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Effect of elevated temperature on eggshell, eggshell powder and eggshell powder mortars for masonry applications

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Abstract

Eggshell powder (ESP) may be an alternative natural sustainable supplementary cementitious material (SCM). Mortar specimens containing 0, 5, 10 and 20 wt. % of ESP as Portland cement replacements were submitted to 20, 150, 300 and 450°C. To gain a better understanding of the organic membranes bonded to the eggshell/ESP, digital images, scanning electron microscopy (SEM) and thermo-gravimetric analysis (TGA) were used after heating of eggshells and ESP. The residual mortar weight loss, porosity, compressive and flexural strengths were determined and compared to the unheated samples. For all temperatures, significant color changes occurred for the eggshells and ESP (e.g. white, pale yellow, light brown and black/gray as temperature increased). SEM showed the interior of the eggshell membranes were not present after 450°C. TGA showed the processed ESP did not contain high amounts of organic membrane. The reduction in compressive and flexural strengths of ESP mortars at room temperature ranged from 21-50% and 8-39%, respectively in contrast to mortars without ESP, while the residual ESP mortar strengths remained below the control. The results showed ESP can be used in amounts up to 20 wt. % as an alternative SCM in mortar applications and still be within the ASTM standard 28-day compressive strength requirements.

Keywords: eggshells; eggshell powder; mortar; temperature; porosity; strength.

1. Introduction

The use of Portland cement (PC) in the building and construction industry has steadily increased over the years. In 2010, the world production of PC was estimated at 3.3 billion metric tonnes per year which increased to 4.10 billion metric tonnes (Gt) per year as of 2017 [1]. In 2009, PC demand was forecasted to be between 3.7-5.5 billion tonnes by 2050 [2] which may have been under-estimated. The general figure to produce one ton of PC releases about one ton of carbon dioxide (CO₂), a greenhouse gas into the environment. Therefore, based on the figures above, in just seven years the increase in CO₂ levels from PC production has increased by about 24%.

In an effort to lower the use of PC in mortars and concrete without affecting strength and durability, synthetic and natural supplementary cementitious materials (SCMs) have been added as partial PC replacements. The three common and most utilized man-made SCMs are obtained from waste product industries; granulated blast furnace slag (metal fabrication), fly ash (coal power generation) and silica fume (ferrosilicon industry). Natural SCMs are calcined shale, calcined clay or metakaolin [3]. Limestone is a natural SCM generally obtained from sedimentary rocks and used as an inert mineral filler in PC. Environmental and social responsibility from industry has led the research community to search for new alternative sustainable SCMs. One of these are bio-based limestone fillers from various seashell wastes used as PC replacements [4, 5]. Another limestone bio-filler type can be derived from eggshell (ES) waste. Eggshell powders (ESP) were previously evaluated to have a composition of approximately 96.9% calcium carbonate CaCO₃ with a crystal structure of calcite and 1-3% organic matter by weight (wt.%) [6]. However, the structure of the calcite in ESP is porous [7] which may modify properties of the mortar.

Common eggs are available in white or brown colour, however in a related study it was found the colour was not a determining factor in the content of CaCO_3 and were considered to be equivalent in composition [8]. The CaCO_3 composition of eggshells is similar to natural limestone used in PC. For instance, depending on the geological nature of the formed limestone, it inherently contains impurities. According to DIN EN ISO 3262, part 5, natural limestone purity is classified by categories A through D which provide CaCO_3 purity content ranging from 99-90%, respectively [9]. Large amounts of waste eggshells could be acquired from egg breaking plant industries designed to extract white and yellow liquid egg products. In return they have an abundance of eggshells to dispose. Recently, there has been an interest to recuperate waste eggshells for use in high value added products. Research laboratories/start-up companies have shown interest in medium to large-scale eggshell processing facilities to produce fine ESP; Eco-SHELL (Spain), Just Egg (Chilled Foods) Ltd. (United Kingdom), Burnbrae Farms Ltd. (Canada), Ateknea Solutions Hungary LLC (Hungary) and Uroc (Belgium). In the near future there will be a need to find niches for ESP. ESP has been studied as a PC replacement in mortars for its hardened room temperature properties. Generally, mortars rather than concrete are studied to determine the behaviour of SCM without the effects of large aggregates. For example, Pliya and Cree [8] studied mortars containing white and brown ESP as replacements in PC-Type I of 0, 5, 10, 15 and 20 wt.% having a particle sizes of 63 μm and water/cement (w/c) ratio of 0.5. The maximum size of the fine sand particles was 2 mm and the specimens were cured by immersing in a water bath. The compressive and flexural strengths were reduced at all levels of ESP replacement compared to mortars without ESP. When 5 wt. % white and brown ESP was substituted for PC, the compressive strengths both decreased by 14%, while the flexural strengths reduced by 18% and 8%, respectively. However the authors observed the strengths reductions were not significantly affected and were still acceptable according to the ASTM C270 [10]. In contrast,

Al-Safy [11] observed mortar compressive and flexural strength improvements using 75 μm ESP powers in PC-Type I replacements of 0, 1, 3, 5, 7 and 10 wt.%. The mortars contained a maximum size of fine aggregates of 4.75 mm and had a w/c ratio of 0.4. The samples were cured at ambient temperature for 24 hours followed by placement in curing tanks until tested. With 5 wt. % ESP, the highest compressive 28-day strength enhanced by about 12%, while the flexural strength improved by about 9% compared to mortars without ESP. In a more recent study, Abdulabbas [12] produced mortar specimens by replacing PC-Type I with 0, 5, 7.5, and 10 wt. % of 75 μm ESP powders. The fine aggregates passed through a sieve size of 2.36 mm and the w/c ratio was 0.45. The specimens were cured in water tanks until tested. The 28-day compressive strength of mortars containing 5 and 7.5 wt. % ESP, increased by 10 and 8%, respectively, but decreased to 23% when 10 wt. % ESP was substituted. Elevated temperature residual strengths on mortars containing natural or ESP limestone has not been studied to a great extent. For example, El-Kurdi et al. [13] investigated elevated temperature residual tests on concrete containing 10 and 15 wt. % natural limestone (<75 μm) replacements of PC. The specimens were heated at 20, 200, 400 and 600 $^{\circ}\text{C}$ (heating rate not reported) and held for 2 hours before cooling to room temperature. The residual compressive strengths reduced by 2, 5, 11 and 18% and 12, 23, 34 and 35 %, respectively, while the residual flexural strengths decreased for both 10 and 15 wt. % limestone replacements compared to concrete without limestone. The authors attributed the increased loss with limestone filler was due to the dilution of the cement.

In the event of a fire, it is helpful to understand the behaviour of fire damaged mortar/masonry used in general purpose applications. The goal of this study was to investigate the effect of ESP replacements in PC mortars submitted to elevated temperatures and residual properties evaluated. Initially, digital images and scanning electron microscopy (SEM) were used to understand the behaviour of ES in terms of color and interior membrane removal after heating

to elevated temperatures. The processed ESP was evaluated by thermo-gravimetric analysis (TGA) to detect if organic membranes remained on the ESP particles after a grinding and washing process. The mortar weight loss, porosity, residual compressive and flexural strengths were also studied. Given the unique composition and morphology of ESP, the outcome of this study may provide an alternative SCM derived from a waste product for the production of cement mortars.

2. Experimental program

2.1. Materials and mixtures

Mortar specimens were produced with and without ESP as PC replacements. Two batches of mortars were fabricated: mortars without ESP (M-0%) and mortars with 50% - /50% (white ESP - brown ESP) by weight of cement. The specimens were prepared from Portland cement CEM I 52.5 R CE CP2 NF with a density of 3140 kg/m^3 and Blaine surface area of $444.9 \text{ m}^2/\text{kg}$. Fine aggregates were natural washed semi-crushed siliceous-calcareous sand with a density of 2630 kg/m^3 . The sand fractions were 0/4 mm. The ESP was processed in a previous study [8] and sieved to a mesh size of $63 \mu\text{m}$ (65% under $63 \mu\text{m}$). Both white and brown ESP had density of 2500 kg/m^3 and the Blaine surface areas were 367 and $307 \text{ m}^2/\text{kg}$, respectively [8].

Specimens were table vibrated for better compaction and removal of entrapped air. Based on the DIN EN ISO 3262-5 [9] which outlines the categories for purities of CaCO_3 , eggshells in this study were between categories B and C with an average CaCO_3 contents of 96.9%, measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) [6]. The chemical characteristics of the white and brown eggshells have been characterized in a previous work [8] where CaCO_3 , chloride, sulphate and sulphur contents for white and brown eggshells were 98.3, 0.058, 0.034, 0.067% and 97.8, 0.033, 0.022 and 0.063%, respectively. All mortar compositions had PC replaced with ESP in amounts of 0, 5, 10 and 20 % by

weight (wt. %), using a water/(cement and ESP) ratio of 0.5. Table 1 provides details of the mixture proportions for the mortar with and without ESP.

Table 1. Mix proportions for mortar with different ESP additions.

Components (kg/m ³)	Percent of PC replacement (wt. %)			
	0	5	10	20
Cement	504	479	454	404
Eggshell powder (ESP)	0	25	50	101
Sand	1513	1513	1513	1513
Water	252	252	252	252
ESP (wt. % of component)	0	1.1	2.2	4.4

2.2. Eggshells and ESP heat treatments

2.2.1. Heating tests

Eggshells and ESP containing interior membranes were initially dried at 105°C for 24 hours followed by submitting to elevated temperature oxidation treatments of 150°C, 300°C, 450°C and 600 °C at a heating rate of 10°C/min in air using a Lindberg/Blue M box furnace. The initial and final weight for three samples of each configuration were averaged.

2.2.2. Digital image and scanning electron microscopy (SEM)

To visually understand the behaviour of ES and ESP during heating, digital photos were taken of the raw ES and ESP submitted to elevated temperatures from 20 to 600°C. In addition, SEM was used to investigate how the exterior and interior surfaces of eggshells are altered as they were heated from 20 to 600°C. The aim was to provide a better understanding of how eggshell membranes can be removed by oxidation treatments (calcined) at different temperatures. The lowest temperature for membrane removal would consume the least

energy. The eggshell surfaces were observed in an SEM operated at 10 kV. The samples were initially coated with a thin layer of gold prior to viewing.

2.2.3. Thermo-gravimetric analysis

The raw eggshells were processed by crushing, fine grinding and washing several times with tap water [8]. Thermal degradation of the ESP was conducted to determine if organic membranes remained on the ESP particles. The TGA experiments were carried out from 20°C to 500°C at a heating rate of 2°C/minute under nitrogen gas flow.

2.3. Cure condition and mechanical tests

Mortar prisms specimens with dimensions of 40 x 40 x 160 mm³ were cast. The samples were de-molded after 24 hours and placed in a water bath for 28 days of curing. After curing, the samples were removed from the water and allowed to surface dry prior to conducting the mechanical tests. Compressive and flexural strength tests were carried out on the prisms at room temperature using loading rates of 2.4 kN/s and 0.5 kN/s, respectively according to the NF EN 196-1 standard [14]. Three specimens were evaluated for each test and averaged.

2.4. Mortar heating-cooling tests

Specimens subjected to high temperatures were initially left at room temperature for three days prior to the heating test. Three mortar samples of each mix were subjected to various heating-cooling cycle from room temperature to 150°C, 300°C and 450°C. The heating rate was 2°C/minute with one hour of dwell temperature. The weight loss, porosity, residual compressive and flexural strengths were studied after cooling to room temperature. The porosity tests were carried out according to NF-P18-459 standard [15].

3. Results and discussion

3.1. Eggshells and ESP heat treatment

3.1.1. Digital images

Digital images of ESP and raw ES after oxidation treatments from 20 to 600°C in air are shown in Fig. 2. At 20°C, both ESP and ES are white in color as expected. As the temperature increased to 150°C, both ESP and ES begin to change to a pale yellow color. At 300°C, there is a more pronounced change to light brown for both ESP and EP where the organic membrane begins to breakdown/decompose. At 450°C, the membrane has calcined as noted by the black residue, while the dark gray is the remaining CaCO₃. Increasing the temperature to 600°C, both ESP and ES are dark gray with little remaining of the organic membranes.

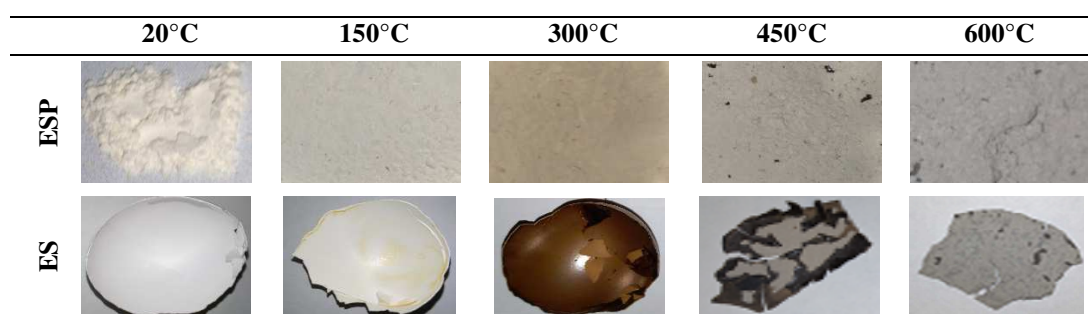


Fig. 2. Behaviour of eggshells powder (ESP) and eggshells (ES) after heating in air from 20-600°C.

Chemical analyzes was performed by Kumar et al. [16] on the ESP and showed it contained chemical compounds of CaO (60-67%), SiO₂ (17-25%), Al₂O₃ (3-8%), Fe₂O₃ (0.5-6%) and MgO (0.1-4%). In addition to these compounds possibly reacting at elevated temperature, such as silica (SiO₂), hematite (Fe₂O₃), and alumina (Al₂O₃) which often lead to the formation of brown or pinkish color at 300°C. Further chemical studies at each oxidation temperature are needed to better explain the reasons for color change.

Furthermore, changes in ESP resulted in shade modifications of mortar specimens after each heating. For example, Fig. 3 shows specimens M-0%, M-5%, M-10% and M-20% after heating-cooling cycles to 450°C. Compared to the dark gray M-0% and M-5% mortars, a slight color change occurred to light gray for mortars M-10% and M-20%. As illustrated in Fig. 2, when ESP was heated alone, variations in color were observed which may contribute more to color change when added to mortar in larger quantities. The addition of ESP in a

mortar mixture could be a drawback or find benefit where desired colors are required without the addition of pigments.

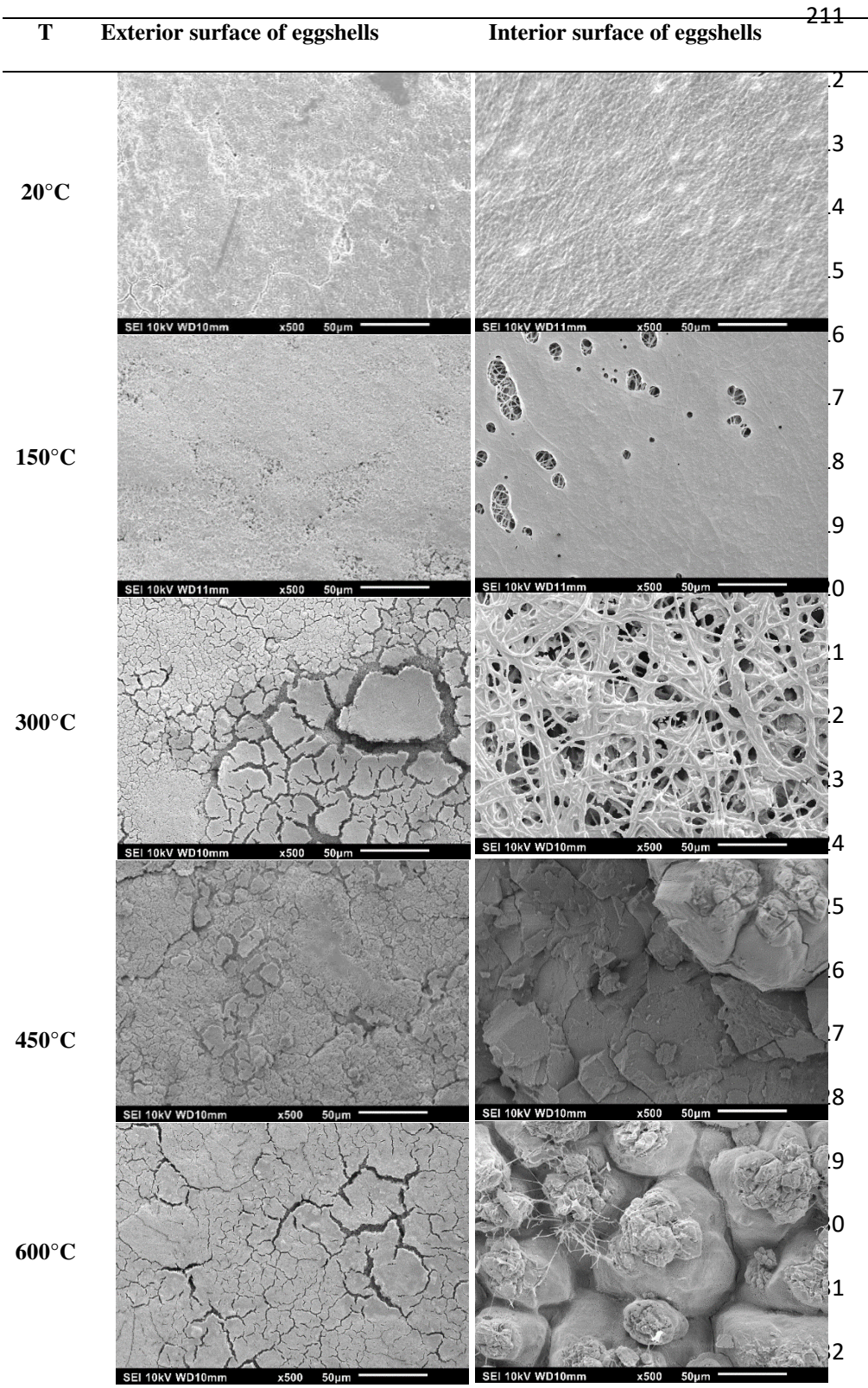


Fig. 3. Color change of mortar samples M-0%, M-5%, M-10% and M-20% when heated to 450°C.

3.1.2. Scanning electron microscopy

The gradual change of the eggshell structure for the exterior and interior surfaces during heating from 20-600°C are shown in Fig. 4. At 20°C, the cuticle layer is shown as the exterior surface which has a relatively rough and slightly porous appearance. Some microcracks are visible in the cuticle due to drying of the membrane. Similarly, the interior or inner membrane of the eggshells appears smooth with wart-like surfaces. At 150°C, the cuticle is still intact with its rough surface appearance. Very little thermal degradation was observed at this temperature on the exterior or interior surfaces. However, small pores begin to form on the exterior surface. Gradual, more pronounced changes of the ES surfaces are shown between 300-600°C. At 300°C, the cuticle is still visible with larger cracks as it is made of hydroxyapatite. Decomposition of hydroxyapatite occurs beyond 1250°C [17]. At this temperature, the entire inner membrane is removed since organic based materials have been reported to decompose around 240°C [18]. Below this membrane, a mesh of fibers are visible. These fibers are organic materials originating from collagen and organic proteins [19].

209
210



233 **Fig. 4.** Exterior and interior of a raw eggshells after heat treatment from 20-600°C.

The mammillary knobs can be faintly seen below this fibrous scaffold. At 450°C, the majority of fiber mesh has disappeared and the mammillary knobs are visible. At 600°C, the residual materials are the mammillary knobs and the palisade layer as observed by its porous structure. Such observations were also made by Tsuboi and Koga [20]. To remove the organic membranes in ES or ESP, the lowest heating temperature suggested from these results is 450 °C.

3.1.3. Thermo-gravimetric analysis

Thermal properties were investigated using TGA to determine if the interior membranes of the eggshells were removed during processing of the waste eggshells. TGA was conducted on three samples: processed ESP, ES containing an attached interior membrane and an ES with interior membrane physically removed. The results are shown in Fig. 5.

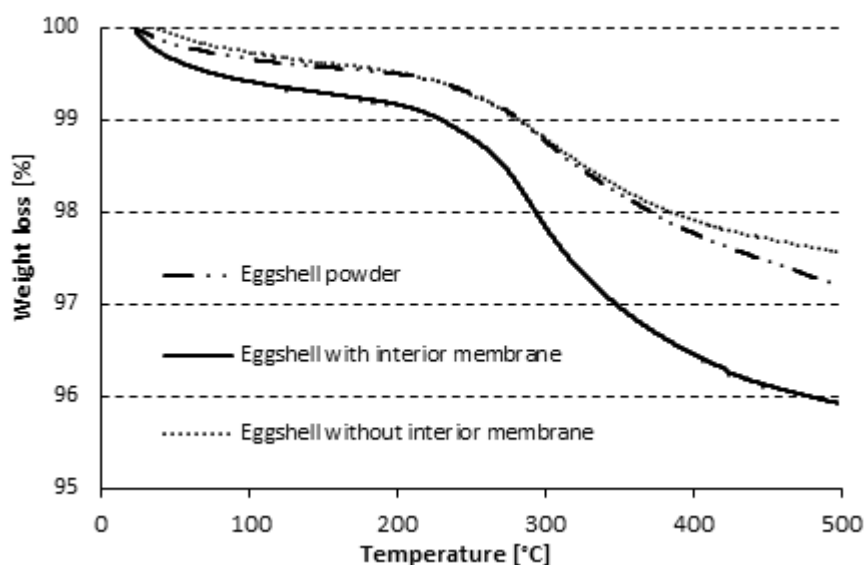


Fig. 5. TGA of eggshells powder and eggshells with and without interior membranes.

Two phenomena in weight loss occurred between the ESP, ES with membranes and ES without membranes. With ES containing the interior membrane, the weight loss takes place in three phases. A first phase occurs from room temperature up to the temperature of 100°C and is characterized by a rapid removal of water adsorbed on the surface or in the pores of the outer and inner membranes. The second phase shows a progressive decrease in weight loss of

about 1% up to the temperature of 200-250°C. Beyond this temperature, the weight loss becomes greater and reaches 4% at a temperature of 480°C. This behaviour corroborates the analyzes of images made on eggshells containing the membranes. For example, at 150°C the SEM images (Fig. 4) showed the inner membrane beginning to decompose while the digital images in Fig. 2 showed the eggshells color change to a pale yellow. At 300°C, the SEM image shows the inner membrane vanished with possible initial breakdown of the outer membrane. In addition, the digital images show a drastic color change of the eggshells to light brown which explains the decomposition phase accompanied by a rapid loss of material and its combustion. Analyzes of the ESP and ES without the interior membrane showed a similar deterioration up to 360°C. The weight loss of the two materials can be grouped into two phases. The first corresponding to a gradual decline to 250°C which corresponds to a 0.75% weight loss similar to the eggshells containing the interior membranes. Above 250-300°C, the weight loss is much lower than that with the attached interior membranes which indicates the processed ESP contained minimal membranes. As shown in Fig. 3, above 450°C, only the layers making up the calcified shell skeleton remain. At the temperature of 500°C, the weight loss of ESP and ES without the interior membrane is 2.8% and 2.5%, respectively. This difference could be attributed to the presence of organic matter in the eggshells.

3.1.4. Eggshells oxidation treatments

To better understand the weight loss phenomenon of ESP mortars at elevated temperatures oxidation experiments on ESP and ES containing interior membranes were carried out at 150, 300 and 450°C. Small weight losses were noted for ES with interior membranes ($1.4\% \pm 0.4$) and ESP ($0.9\% \pm 0.3$) after heating to 150°C. These weight losses can be attributed to a departure of free and bound water contained in the materials. The ES with interior membranes had a greater loss due to the higher water content of the organic membranes. Fig. 2 shows both ESP and ES with interior membranes at 20°C and 150°C where the color changed from

white to pale yellow for both materials which suggests the beginning of the decomposition phase. At 300°C and 450°C, ES with interior membranes ($2.7\% \pm 0.8$ and $7.8\% \pm 1.8$) lost two and three times more weight than the ESP ($1.2\% \pm 0.5$ and $3.0\% \pm 0.3$), respectively. The results showed the processing method of crushing, grinding and rinsing with water was able to remove the majority of organic membranes, but heating the ES or ESP would provide repeatable conditions. In a related study, Intharapat et al. [21] showed a weight loss of 3% for crushed eggshells heated between 250°C to 380°C. The authors suggests the loss was the result of decomposition of the organic matter. Interestingly, eggshells contains about 97% CaCO_3 and 3% organic matter [6].

3.2. ESP mortar heating-cooling tests

3.2.1. Mortar weight loss

Fig. 6 shows the evolution of weight loss for mortars with increase in temperature. The results showed mortars containing 0, 5, 10 and 20 wt. % ESP had a progressive loss in weight as the temperature increased. After heating from room temperature to 150°C, a higher weight loss for M-10% and M-20% mortars was observed (+1.5% on average) compared to M-0% and M-5% mortars. Eggshells are naturally porous. Bashir and Manusamy [22] viewed ESP particles using SEM. They observed the ESP particles had high porosity which were concluded to be integral to the eggshells structure and are used for gas exchange of the embryo. Higher contents of ESP (M-10% and M-20%) in the mortars would tend to absorb more water due to the porous structure of the ESP. The increased physical adsorbed surface and/or pore water can explain the important weight loss at 150°C for M-10% and M-20% mortars. Beyond 150°C, the weight loss varies very little between the different mortars due to the evaporated water. Mortars M-5%, M-10% and M-20% contained PC replacements of ESP of 1.1, 2.2 and 4.4% (wt.% of mortar component), respectively as given in Table 1. Between 200-450 °C, the calcium silicate hydrate (CSH gel), the main hydration product of PC begins

to decrease due to dehydration [23]. The outcome of heating ESP at temperatures of 150, 300 and 450°C showed the greatest weight loss when heated to 450°C on the order of 3.1%. This corresponds to about 0.1% weight loss for the M-20% mortar compared to the M-0% mortar. The small reduction in weight due to ESP additions into the mortar was not significant.

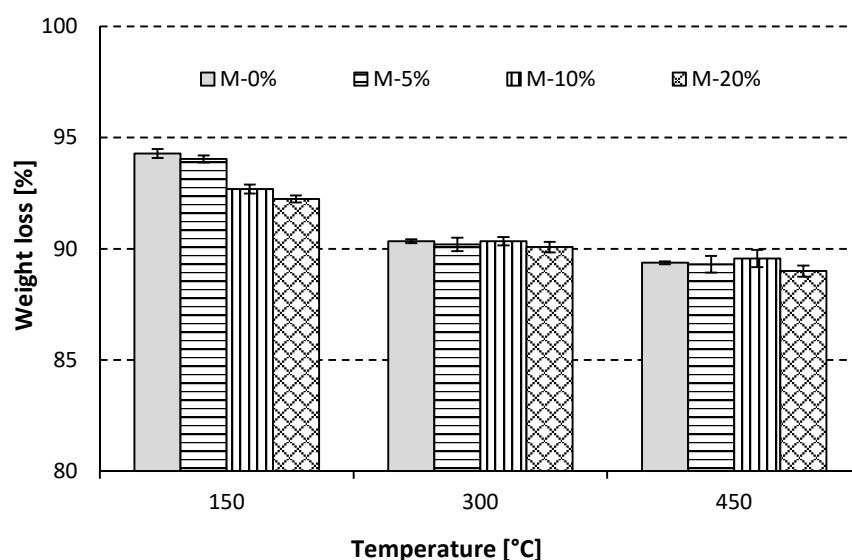


Fig. 6. Evolution of the weight loss (from 0 to 20%) according to the heating temperature.

3.2.2. Mortar specimen porosity

Fig. 7 shows the porosity evolution of the mortars with and without ESP as a function of temperature. The porosity of mortars containing ESP varied little compared to that of mortars without ESP at 150°C. The small variation in porosity showed ESP had a low impact on the cement matrix. Although there was a significant weight loss for mortars M-10% and M-20% when heated to 150°C as shown in Fig. 6, the porosity was not affected due to the interior membranes not fully decomposed at this temperature as illustrated in Fig. 4. At 300°C the ESP mortars had slightly higher porosity than M-0% mortars due to decomposition of the interior membranes. The removal of the membranes with heat is presumed to have generated small spaces/pores between the ESP particle interface and cement paste. At 450°C, the additional porosity of all mortars were relatively small and considered equivalent which can be attributed to further breakdown of the PC. During hydration of the PC paste, the reaction

products responsible for strength are calcium silicate hydrate (C-S-H) gel and to a lesser extent portlandite or calcium hydroxide (CH). It has been reported C-S-H begins dehydration at 105°C and its deterioration becomes more important between 200-300°C, while CH begins dehydration around 400°C and completely decomposes at 600°C [24]. In a related study, PC pastes were submitted to elevated temperatures where an increase in the percentage of pores occurred in the temperature range of 300-500°C. The authors concluded both decomposition of hydration products and changes in pore structure influenced the increased porosity [25].

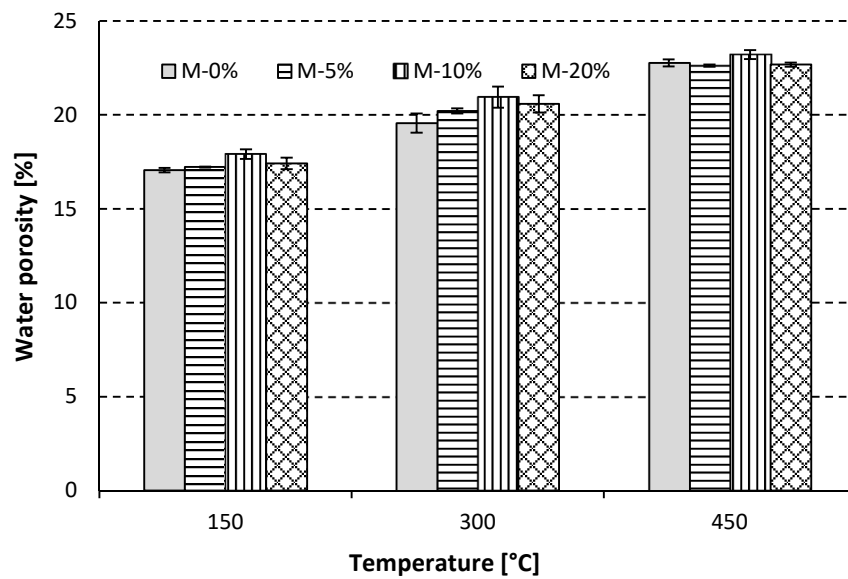


Fig. 7. Evolution of water porosity with temperature for M-0%, M-5%, M-10% and M-20% mortars.

3.2.3. Compressive strength

Fig. 8 shows the evolution of compressive strength as a function of temperature for M-0%, M-5%, M-10% and M-20% mortars.

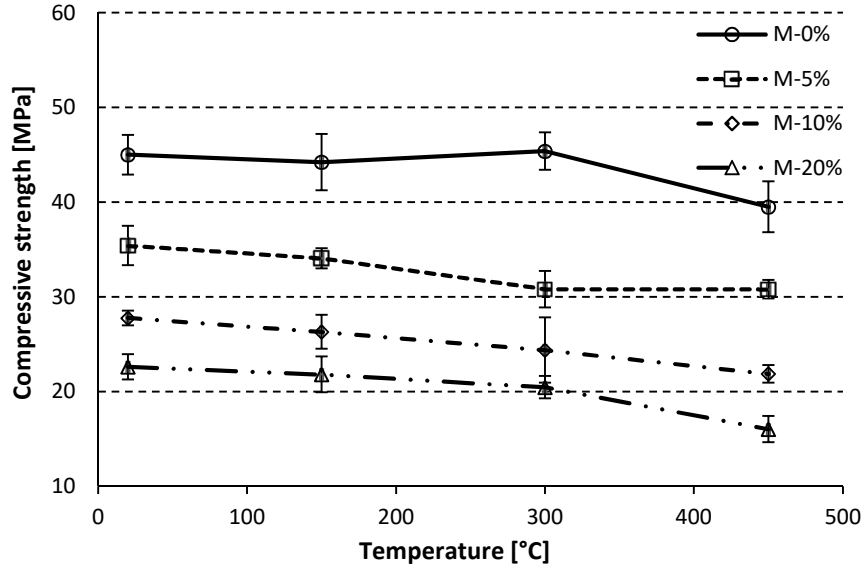


Fig. 8. Evolution of residual compressive strength with temperature.

3.2.3.1 Unheated compressive strength

The compressive strength of M-0%, M-5%, M-10% and M-20% mortars at room temperature was $45.0 \text{ MPa} \pm 2.2$, $35.4 \text{ MPa} \pm 2.1$, $27.8 \text{ MPa} \pm 0.8$ and $22.6 \text{ MPa} \pm 1.3$, respectively. The unheated mortars containing ESP decreased in compressive strength as the ESP percent replacement increased. For example, compared to mortars without ESP, the ESP mortars declined on average from 21% to 50% for replacement proportions ranging from 5 to 20 wt.%, respectively. Studies previously conducted by Pliya and Cree [8] have shown unheated room temperature compressive strengths of ESP mortars decreased in the range from 14% to 54% using the same replacement proportions. The reductions in strength due to substitution of ESP for PC may be ascribed to the irregularity of morphology and size distribution of ESP particles which may be related to the ESP powder manufacturing method. This irregularity can have an impact on distribution and adhesion between the cement matrix, the fine aggregates and the ESP particles. El-Hawary and Nouh [26] suggested mechanical properties could be improved by increasing the filler fineness, when limestone was added to concrete as a filler. Additionally, the amount of limestone filler replacement and particle size were found to have negative effects on the compressive strength of concrete [27]. Although the unheated

compressive strengths reduced with the addition of ESP, the additions of 5-20 wt. % ESP produced 28-day compressive strengths above 17.2 MPa, a value specified for mortars according ASTM C270 [10]. Decreasing the particle size closer to the PC of about 20 μm in a planetary ball mill may improve the particle shape and consistency. The porosity measurements in Fig. 7 suggested the mortars heated to 150°C (still containing majority of the organic membranes) had similar permeabilities for each mortar composition. The drop in compressive strength is therefore not linked to the presence of large pore volumes due to the increased porosity from removal of evaporable water, but rather from an interaction between the ESP particles and the cementitious matrix-aggregates. The presence of organic matter in eggshells could play an important role in lowered strengths. However, a study conducted at room temperature investigated ground waste seashells in mortars and did not find any adverse effect in strength requirements due to the organic materials, but suggested smaller particles have more surface area to improve the filling effect in PC paste [5]. Limestone is an inert material and does not have pozzolanic properties, rather natural limestone was determined to densify the interfacial area between aggregates and cementitious matrix and improve the performance of concrete [28]. Similarly, ESP has a high CaCO_3 content and therefore would fall into the category of limestone as an inert SCM material without pozzolanic properties.

3.2.3.2. Residual (after heating) compressive strength

In the same way as unheated specimens, when mortars were heated, a gradual decrease in compressive strength was noticed for mortars with or without ESP at all temperatures studied as shown in Fig. 8. After heating to 150°C, the loss of strength in mortars without ESP was below 2% compared to the room temperature strength, while mortars with ESP had a slight loss in residual compressive strength of 4-5% compared to its unheated strengths. At a temperature of 300°C, the mortar without ESP retained its initial strength and slightly increased by 1%. However, ESP mortars lost on average 11% of their initial compressive

strengths. Compared to the strengths at 20°C, the effect of varying the ESP replacement rate was not remarkable. At temperatures of up to 300°C, internal autoclaving, a phenomenon which hydrates non-hydrated cement particle due to the formation of steam acts to increase the compressive strength of PC paste [24]. At 300°C, the residual strength of M-0% improved since it contained only PC, while internal autoclaving did not appear to occur for mortars containing ESP possibly due to the reduced content of PC. At a temperature of 450°C, the loss of strength of the mortars M-0%, M-5%, M-10% and M-20% was 12%, 13%, 21% and 29%, respectively compared to the control specimen. Mortars M-0% and M-5% had similar strength losses, while the replacement rate effect became noticeable above 10% replacements. The loss of strength at 450°C is strongly related to the decomposition of C-S-H and CH in the PC matrix. For example, the M-0% mortar had a sharp drop in strength from 300 to 450°C compared to the ESP mortars. This severe decrease in strength was not observed for M-5%, M-10% and M-20% mortars possibly due to the reduction of PC in the mortars.

3.2.4. Unheated and residual flexural strength

The evolution of flexural strengths as a function of temperature for M-0%, M-5%, M-10% and M-20% mortars are provided in Fig. 9.

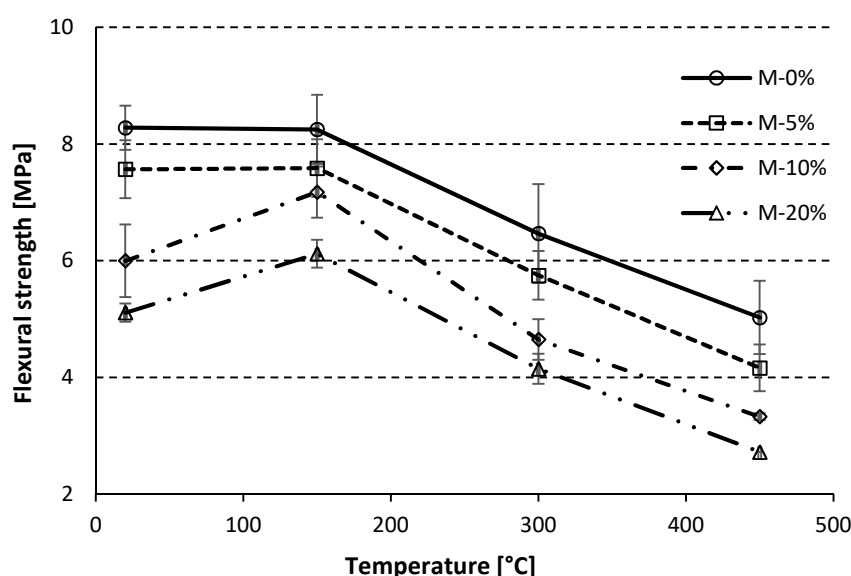


Fig. 9. Evolution of residual flexural strength with temperature.

At room temperature, the unheated flexural strengths varied with degree of ESP replacement. The flexural strength of M-0%, M-5%, M-10% and M-20% mortars was $8.3 \text{ MPa} \pm 0.4$, $7.6 \text{ MPa} \pm 0.5$, $6.0 \text{ MPa} \pm 0.6$ and $5.1 \text{ MPa} \pm 0.3$, respectively. Decreases in strength varied from 8% to 39% for replacement ratios of 5 to 20 wt.%, respectively compared to the mortar without ESP. The residual strength of mortars after being submitted to 150°C , were not affected for M-0% and M-5% and remained identical to the room temperature strengths. For M-10% and M-20%, the residual strengths were higher than the room temperature strengths by 20%.

Beyond 150°C , a progressive decrease in strength was observed. At 300°C M-0%, M-5%, M-10% and M-20% had residual strength reductions of 22%, 24%, 22% and 20% respectively. At 450°C , the ESP mortars lost an average 6% compared to mortars without ESP which suggests the flexural strength loss of ESP mortar at 450°C was not strongly related to the ESP replacement rate. The decomposition of the membrane in the ESP powder may play an important role in the strength drop beyond 150°C for flexural specimens.

4. Conclusion

The goal of this study was to investigate the effect of ESP replacements in PC for mortar samples submitted to high temperature. Various investigations have been conducted on ES and ESP to better understand and explain the behavior of heated mortar specimens. Several conclusions could be made from this study:

- As observed in the digital images, ES and ESP were heated at different temperatures and the results showed their decompositions were accompanied by color changes. These color changes were also observed on the surface of heated mortars specimens. Heated ESP should not be thought of as a disadvantage, but could find benefit in mortars where desired colors are required without the addition of pigments. Further

studies are needed to identify the reasons for color change at different elevated temperatures.

- SEM analyzes of the exterior and interior surfaces from room temperature to 600°C showed gradual thermal degradation. Heating waste eggshells to 450°C would allow the organic membrane to be removed prior to crushing and grinding into powder form without changing the composition of CaCO_3 .
- TGA results at 500°C showed 3-4% weight loss which was attributed to the organic membranes of the eggshells. Up to about 500°C, the ES and ESP without interior (inner) membrane have similar weight losses which signified the manual method used for crushing, grinding and washing/rinsing ESP was able to remove a majority of the membranes. An industrialized process would improve the membrane removal process.
- At all elevated temperatures, the residual porosity of mortars containing various amounts of ESP was similar to mortars without ESP.
- The compressive strengths at room temperature for M-5%, M-10% and M-20% mortars decreased by 21%, 38 % and 50%, while the flexural strengths were reduced by 8%, 28% and 39% , respectively compared to the control (M-0%) samples. The lowest strength loss was with 5 wt. % of ESP. Although the use of ESP in mortar had a slightly negative effect on the compressive strengths, the strength requirements were higher than those required by ASTM standard even with 20 wt. % ESP.
- The residual compressive strength of the mortar without ESP increased in strength by 1%, but decreased by 9-13% for mortars containing ESP. The internal autoclaving effect may have been disrupted due to the lower amount of PC in the ESP mortars. Heating to 300°C, the residual flexural strength losses were similar for mortars with and without ESP having decreased by 20-24%. To improve the overall mechanical

properties it is suggested to decrease the ESP particle size in a planetary ball mill to smaller than 63 μm which may improve the particle shape and consistency.

- Utilization of waste eggshells in masonry finds benefit as an alternative construction material. The goal of using ESP in mortar is not to entirely replace limestone derived from rocks but divert discarded eggshells from landfills.

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