%	%	%	%	%	%	%	%	%	%	%
LS	0.38	-	55.79	44.21	43.82	39.87	55.78	44.22	43.84	39.92	99.62
ES1	1.14	1.63	54.83	45.17	42.40	39.18	54.44	45.56	42.79	38.96	97.23
ES2	0.94	3.35	53.61	46.39	42.10	38.31	53.59	46.41	42.12	38.36	95.72
ES3	1.24	2.89	51.76	48.24	44.11	36.99	53.68	46.32	42.19	38.42	95.87
ES4	0.91	2.00	54.23	45.77	42.86	38.76	54.36	45.64	42.73	38.91	97.09
ES5	1.09	2.08	55.29	44.71	41.54	39.51	54.22	45.78	42.61	38.80	96.83
ES6	1.15	2.46	53.70	46.30	42.69	38.37	53.97	46.03	42.42	38.63	96.39
ES7	1.30	1.99	53.61	46.39	43.10	38.31	54.15	45.85	42.56	38.76	96.71

ES8	1.22	2.37	55.92	44.08	40.50	39.96	53.98	46.02	42.43	38.64	96.41
ES9	1.05	2.23	53.95	46.06	42.77	38.55	54.15	45.85	42.56	38.76	96.71
ES10	1.22	2.10	55.93	44.08	40.76	39.97	54.14	45.86	42.55	38.75	96.69
ES11	1.34	2.58	52.98	47.02	43.10	37.86	53.80	46.20	42.28	38.50	96.08
ES12	1.51	2.11	55.27	44.73	41.11	39.49	53.97	46.03	42.42	38.62	96.38
ES13	1.23	3.42	54.18	45.82	41.17	38.72	53.39	46.61	41.96	38.21	95.35
ES14	1.01	2.28	53.73	46.27	42.98	38.40	54.15	45.85	42.56	38.76	96.72
ES15	1.09	2.47	55.28	44.72	41.15	39.51	54.00	46.00	42.44	38.65	96.44
ES16	1.34	4.01	53.51	46.49	41.15	38.24	53.00	47.00	41.66	37.93	94.65
Aver.	1.17	2.50	54.24	45.76	42.09	38.76	53.94	46.06	42.39	38.61	96.33

[1] Organic and volatile components. [2] Mineral components. [3] organic components. [4] Volatile components.

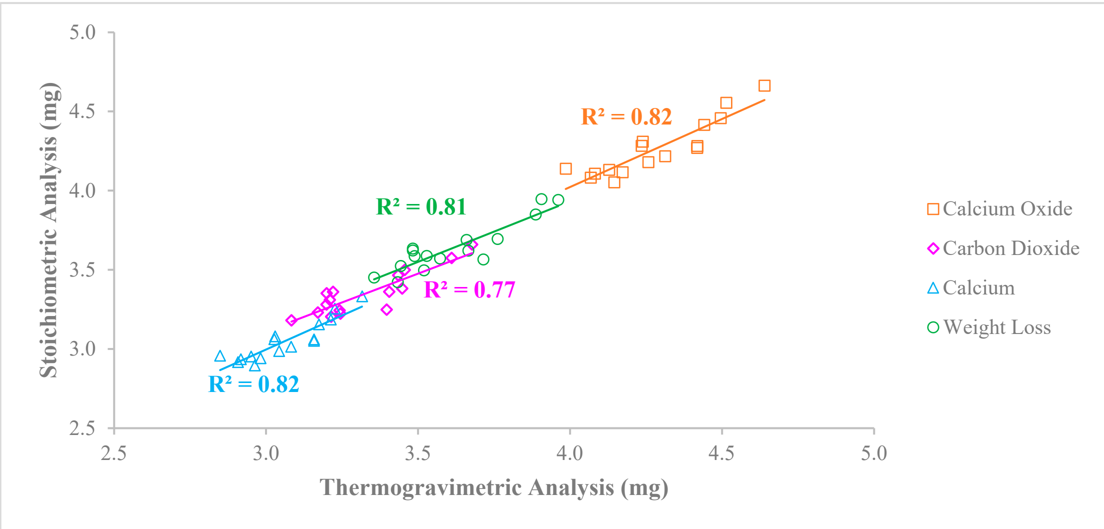


Figure 4. Correlation between the stoichiometric analysis and thermogravimetric analysis of sample eggshells for mineral part.

Table 7. Comparison of average composition of eggshells from different countries and extra pure limestone (LS).

Component	Stochiometric Analysis	Thermogravimetric Analysis		
		Extra Pure Limestone	Eggshells from different countries	Difference
%	%	%	%	%
Ca	40.08	40.03	40.24	0.21
C	11.99	12.01	11.93	0.08
O	47.93	47.97	47.83	0.13
CO_2	43.92	43.99	43.70	0.30

CaO	56.08	56.01	56.30	0.30

3.3. Application of Eggshells as a Cement Replacement

3.3.1. Selection of Eggshells and their Properties

To replace the cement with eggshells, three types of eggshells from the sample eggshells were selected based on their popularity and mineral contents, i.e., low, medium, and high. Among them were American eggshells (ES7) with $CaCO_3$ 96.71%, Chinese eggshells (ES13) with $CaCO_3$ 95.35%, and Japanese eggshells (ES16) with $CaCO_3$ 94.65%. All these selected eggshells were also calcined under the above-mentioned calcination condition to get the calcined eggshells. The corresponding calcined American eggshells were designated as CES7, calcined Chinese eggshells as CES13, and calcined Japanese eggshells as CES16.

Since the fineness of cement additives plays an essential role in hydration kinetics and strength development, it is prime important to investigate the PSD of OPC, LS, ES, and CES. For this purpose, the PSD curve for each type of material is shown below in Figure 5, along with D[4,3], D(50), and D(90) particle sizes in Table 8.

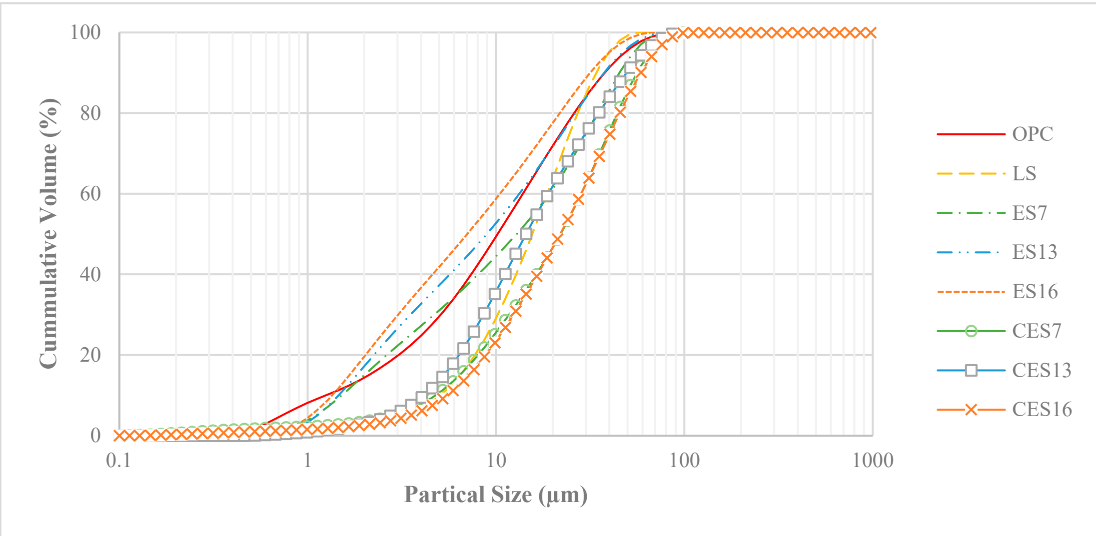


Figure 5. Particle Size Distribution (PSD) cure of OPC, LS, ESs and CESs.

Table 8. Details of D[4,3], D(50), and D(90) particles sizes of OPC, LS, ESs, and CES.

Material	D [4,3] (µm)	D (50) (µm)	D (90) (µm)
OPC	17.53	11.56	42.86
LS	20.27	17.74	38.90
ES-7	21.26	14.62	51.45
ES-13	16.76	10.14	42.67
ES-16	13.94	8.00	35.98
CES-7	30.21	24.98	63.83
CES-13	24.09	16.43	56.25

CES-16	31.27	24.87	66.68

The calcium carbonate in ES, when calcined at a certain temperature, converts into CaO along with the liberation of CO_2. Later, the CaO, because of its high reactivity with water vapors in the atmosphere, converts into $Ca(OH)_2$ [114]. Therefore, the partially decomposed calcium carbonate may likely consist of a mixture of $CaCO_3$, $Ca(OH)_2$, and CaO. In the given case, all the calcined eggshells consisted of a mixture of all these three components, as shown below in an XRD spectrum of LS, ES, and CES in Figure 6. Whereas the quantities of this phase composition by Rietveld refinement in Match software and are shown below in Table 9. It can be seen that $Ca(OH)_2$ is the major phase due to the reaction of CaO with the water vapors in the atmosphere. Therefore, the formation of $Ca(OH)_2$ may vary depending upon the relative humidity of the environment.

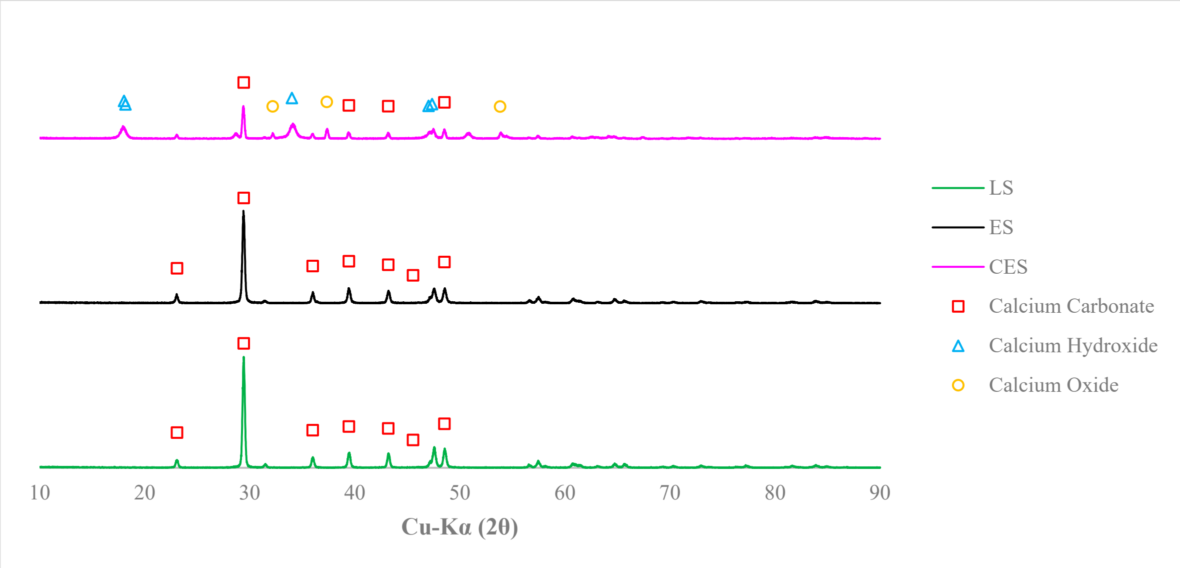


Figure 6. XRD spectrum of CES indicates the existence of a blend of calcium carbonate, calcium hydroxide, and calcium oxide in comparison with LS and ES.

Table 9. Quantities of different phases after Rietveld analysis.

S. No	Calcined Eggshells	$CaCO_3$	$Ca(OH)_2$	CaO
		%	%	%
1	CES7	37.5	55.3	7.2
2	CES13	37.6	55.1	7.4
3	CES16	36.7	54.6	8.7

3.3.2. Compressive Strength and Relative Strength (RS) of Concrete Specimens

It has been found that replacing cement either with uncalcined eggshells or calcined eggshells is viable based on the compressive strength, as shown below in Figure 7(a). Both provide adequate strength, while the Relative Strength (RS) is shown in Figure 7(b). It can be seen that calcined eggshells are showing higher strength as compared to uncalcined eggshells. The average 7th-day compressive strength for mixes containing eggshells is 36.33Mpa, while for mixes containing calcined eggshells is 40.00Mpa. Similarly, the average 28th-day compressive strength is 49.33MPa and 54.33Mpa for mixes containing eggshells and calcined eggshells, respectively. Furthermore, the eggshells with the highest mineral content (i.e., ES7) show higher compressive strength both in calcined and uncalcined states and vice versa.

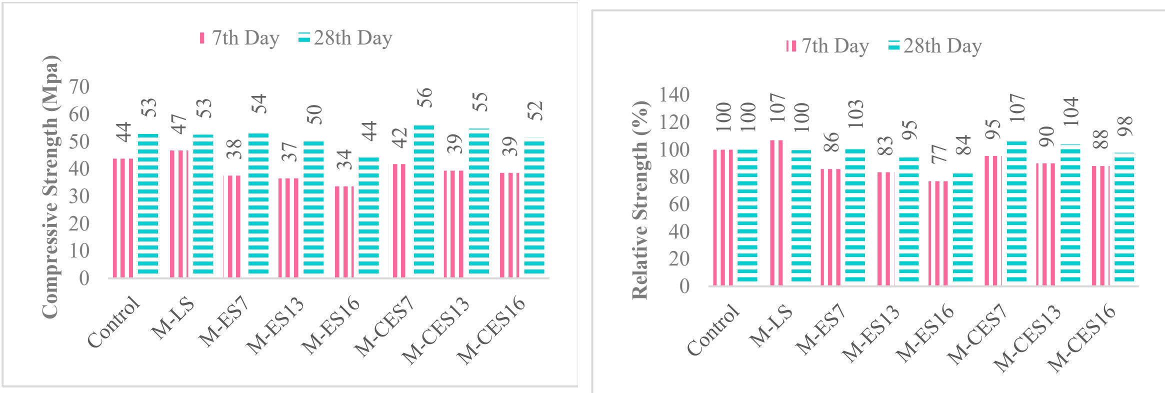


Figure 7. (a) Compressive strength for 7th and 28th day, (b) Relative strength (RS) for 7tha and 28th day.

4. Discussions

4.1. Calcium Carbonate vs Specific Gravity in Uncalcined Eggshells

As explained earlier, measuring specific gravity is a direct way to measure the quality of eggshells. Similarly, the quantity of minerals can also affect the quality of the eggshell and make it harder or softer [72]. However, the quality of eggshells also varies with some other factors as well. A correlation is shown below in Figure 8 between both parameters of quality assessment i.e., $CaCO_3$ and the specific gravity of sampled eggshells. The specific gravity varies linearly with the $CaCO_3$ content in the given eggshells whereas this correlation is a bit lower. There could be many reasons behind this low correlation, the most straightforward reason is the presence of residual shell membrane [109]. It is a bit hard to remove the complete organic membrane from the eggshells during physical washing and cleaning. There is also an internal shell membrane in addition to the external shell membrane and that can only be removed by rubbing the internal surface of the shell membrane. To completely remove the organic part, it is necessary to do heat treatment like calcination [105] or a chemical treatment like a reaction with bleach solution [115].

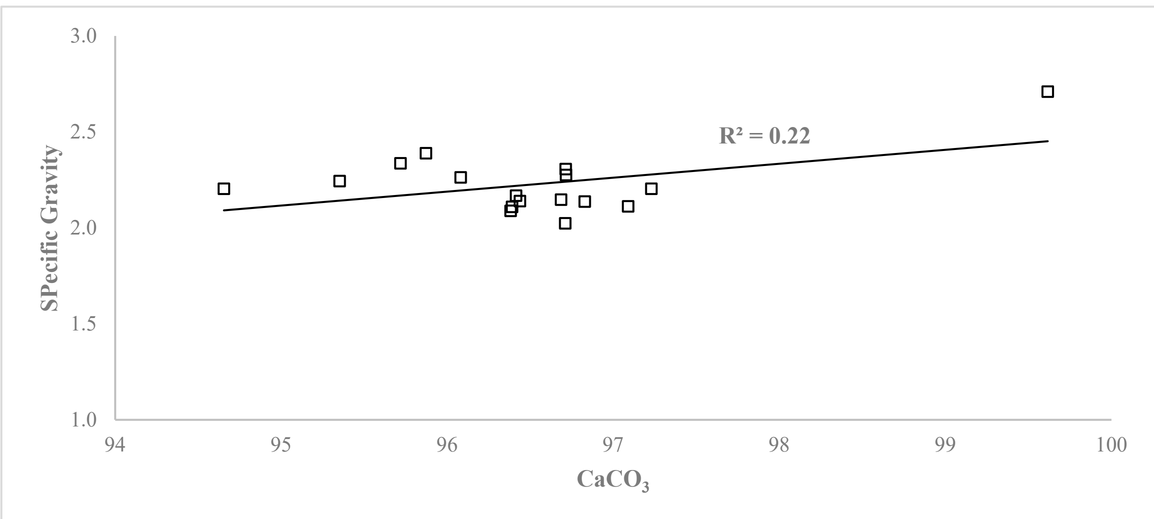


Figure 8. Correlation between specific gravity and the $CaCO_3$ in ES and LS.

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In addition, the low correlation depicts that both specific gravity and $CaCO_3$ contents are not enough to describe the quality of eggshells from different regions of the world. The brown pigmentation imparts strength and the eggshell quality while it does not correlate with the egg's internal quality [116]. Therefore, the brown eggshells are linked to the higher specific gravity [117]. This also justifies the given case like ES2, ES3, ES7, ES11, ES13, and ES14 are heavier eggshells and are either dark brown or light brown. Unlike specific gravity, brown pigmentation has no clear link with the mineral content in the given case. This is controversial to some of the previous studies because brown eggshells have more mineral content as compared to white eggshells [50,72,82]. For example, a study reports that brown eggshells have 96%-97% $CaCO_3$ while this quantity is around 94% in white eggshells [118]. However, there is also a conflicting opinion in some previous studies as well which indicates that brown pigmentation is not a reliable tool for assessing the quality of eggshells [117,119]. Therefore, the micro-structure is another factor that can affect both specific gravity and $CaCO_3$, and ultimately the quality of eggshells. Bain [120] suggested the orientation of palisade columns in the palisade layer affects the shell quality in addition to the crystal size. Since the palisade layer is the biggest layer that defines the major structural part, therefore, it is highly likely that a change in the palisade layer may affect the whole structure of an eggshell. Moreover, the housing system of egg-laying hens is an important factor that can affect the microstructure of a shell and ultimately the shell thickness and strength. It has been observed that higher numbers of pores are present in cage housing systems than in litter housing systems [121]. Hence, the cage housing system accounts for more cracked and broken eggs [122]. Although the housing system for the sampled eggshells in the present study is not known, an inference can be made that there is a diversity in the structure or pores of the eggshells which is the cause of the low correlation between specific gravity and the mineral content in addition to the presence of residual membrane. Moreover, it must be noted here that this correlation also includes the LS which has higher specific gravity due to its higher mineral content and non-pores micro-structure as compared to eggshells. In general, the quality of eggshells from different regions should be defined by their structure in addition to their mineral content and specific gravity.

4.2. Role of Calcium Carbonate

4.2.1. Calcium Carbonate vs Strength Development

The use of eggshells in uncalcined form from different regions in the given case is viable to use as a cement replacement. There is some variation as compared to the control mix and the mix with LS depending upon the mineral content, but this variation is within the acceptable limit. It is necessary to understand the determinants involved in strength development. Eggshells in an uncalcined state are an impure form of limestone and thus produce inferior strength [50]. A good correlation has been established between the strength development and the mineral content as shown below in Figure 9. The $CaCO_3$ is both inert and reactive, having complete reactivity up to 5% replacement [2]. The $CaCO_3$ reacts with the C_3A and C_4AF and forms additional hydrates like carboaluminates which imparts strength [2,123]. The quantity of $CaCO_3$ is the main strength contributing factor in addition to the clinker; therefore, those mixes containing the highest $CaCO_3$ quantity (i.e., M-ES7 and M-CES7) showing the highest strength as compared to the mixes with lowest $CaCO_3$ (i.e., M-ES16 and M-CES16). It can also be seen that the correlation for 28th day strength is a bit lower as compared to the correlation for 7th-day strength and the LS significantly improves the 7th-day strength in contrast to 28th-day strength by providing additional sites for nucleation and growth of hydrates [8,124–127]. The more variation or uncertainty in 28th-day strength is due to the dilution effect [5,8,128,129]. This is because the mixes containing the LS and eggshells require less water due to the decrease of cementing part and causes the increase of w/c ratio [8,118]. Incorporation of $CaCO_3$ improves the compressive strength due to improvement in the degree of hydration at a low w/c ratio but the w/c ratio is high in the given case which is causing the dilution effect and the impairment of compressive strength at later ages [130].

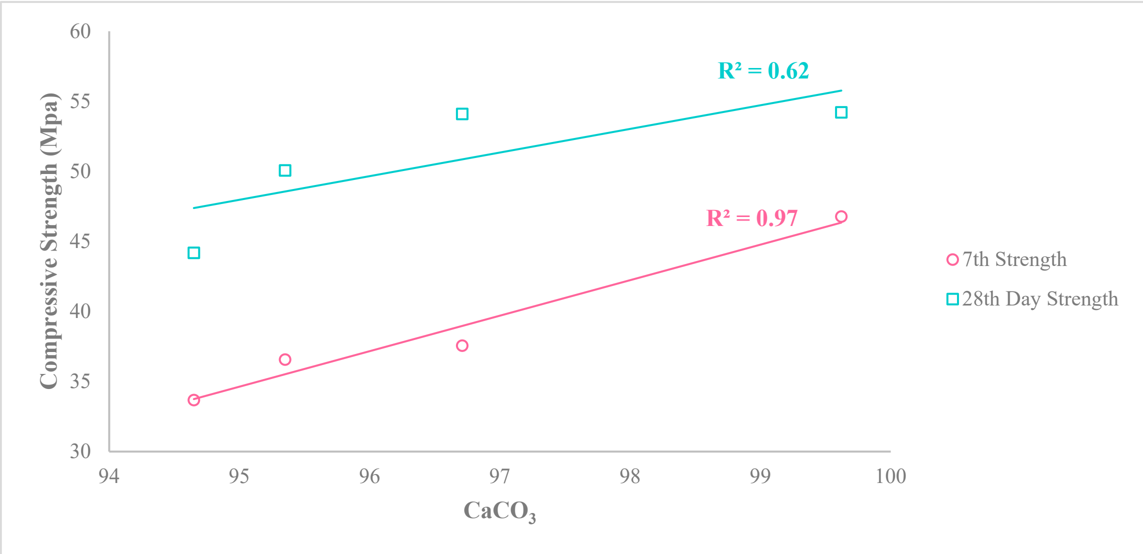

Figure 9. Correlation between compressive strength and the $CaCO_3$ content in mixes with uncalcined eggshells.

4.2.2. Filler Effect and Heterogenous Nucleation

The strength development due to the addition of $CaCO_3$ is due to the filler effect in which the finer particles of $CaCO_3$ fill up the voids in cement. The filler effect produces more denser microstructure and increases the packing density. However, this filler effect cannot be seen if the particle size of $CaCO_3$ is comparable to or bigger than cement's particle size [131]. In the given case, the D[4,3] particle size of LS, ES, and CES ranges between 13.94µm – 31.27µm which is comparable to or bigger than cement (i.e., 17.53µm). Similarly, the D(50) and D(90) particle sizes are also bigger than cement (i.e., D(50)=11.56 & D(90)=42.86) in most of the specimens. Therefore, a reduction in strength can be seen due to the dilution effect, particularly in the specimens with uncalcined eggshells. However, strength development in the specimens with LS is comparable with the control mix because D(90) particle size is lower than cement and also there is the absence of an organic matrix. In contrast, the strength development in specimens with CES is comparatively more while the quantity of $CaCO_3$ is relatively less due to its decomposition. There is a need to justify this phenomenon which will be justified in the next section.

In addition to the filler effect, heterogeneous nucleation is another phenomenon that can improve hydration due to the addition of $CaCO_3$. Unlike homogenous nucleation, the $CaCO_3$ particles behave as a nucleation site for C-S-H and improve the degree of hydration [128]. This is because the planar configuration of Ca and O atoms in the $CaCO_3$ particles is very similar to the Ca and O atoms in the C-S-H [132]. The factors influencing the heterogenous nucleation are the particle sizes [133], surface structure [134], and the quantity of $CaCO_3$[135]. The surface energy and absorption capacity of $CaCO_3$ particles increases with the decrease of particle sizes for the formation of heterogeneous nucleation. Likewise, the potential for the formation of heterogeneous nucleation also increases with the increase of $CaCO_3$ content. However, the part contribution of different factors has not been understood yet [8]. Since the quantity of $CaCO_3$ is constant in the given case, therefore, it can be assumed that both the filler effect and the heterogenous nucleation depend on the particle sizes. While the particle sizes in all non-control mixes are either comparable or greater than the cement particle sizes so dilution effect is quite explicit. Therefore, only part of the particles which are smaller than cement is taking part in the strength development due to the filler effect and heterogenous nucleation in addition to the $CaCO_3$ content. Despite the dilution effect, the variation in the strength of both mixes with uncalcined and calcined eggshells is acceptable.

4.3. Role of Calcium Oxide in Strength Development in Mixes with CES

Specimens containing calcined eggshells are showing better strength despite having a low quantity of $CaCO_3$. Therefore, it needs to investigate the strength contributing factor for the mixes with calcined eggshells. The major reason is the absence of an organic matrix, which decomposed during the calcination process. In this case, the strength contributing factor is the CaO in addition to the $CaCO_3$, which contributes to a slight increase in the strength development up to a certain limit [136,137] while the $Ca(OH)_2$ does not affect the strength [138]. This additional CaO accounts for more heat of hydration at an early stage due to its exothermic reaction with water [14,139]. Also, adding a given CES consisting of free CaO in the binder matrix can increase the strength of the concrete by improving the Hydraulic Modulus (HM) and Lime Saturation Factor (LSF) [140]. Given below are the mathematical equations for the estimation of HM and LSF.

$$\mathrm{HM} = \frac{\mathrm{CaO}}{\mathrm{SiO_2 + Al_2O_3 + Fe_2O_3}}$$

$$\mathrm{LSF} = \frac{\mathrm{CaO}}{\mathrm{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3}}$$

It must be noted here that CaO content for binder mix with CES consists of both CaO from XRF of OPC and from Rietveld analysis of CES. The details of HM and LSF for OPC and the binders with 5% CES replacement are shown below in Table 10. Since most of the CaO was converted into $Ca(OH)_2$ and the replacement level is only 5%, therefore, an extremely slight increase can be observed in HM and LSF of binders with CES. It means that the quantity of free CaO from the CES contributing to the strength is negligible while $CaCO_3$ is still present and contributing the strength. It is hard to find which phase is contributing more to strength in addition to the absence of the organic part but both CaO and $CaCO_3$ are the strength contributors. Furthermore, it is recommended to incorporate pozzolanic materials along with CES with decomposed calcium carbonate to consume the additional $Ca(OH)_2$ produced during the calcination for achieving high durability.

Table 10. HM and LSF for the OPC and the OPC with 5% CES.

Mix	CaO in CES	CaO in OPC	SiO_2	Al_2O_3	Fe_2O_3	HM	LSF
	%	%	%	%	%		
OPC	-	65.5	19.1	5.45	3	2.377	1.057
M-CES7	7.2	65.5	19.1	5.45	3	2.391	1.063
M-CES13	7.4	65.5	19.1	5.45	3	2.392	1.063
M-CES16	8.7	65.5	19.1	5.45	3	2.394	1.064

5. Conclusions

This study was carried out to assess the suitability of waste eggshells from different countries of origin for application in cementitious materials as a cement replacement. The focus was on the extent of variation in eggshells quality and its effect on the cement concrete when replaced with cement. The following conclusions can be drawn based on a detailed investigation of sixteen different eggshells from different countries of origin.

- The specific gravity of eggshells from across the world is lower as compared to the extra pure limestone due to the presence of an organic matrix. Thus, the eggshells are impure biological limestone having less mineral content as compared to extra pure limestone. The brown pigmentation in eggshells causes higher specific gravity but it does not affect the mineral content. Furthermore, the quality of eggshells from different regions across the world can be defined by their micro-structure in addition to their specific gravity and mineral contents.

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- The eggshells from different regions across the globe both in uncalcined state and calcined state with decomposed $CaCO_3$ are viable to use as a replacement of cement. The variation in the strength due to the variation in mineral content is acceptable. However, the strength of mixes with calcined eggshells is closer to the control mix and mix with limestone. The $CaCO_3$ content is the major contributor towards strength development by producing filler/dilution effect and heterogenous nucleation depending upon the size of particles in addition to the $CaCO_3$ content whereas CaO is another factor towards strength development by increasing the quantity of free CaO in the cementitious matrix containing calcined eggshells.

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References

1. R.M. Andrew, Global CO2 emissions from cement production, 1928-2018, Earth Syst. Sci. Data. 11 (2019) 1675–1710. https://doi.org/10.5194/essd-11-1675-2019.
2. T. Matschei, B. Lothenbach, F.P. Glasser, Thermodynamic properties of Portland cement hydrates in the system CaO–Al2O3–SiO2–CaSO4–CaCO3–H2O, 37 (2007) 1379–1410. https://doi.org/10.1016/j.cemconres.2007.06.002.
3. ASTM, ASTM C125-Standard Terminology Relating to Concrete and Concrete Aggregates, in: ASTM Stand., West Conshohocken, PA, 2003: pp. 1–4. https://doi.org/10.1520/C0125-15B.2.
4. S. Tsivilis, E. Chaniotakis, E. Badogiannis, G. Pahoulas, A. Ilias, A study on the parameters affecting the properties of Portland limestone cements, Cem. Concr. Compos. 21 (1999) 107–116. https://doi.org/10.1016/S0958-9465(98)00031-6.
5. V. Bonavetti, H. Donza, G. Menéndez, O. Cabrera, E.F. Irassar, Limestone filler cement in low w/c concrete: A rational use of energy, Cem. Concr. Res. 33 (2003) 865–871. https://doi.org/10.1016/S0008-8846(02)01087-6.
6. ASTM, ASTM C150-Standard Specification for Portland Cement, in: ASTM Stand., West Conshohocken, PA, 2015: pp. 1–10. https://doi.org/10.1520/C0150.
7. BSI, Methods of testingComposition, Specifications and Conformity Criteria for Common Cements, in: BS EN 197-1, 2011: p. 50.
8. D. Wang, C. Shi, N. Farzadnia, Z. Shi, H. Jia, A review on effects of limestone powder on the properties of concrete, Constr. Build. Mater. 192 (2018) 153–166. https://doi.org/10.1016/j.conbuildmat.2018.10.119.
9. M. Afzal, Y. Liu, J.C.P. Cheng, V.J.L. Gan, Reinforced concrete structural design optimization: A critical review, J. Clean. Prod. 260 (2020) 120623. https://doi.org/https://doi.org/10.1016/j.jclepro.2020.120623.
10. S. Tsivilis, G. Batis, E. Chaniotakis, G. Grigoriadis, D. Theodossis, Properties and behavior of limestone cement concrete and mortar, Cem. Concr. Res. 30 (2000) 1679–1683. https://doi.org/10.1016/S0008-8846(00)00372-0.
11. M. Afzal, S. Maqsood, S. Yousaf, Performance Evaluation of Cost Saving Towards Sustainability in Traditional Construction Using Prefabrication Technique, Int. J. Res. Eng. Sci. ISSN. 5 (2017) 73–79. www.ijres.org.
12. ASTM, ASTM C911-Standard Specification for Quick Lime, Hydrated Lime, and Limestone for Selected Chemical and Industrial Uses, in: ASTM Stand., West Conshohocken, PA, 2011: pp. 6–8. https://doi.org/10.1520/C0911-06R11.
13. F. Ujin, K.S. Ali, Z.Y.H. Harith, Viability of Using Eggshells Ash Affecting the Setting Time of Cement, Int. J. Civil, Environ. Struct. Constr. Archit. Eng. 10 (2016) 327–331.
14. S. Maqsood, L.S.S. Eddie, Effect of using Calcined Eggshells as a Cementitious Material on Early Performance, (n.d.) 1–19.
15. Y. Liu, M. Afzal, J.C.P. Cheng, J. Gan, Extension of IFC model schema for automated prefabrication of steel reinforcement in concrete structures, in: 8th Int. Conf. Innov. Prod. Constr. (IPC 2020), Hong Kong, China, 2020. https://hdl.handle.net/1783.1/110080.
16. H. Binici, O. Aksogan, A.H. Sevinc, E. Cinpolat, Mechanical and radioactivity shielding performances of mortars made with cement, sand and egg shells, Constr. Build. Mater. 93 (2015) 1145–1150. https://doi.org/10.1016/j.conbuildmat.2015.05.020.

17. A.H. Sevinç, M.Y. Durgun, A novel epoxy-based composite with eggshell, PVC sawdust, wood sawdust and vermiculite: An investigation on radiation absorption and various engineering properties, Constr. Build. Mater. 300 (2021). https://doi.org/10.1016/j.conbuildmat.2021.123985.
18. D. Cree, P. Pliya, Effect of elevated temperature on eggshell, eggshell powder and eggshell powder mortars for masonry applications, J. Build. Eng. 26 (2019). https://doi.org/10.1016/j.jobe.2019.100852.
19. D. Gowsika, S.S. kokila, K. Sargunan, Experimental Investigation of Egg Shell Powder as Partial Replacement with Cement in Concrete, Int. J. Eng. Trends Technol. 14 (2014) 65–68. https://doi.org/10.14445/22315381/ijett-v14p214.
20. N. Parthasarathi, M. Prakash, K.S. Satyanarayanan, Experimental study on partial replacement of cement with egg shell powder and silica fume, Rasayan J. Chem. 10 (2017) 442–449. https://doi.org/10.7324/RJC.2017.1021689.
21. S. Sohu, N. Bheel, A.A. Jhatial, A.A. Ansari, I.A. Shar, Sustainability and mechanical property assessment of concrete incorporating eggshell powder and silica fume as binary and ternary cementitious materials, Environ. Sci. Pollut. Res. (2022) 58685–58697. https://doi.org/10.1007/s11356-022-19894-5.
22. A. Teara, D. Shu Ing, Mechanical properties of high strength concrete that replace cement partly by using fly ash and eggshell powder, Phys. Chem. Earth. 120 (2020) 102942. https://doi.org/10.1016/j.pce.2020.102942.
23. A. Teara, S.I. Doh, S.C. Chin, Y.J. Ding, J. Wong, X.X. Jiang, Investigation on the durability of use fly ash and eggshells powder to replace the cement in concrete productions, in: IOP Conf. Ser. Earth Environ. Sci., 2019. https://doi.org/10.1088/1755-1315/244/1/012025.
24. F. Fatahillah, A. Sumarno, The Effect of Concrete Mixture on Usage Fly Ash and Chicken Egg Shell Powder as Cement Substitutions in Concrete Compressive Strength, Neutron. 22 (2022) 24–30. https://doi.org/10.29138/neutron.v22i01.173.
25. N.S. Afizah Asman, S. Dullah, J. Lynn Ayog, A. Amaludin, H. Amaludin, C.H. Lim, A. Baharum, Mechanical Properties of Concrete Using Eggshell Ash and Rice Husk Ash As Partial Replacement of Cement, in: MATEC Web Conf., 2017: pp. 4–9. https://doi.org/10.1051/matecconf/201710301002.
26. C. Oliko, C.K. Kabubo, J.N. Mwero, Rice Straw and Eggshell Ash as Partial Replacements of Cement in Concrete, Eng. Technol. Appl. Sci. Res. 10 (2020) 6481–6487. https://doi.org/10.48084/etasr.3893.
27. V. Chandrasekaran, M. Vasanth, S. Thirunavukkarasu, Experimental Investigation of Partial Replacement of Cement with Glass Powder and Eggshell Powder Ash in Concrete, Civ. Eng. Res. J. 5 (2018) 1–9. https://doi.org/10.19080/cerj.2018.05.555662.
28. M.E. Mohamad, A.A. Mahmood, A. Yik Yee Min, A.R. Nur Nadhira, Palm Oil Fuel Ash (POFA) and Eggshell Powder (ESP) as Partial Replacement for Cement in Concrete, E3S Web Conf. 34 (2018) 1–8. https://doi.org/10.1051/e3sconf/20183401004.
29. H. Hamada, B. Tayeh, F. Yahaya, K. Muthusamy, A. Al-Attar, Effects of nano-palm oil fuel ash and nano-eggshell powder on concrete, Constr. Build. Mater. 261 (2020) 119790. https://doi.org/10.1016/j.conbuildmat.2020.119790.
30. N.H. Abd Khalid, N.N. Abdul Rasid, A.R. Mohd Sam, N.H. Abdul Shukor Lim, L. Zardasti, M. Ismail, A. Mohamed, Z.A. Majid, The hydration effect on palm oil fuel ash concrete containing eggshell powder, IOP Conf. Ser. Earth Environ. Sci. 220 (2019). https://doi.org/10.1088/1755-1315/220/1/012047.
31. N.H.A. Khalid, N.N.A. Rasid, A.R. Mohdsam, N.H.A.S. Lim, M. Ismail, L. Zardasti, A. Mohamed, Z.A. Majid, N.F. Ariffin, Characterization of palm oil fuel ash and eggshell powder as partial cement replacement in concrete, IOP Conf. Ser. Mater. Sci. Eng. 431 (2018). https://doi.org/10.1088/1757-899X/431/3/032002.
32. M. Amin, M.M. Attia, I.S. Agwa, Y. Elsakhawy, K.A. El-hassan, B.A. Abdelsalam, Effects of sugarcane bagasse ash and nano eggshell powder on high-strength concrete properties, Case Stud. Constr. Mater. 17 (2022). https://doi.org/10.1016/j.cscm.2022.e01528.
33. S. Kamaruddin, W.I. Goh, A.A. Jhatial, M.T. Lakhiar, Chemical and Fresh State Properties of Foamed Concrete Incorporating Palm Oil Fuel Ash and Eggshell Ash as Cement Replacement, Int. J. Eng. Technol. 7 (2018) 350–354.
34. L.R. Siong, Water Absorption and Strength Properties of Lightweight Foamed Concrete with 2.5% and 5.0% Eggshell as Partial Cement Replacement Material, Universiti Tunku Abdul Rehman, 2015.

35. O.M. Ofuyatan, A.G. Adeniyi, D. Ijie, J.O. Ighalo, J. Oluwafemi, Development of high-performance self compacting concrete using eggshell powder and blast furnace slag as partial cement replacement, Constr. Build. Mater. 256 (2020) 119403. https://doi.org/10.1016/j.conbuildmat.2020.119403.
36. A.S. Aadi, N.H. Sor, A.A. Mohammed, The behavior of eco-friendly self - Compacting concrete partially utilized ultra-fine eggshell powder waste, J. Phys. Conf. Ser. 1973 (2021). https://doi.org/10.1088/1742-6596/1973/1/012143.
37. N. Hilal, D.M. Al Saffar, T.K.M. Ali, Effect of egg shell ash and strap plastic waste on properties of high strength sustainable self-compacting concrete, Arab. J. Geosci. 14 (2021). https://doi.org/10.1007/s12517-021-06654-x.
38. Y. Liu, M. Afzal, J.C.P. Cheng, J. Gan, Concrete reinforcement modelling with IFC for automated rebar fabrication, in: 8th Int. Conf. Prod. Constr. (IPC 2020) Will Jointly Organ. with 8th Int. Conf. Constr. Eng. Proj. Manag. (ICCEPM 2020), Hong Kong, China, 2020. https://hdl.handle.net/1783.1/110084.
39. M. Afzal, Evaluation and development of automated detailing design optimization framework for RC slabs using BIM and metaheuristics, Hong Kong University of Science and Technology, 2019. https://hdl.handle.net/1783.1/101635.
40. P. Shekhawat, G. Sharma, R.M. Singh, Strength behavior of alkaline activated eggshell powder and flyash geopolymer cured at ambient temperature, Constr. Build. Mater. 223 (2019) 1112–1122. https://doi.org/10.1016/j.conbuildmat.2019.07.325.
41. N. Shiferaw, L. Habte, T. Thenepalli, J.W. Ahn, Effect of eggshell powder on the hydration of cement paste, Materials (Basel). 12 (2019). https://doi.org/10.3390/ma12152483.
42. S. Maqsood, L.S.S. Eddie, Effect of using Calcined Eggshells as a Cementitious Material on Early Performance, Constr. Build. Mater. 318 (2022) 1–15. https://doi.org/10.1016/j.conbuildmat.2021.126170.
43. A.A. Dezfouli, Effect of Eggshell Powder Application on the Early and Hardened Properties of Concrete, J. Civ. Eng. Mater. Appl. 4 (2020) 209–221. https://doi.org/10.22034/JCEMA.2020.241853.1036.
44. N. Razali, M.A. Azizan, K.F. Pa'ee, N. Razali, N. Jumadi, Preliminary studies on calcinated chicken eggshells as fine aggregates replacement in conventional concrete, Mater. Today Proc. 31 (2020) 354–359. https://doi.org/10.1016/j.matpr.2020.06.232.
45. Jayasankar.R, Mahindran.N, Langovan.R, Studies on Concrete using Fly Ash , Rice Husk Ash and Egg Shell, Int. J. Civ. Struct. Eng. 1 (2010) 362–372.
46. A. Yerramala, Properties of concrete with eggshell powder as cement replacement, Indian Concr. J. 88 (2014) 94–102.
47. D. Gowsika, S. Sarankokila, K. Sargunan, Experimental investigation of egg shell powder as partial replacement with cement in concrete, Int. J. Eng. Trends Technol. 14 (2) (2014) 65–68.
48. O.U. Orie, O.J. Omokhiboria, Mechanical Properties of Eggshell and Palm Oil Fuel Ashes Cement Blended Concrete, Res. J. Eng. Appl. Sci. 3 (2014) 401–405.
49. S.I. Doh, S.C. Chin, Eggshell powder: potential filler in concrete, in: Malaysian Tech. Univ. Conf. Eng. Technol., Melaka, Malaysia, 2014.
50. P. Pliya, D. Cree, Limestone derived eggshell powder as a replacement in Portland cement mortar, Constr. Build. Mater. 95 (2015) 1–9. https://doi.org/10.1016/j.conbuildmat.2015.07.103.
51. R.A. Al-safy, Experimental Investigation on Properties of Cement Mortar Incorporating Eggshell Powder, J. Eng. Dev. 19 (2015) 198–209.
52. T.Y. Yu, D.S. Ing, C.S. Choo, The Effect of Different Curing Methods on the Compressive Strength of Eggshell Concrete, Indian J. Sci. Technol. 10 (2017) 1–4. https://doi.org/10.17485/ijst/2017/v10i6/111210.
53. A. Parkash, E.R. Singh, Behaviour of Concrete Containing Egg Shell Powder As Cement Replacing Material, Int. J. Latest Res. Eng. Comput. 5 (2017) 2347–6540. www.ijlrec.com.
54. N. Balouch, K. Rashid, S. Javed, T. Ahmad, Experimental Study on Compressive Strength of Concrete by Partial Replacement with Eggshell Powder, Tech. Journal, Univ. Eng. Technol. Taxila. 22 (2017) 21–27. https://doi.org/10.22214/ijraset.2019.5084.
55. J.O. Afolayan, Experimental Investigation of the Effect of Partial Replacement of Cement with Eggshell Ash on the Rheological Properties of Concrete, Int. J. Eng. Appl. Sci. 4 (2017) 1–7.
56. A.A. Manzoor, E. Anand, Behaviour of Concrete Containing Egg Shell Powder As Cement Replacing Material, Int. J. Sci. Dev. Adn Res. 3 (2018) 2347–6540. ijsdr.org.
57. P. Kalpana, M. Chandu, The Enduringness Moderator in Concrete by Eggshell Powder, Agro Waste and E Waste, in: 12th Int. Conf. Recent Innov. Scieence, Eng. Manag., Srikakulam, 2018: pp. 728–737.

58. Y.Y. Tan, S.I. Doh, S.C. Chin, Eggshell as a partial cement replacement in concrete development, Mag. Concr. Res. 70 (2018) 662–670. https://doi.org/10.1680/jmacr.17.00003.
59. N.A. Gabol, A.M. Fareed, M. Jawaduddin, Z.H. Zardari, Analysis of Eggshell Powder as A Partial Replacing Material in Concrete, Int. J. Mod. Res. Eng. Manag. 2 (2019) 22–31. www.ijmrem.com.
60. H.A. Jaber, R.S. Mahdi, A.K. Hassan, Influence of eggshell powder on the Portland cement mortar properties, Mater. Today Proc. 20 (2020) 391–396. https://doi.org/10.1016/j.matpr.2019.09.153.
61. A.A. Langah, A. Saand, Strength Development of Concrete by Using Eggshell Powder as Partial Replacement of Cement, QUEST Res. J. 18 (2020) 72–79.
62. B. Lejano, R.J. Barron, P.D. Saludo, J.M. Tugade, K. Yokohama, Compressive strength of concrete with seawater and powdered eggshells as partial replacement for cement, Int. J. GEOMATE. 18 (2020) 52–58. https://doi.org/10.21660/2020.69.9113.
63. S. Mohd Arif, O. Rokiah, M. Khairunisa, B.W. Chong, Y.C. Chek, D. Youventharan, P.J. Ramadhansyah, S.I. Doh, Compressive Strength of Concrete containing Eggshell Powder as Partial Cement Replacement, IOP Conf. Ser. Earth Environ. Sci. 682 (2021). https://doi.org/10.1088/1755-1315/682/1/012031.
64. S. Niyasom, N. Tangboriboon, Development of biomaterial fillers using eggshells, water hyacinth fibers, and banana fibers for green concrete construction, Constr. Build. Mater. 283 (2021) 122627. https://doi.org/10.1016/j.conbuildmat.2021.122627.
65. K. Nandhini, J. Karthikeyan, Effective utilization of waste eggshell powder in cement mortar, Mater. Today Proc. 61 (2022) 428–432. https://doi.org/10.1016/j.matpr.2021.11.328.
66. E.M. Shcherban', S.A. Stel'makh, A.N. Beskopylny, L.R. Mailyan, B. Meskhi, V. Varavka, N. Beskopylny, D. El'shaeva, Enhanced Eco-Friendly Concrete Nano-Change with Eggshell Powder, Appl. Sci. 12 (2022). https://doi.org/10.3390/app12136606.
67. C. Shi, Steel Slag—Its Production, Processing, Characteristics, and Cementitious Properties, J. Mater. Civ. Eng. 16 (2004) 230–236. https://doi.org/10.1061/(asce)0899-1561(2004)16:3(230).
68. Z. Zhou, M. Sofi, E. Lumantarna, R.S. Nicolas, G.H. Kusuma, P. Mendis, Strength development and thermogravimetric investigation of high-volume fly ash binders, Materials (Basel). 12 (2019). https://doi.org/10.3390/ma12203344.
69. P. Suraneni, A. Hajibabaee, S. Ramanathan, Y. Wang, J. Weiss, New insights from reactivity testing of supplementary cementitious materials, Cem. Concr. Compos. 103 (2019) 331–338. https://doi.org/10.1016/j.cemconcomp.2019.05.017.
70. M. Kristl, S. Jurak, M. Brus, V. Sem, J. Kristl, Evaluation of calcium carbonate in eggshells using thermal analysis, J. Therm. Anal. Calorim. 138 (2019) 2751–2758. https://doi.org/10.1007/s10973-019-08678-8.
71. A.M. King'ori, A Review of the uses of poultry eggshells and shell membranes, Int. J. Poult. Sci. 10 (2011) 908–912. https://doi.org/10.3923/ijps.2011.908.912.
72. N. Ajayan, S. K. P, A. A. U., S. Soman, Quantitative Variation in Calcium Carbonate Content in Shell of Different Chicken and Duck Varieties, Adv. Zool. Bot. 8 (2020) 1–5. https://doi.org/10.13189/azb.2020.080101.
73. G.D. Butcher, R. Miles, Concepts of Eggshell Quality, (2012) 1–2.
74. Y.O. Suk, C. Park, Effect of breed and age of hens on the yolk to albumen ratio in two different genetic stocks, Poult. Sci. 80 (2001) 855–858. https://doi.org/10.1093/ps/80.7.855.
75. E. Casiraghi, A. Hidalgo, M. Rossi, Influence of weight grade on shell characteristics of marketed hen eggs, in: XI Th Eur. Symp. Qual. Eggs Egg Prod., Doorwerth, Netherlands, 2005: pp. 23–26.
76. H.M. Yang, Z.Y. Wang, J. Lu, Study on the relationship between eggshell colors and egg quality as well as shell ultrastructure in Yangzhou chicken, African J. Biotechnol. 8 (2009) 2898–2902.
77. J. Vlčková, E. Tůmová, M. Ketta, M. Englmaierová, D. Chodová, Effect of housing system and age of laying hens on eggshell quality, microbial contamination, and penetration of microorganisms into eggs, Czech J. Anim. Sci. 63 (2018) 51–60. https://doi.org/10.17221/77/2017-CJAS.
78. A. Galic, D. Filipovic, Z. Janjecic, D. Bedekovic, I. Kovacev, K. Copec, S. Pliestic, Physical and mechanical characteristics of Hisex Brown hen eggs from three different housing systems, South African J. Anim. Sci. 49 (2019) 468–476. https://doi.org/10.4314/sajas.v49i3.7.
79. E. Altuntas, A. Sekeroglu, Mechanical behavior and physical properties of chicken egg as affected by different egg weights, J. Food Process Eng. 33 (2010) 115–127. https://doi.org/10.1111/j.1745-4530.2008.00263.x.

80. R.M.G. Hamilton, Methods and Factors That Affect the Measurement of Egg Shell Quality, Poult. Sci. 61 (1982) 2022–2039. https://doi.org/10.3382/ps.0612022.
81. J.H. Wolford, K. Tanaka, Factors Influencing Egg Shell Quality - A Review, Worlds. Poult. Sci. J. 26 (1970) 763–780. https://doi.org/10.1079/WPS19700033.
82. P. Hunton, Research on eggshell structure and quality : An historical overview, Brazilian J. Poult. Sci. 7 (2005) 67–71.
83. J.R. Robert, Factors Affecting Egg Internal Quality and Egg Shell Quality in Laying Hens, J. Poult. Sci. 41 (2004) 161–177. https://doi.org/10.2141/jpsa.41.161.
84. H.K. Muiruri, P.C. Harrison, Effect of roost temperature on performance of chickens in hot ambient environments., Poult. Sci. 70 (1991) 2253–2258. https://doi.org/10.3382/ps.0702253.
85. A. Nardone, B. Ronchi, N. Lacetera, M.S. Ranieri, U. Bernabucci, Effects of climate changes on animal production and sustainability of livestock systems, Livest. Sci. 130 (2010) 57–69. https://doi.org/10.1016/j.livsci.2010.02.011.
86. N. Dayyani, H. Bakhtiari, Heat stress in poultry: background and affective factors, Int. J. Adv. Biol. Biomed. Res. 1 (2013) 1409–1413. http://www.ijabbr.com.
87. J.R. Roberts, Factors affecting egg shell and internal egg quality, in: Proc. 18th Annu. ASAIM SE Asian Feed Technol. Nutr. Work. Le Meridien Siem Reap, Cambodia, 2010: pp. 1–9.
88. M.E. Mohamad, A.A. Mahmood, A.Y.Y. Min, N.H.A. Khalid, A Review of the Mechanical Properties of Concrete Containing Biofillers, IOP Conf. Ser. Mater. Sci. Eng. 160 (2016). https://doi.org/10.1088/1757-899X/160/1/012064.
89. Dhanalakshmi M, Dr Sowmya N J, Dr Chandrashekar A, A Comparative Study on Egg Shell Concrete with Partial Replacement of Cement by Fly Ash, Int. J. Eng. Res. V4 (2015). https://doi.org/10.17577/ijertv4is051303.
90. V.H. Yadav, H. Eramma, Experimental Studies on Concrete for the Partial Replacement of Cement By Egg Shell Powder and Ggbs, Int. Res. J. Eng. Technol. 4 (2017) 144–150. https://irjet.net/archives/V4/i8/IRJET-V4I827.pdf.
91. S. Karthikeyan, C. Suresh, S. Manikandan, M. Divya, R. Nandhakumar, An experimental investigation of eggshell concrete, J. Chem. Pharm. Sci. 8 (2015) 851–852.
92. T. Prasanth, B. Sasidharan, M.R. Udhayakumar, V. Yuvasakthi, Hameed A. A., Replacement of cement using eggshell and fully replacement by red sand, Int. J. Intellect. Adv. Res. Eng. Comput. 6 (2018) 1133–1136.
93. R.R. Kumar, R. Mahendran, S.G. Nathan, D. Sathya, K. Thamaraikannan, an Experimental Study on Concrete Using Coconut Shell Ash and Egg Shell Powder, South Asian J. Eng. Technol. 3 (2017) 151–161.
94. and T.A. N. Balouch, K. Rashid, S. Javed, Experimental Study on Compressive Strength of Concrete by Partial Replacement of Cement with Eggshell Powder, Int. J. Res. Appl. Sci. Eng. Technol. 7 (2019) 502–503. https://doi.org/10.22214/ijraset.2019.5084.
95. R.H. Harms, Specific gravity of eggs and eggshell weight from commercial layers and broiler breeders in relation to time of oviposition., Poult. Sci. 70 (1991) 1099–1104. https://doi.org/10.3382/ps.0701099.
96. P.S.B. N. Mesha, A. Roopa, A Thesis on Partial Replacement of Cement by Eggshell Powder and Fine Aggregate by Crushed Gullet Pieces, Int. Journals Adv. Res. Comput. Sci. Softw. Eng. ISSN 2277-128X (Volume-8, Issue-4). (2018) 347–354.
97. M.K. Kiran, M.A. Sharma, An experimental study on partial replacement of cement with brick dust (surkhi) in concrete, J. Civ. Constr. Eng. 3 (2017).
98. F. Adogla, P. Paa Kofi Yalley, M. Arkoh, Improving Compressed Laterite Bricks using Powdered Eggshells, Int. J. Eng. Sci. 5 (2016) 65–70.
99. G. Mishra, N. Pathak, Strength and Durability study on Standard Concrete with Partial Replacement of Cement and Sand using Egg Shell Powder and Earthenware Aggregates for Sustainable Construction, Int. J. Res. Dev. Technol. 8 (2017) 360–371.
100. FAO, FAOSTAT - Food Balances, Food Agric. Organ. (2023). https://www.fao.org/faostat/en/#data/FBS (accessed December 25, 2023).
101. OEC, Trade Balance of Eggs in Hong Kong, Obs. Econ. Complex. (2021). https://oec.world/en/profile/bilateral-product/eggs/reporter/hkg?yearExportSelector=exportYear1. (accessed June 28, 2023).

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 27 December 2023 doi:10.20944/preprints202310.1834.v2

102. S. Maqsood, L.S.S. Eddie, N.H. Yi, M. Afzal, An Insight on the Sufficiency of Waste Eggshells in Hong Kong for Sustainable Commercial Applications in Cementitious Products, Preprints. (2023). https://doi.org/10.20944/preprints202309.2056.v1.
103. V. Kattimani, G.S.K. PANGA, G. Ek, Eggshell membrane separation methods-waste to wealth-a scoping review, Poult. Stud. 19 (2022) 11–18. https://doi.org/10.34233/jpr.1131361.
104. R.H. Wang, F.Z. Ren, Z.J. Huang, H. Zhao, H.Y. Guo, J.Y. Cui, Research of jointing impact crushing, flotation and acid treatment of avian eggshell membrane extraction method, Sci. Technol. Food Ind. 33 (2012) 291–299.
105. S. Yoo, J.S. Hsieh, P. Zou, J. Kokoszka, Utilization of calcium carbonate particles from eggshell waste as coating pigments for ink-jet printing paper, Bioresour. Technol. 100 (2009) 6416–6421. https://doi.org/10.1016/j.biortech.2009.06.112.
106. R. Mohadi, K. Anggraini, F. Riyanti, A. Lesbani, Preparation Calcium Oxide From Chicken Eggshells, Sriwij. J. Environ. 1 (2016) 32–35. https://doi.org/10.22135/sje.2016.1.2.32-35.
107. L. Dupoirieux, D. Pourquier, F. Souyris, Powdered eggshell: a pilot study on a new bone substitute for use in maxillofacial surgery, J. Cranio-Maxillofacial Surg. 23 (1995) 187–194. https://doi.org/10.1016/S1010-5182(05)80009-5.
108. Z. Li, Materials for Making Concrete, in: Adv. Concr. Technol., John Wiley and Sons, Hoboken, New Jersey, 2011: pp. 23–92.
109. W.T. Tsai, J.M. Yang, C.W. Lai, Y.H. Cheng, C.C. Lin, C.W. Yeh, Characterization and adsorption properties of eggshells and eggshell membrane, Bioresour. Technol. 97 (2006) 488–493. https://doi.org/10.1016/j.biortech.2005.02.050.
110. S.M. Hama, Improving mechanical properties of lightweight Porcelanite aggregate concrete using different waste material, Int. J. Sustain. Built Environ. 6 (2017) 81–90. https://doi.org/10.1016/j.ijsbe.2017.03.002.
111. H.M. Hamada, B.A. Tayeh, A. Al-Attar, F.M. Yahaya, K. Muthusamy, A.M. Humada, The present state of the use of eggshell powder in concrete: A review, J. Build. Eng. 32 (2020) 101583. https://doi.org/10.1016/j.jobe.2020.101583.
112. F.S. Murakami, P.O. Rodrigues, C.M.T. De Campos, M.A.S. Silva, Physicochemical study of CaCO3 from egg shells, Cienc. e Tecnol. Aliment. 27 (2007) 658–662. https://doi.org/10.1590/S0101-20612007000300035.
113. T. Witoon, Characterization of calcium oxide derived from waste eggshell and its application as CO2 sorbent, Ceram. Int. 37 (2011) 3291–3298. https://doi.org/10.1016/j.ceramint.2011.05.125.
114. A. Lesbani, P. Tamba, R. Mohadi, Fahmariyanti, Preparation of calcium oxide from Achatina fulica as catalyst for production of biodiesel from waste cooking oil, Indones. J. Chem. 13 (2013) 176–180. https://doi.org/10.22146/ijc.21302.
115. D. Cree, A. Rutter, Sustainable Bio-Inspired Limestone Eggshell Powder for Potential Industrialized Applications, ACS Sustain. Chem. Eng. 3 (2015) 941–949. https://doi.org/10.1021/acssuschemeng.5b00035.
116. H.M. Yang, Z.Y. Wang, J. Lu, Study on the relationship between eggshell colors and egg quality as well as shell ultrastructure in Yangzhou chicken, African J. Biotechnol. 8 (2009) 2898–2902. https://www.cabdirect.org/cabdirect/abstract/20093204107.
117. N.S. Joseph, N.A. Robinson, R.A. Renema, F.E. Robinson, Shell Quality and Color Variation in Broiler Breeder Eggs, J. Appl. Poult. Res. 8 (1999) 70–74. https://doi.org/10.1093/japr/8.1.70.
118. P. Pliya, D. Cree, Limestone derived eggshell powder as a replacement in Portland cement mortar, Constr. Build. Mater. 95 (2015) 1–9. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2015.07.103.
119. P.D.G. Richards, D.C. Deeming, Correlation between shell colour and ultrastructure in pheasant eggs, Br. Poult. Sci. 42 (2001) 338–343. https://doi.org/10.1080/00071660120055304.
120. S.E. Solomon, Egg & eggshell quality., Iowa State University Press, 1997.
121. E. Tumova, M. Englmaierova, Z. Ledvinka, and V Charvatova, Interaction between housing system and genotype in relation to internal and external egg quality parameters, Czech J. Anim. Sci. 56 (2011) 490–498.
122. M. Ketta, E. Tůamová, Eggshell structure, measurements, and quality-affecting factors in laying hens: A review, Czech J. Anim. Sci. 61 (2016) 299–309. https://doi.org/10.17221/46/2015-CJAS.
123. A. Ipavec, R. Gabrovšek, T. Vuk, V. Kaučič, J. MačEk, A. Meden, Carboaluminate phases formation during the hydration of calcite-containing Portland cement, J. Am. Ceram. Soc. 94 (2011) 1238–1242. https://doi.org/10.1111/j.1551-2916.2010.04201.x.
124. R.L. Sharma, S.P. Pandey, Influence of mineral additives on the hydration characteristics of ordinary Portland cement, Cem. Concr. Res. 29 (1999) 1525–1529. https://doi.org/10.1016/S0008-8846(99)00104-0.

 doi:10.20944/preprints202310.1834.v2

125. J.J. Thomas, H.M. Jennings, J.J. Chen, Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement, J. Phys. Chem. C. 113 (2009) 4327–4334. https://doi.org/10.1021/jp809811w.
126. E.H. Kadri, S. Aggoun, G. De Schutter, K. Ezziane, Combined effect of chemical nature and fineness of mineral powders on Portland cement hydration, Mater. Struct. Constr. 43 (2010) 665–673. https://doi.org/10.1617/s11527-009-9519-6.
127. A. Schöler, B. Lothenbach, F. Winnefeld, M. Ben Haha, M. Zajac, H.M. Ludwig, Early hydration of SCM-blended Portland cements: A pore solution and isothermal calorimetry study, Cem. Concr. Res. 93 (2017) 71–82. https://doi.org/10.1016/j.cemconres.2016.11.013.
128. M. Cyr, P. Lawrence, E. Ringot, Efficiency of mineral admixtures in mortars: Quantification of the physical and chemical effects of fine admixtures in relation with compressive strength, Cem. Concr. Res. 36 (2006) 264–277. https://doi.org/10.1016/j.cemconres.2005.07.001.
129. Q. Wang, J. Yang, H. Chen, Long-term properties of concrete containing limestone powder, Mater. Struct. Constr. 50 (2017) 1–13. https://doi.org/10.1617/s11527-017-1040-8.
130. X.Y. Wang, Modeling of hydration, compressive strength, and carbonation of portland-limestone cement (PLC) concrete, Materials (Basel). 10 (2017). https://doi.org/10.3390/ma10020115.
131. G. De Schutter, Effect of limestone filler as mineral addition in self compacting concrete, in: 36th Conf. Our World Concr. Struct. "Recenet Adv. Technol. Fresh Concr., Ghent University, Department of Structural Engineering, Ghent, 2011: pp. 49–54. https://biblio.ugent.be/publication/2939937.
132. S. Rode, N. Oyabu, K. Kobayashi, H. Yamada, A. Kühnle, True atomic-resolution imaging of (1014) calcite in aqueous solution by frequency modulation atomic force microscopy, Langmuir. 25 (2009) 2850–2853. https://doi.org/10.1021/la803448v.
133. K. Vance, M. Aguayo, T. Oey, G. Sant, N. Neithalath, Hydration and strength development in ternary portland cement blends containing limestone and fly ash or metakaolin, Cem. Concr. Compos. 39 (2013) 93–103. https://doi.org/10.1016/j.cemconcomp.2013.03.028.
134. D.P. Bentz, A. Ardani, T. Barrett, S.Z. Jones, D. Lootens, M.A. Peltz, T. Sato, P.E. Stutzman, J. Tanesi, W.J. Weiss, Multi-scale investigation of the performance of limestone in concrete, Constr. Build. Mater. 75 (2015) 1–10. https://doi.org/10.1016/j.conbuildmat.2014.10.042.
135. P. Thongsanitgarn, W. Wongkeo, A. Chaipanich, C.S. Poon, Heat of hydration of Portland high-calcium fly ash cement incorporating limestone powder: Effect of limestone particle size, Constr. Build. Mater. 66 (2014) 410–417. https://doi.org/10.1016/j.conbuildmat.2014.05.060.
136. R. Gagné, Expansive agents, in: Sci. Technol. Concr. Admixtures, Elsevier Ltd, 2016: pp. 441–456. https://doi.org/10.1016/B978-0-08-100693-1.00022-9.
137. N.H. Mtarfi, Z. Rais, M. Taleb, Effect of clinker free lime and cement fineness on the cement physicochemical properties, J. Mater. Environ. Sci. 8 (2017) 2541–2548.
138. P.C. Aïtcin, Portland cement, in: Sci. Technol. Concr. Admixtures, Elsevier Ltd, 2016: pp. 27–51. https://doi.org/10.1016/B978-0-08-100693-1.00003-5.
139. C. Ju, Y. Liu, M. Jia, K. Yu, Z. Yu, Y. Yang, Effect of calcium oxide on mechanical properties and microstructure of alkali-activated slag composites at sub-zero temperature, J. Build. Eng. 32 (2020) 101561. https://doi.org/10.1016/j.jobe.2020.101561.
140. P.H. Shih, J.E. Chang, L.C. Chiang, Replacement of raw mix in cement production by municipal solid waste incineration ash, Cem. Concr. Res. 33 (2003) 1831–1836. https://doi.org/10.1016/S0008-8846(03)00206-0.