

CREATION OF A POZZOLANIC MATERIAL FROM WASTE CALCIUM HYDROXIDE AND RECYCLED GLASS POWDER

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Abstract

The use of consumer and industrial waste as supplementary cementitious materials is one solution to the development of sustainable Portland cement. This research studied the partial replacement of cement with a pozzolanic mixture of recycled soda-lime glass powder (GP) and waste calcium hydroxide (CH). The optimal weight ratio of CH and GP was selected from five ratios between 30/70 to 70/30 (CH/GP), using thermal gravimetric analysis and X-ray diffraction. It was found that CH deficient ratios contained residual glass powder, while CH rich ratios contained residual calcium hydroxide and had undesirable carbonation of the CH. The 60/40 pozzolan was selected due to the large amount of calcium silicate hydrate (C-S-H) gel that was formed, the absence of residual GP and a minimum of excess CH. Portland cement (PC) specimens with 20 to 40 wt.% replacement by the 60/40 pozzolan were characterized for porosity and compressive strength at aging times from 3 to 28 days. The PC with 20 to 40 wt.% pozzolan had slightly increased porosity due to an increased amount of unreacted water from the batch. The porosity decreased with increased aging time. The PC with 30 wt.% pozzolan had a compressive strength equal to the reference PC, but only after 7 days or longer of aging. This was likely due to the slower reaction rate of the pozzolan. The 60/40 CH/GP pozzolan appears to be a viable partial replacement for PC when used at 30 wt.%.

Keywords: Cement Replacement, Pozzolan, Recycled Glass, Waste Calcium Hydroxide

Introduction

Portland cement is used extensively in the modern world. It is a primary constituent of the concrete used for the construction of homes and commercial buildings, and infrastructure such as roads, bridges and dams. The manufacturing of cement is estimated to contribute 6 to 7% of the global emissions of carbon dioxide (CO₂), a potent

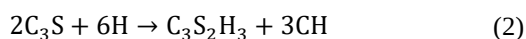
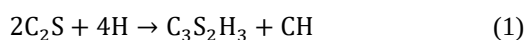
greenhouse gas (Imbabi *et al.*, 2012; Aprianti, 2017). With the ever-increasing demand for cement, there is interest in trying to reduce the environmental impact of cement manufacturing. At the same time, the ever-increasing demand for goods and materials leads to increased consumer and industrial wastes, much of which does not see

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significant utilization. Due to their amenable chemistries, several of these waste materials, such as fly ash and furnace slags, are suitable for use as cement replacement materials also called supplementary cementitious materials or SCMs (Paris *et al.*, 2016). As such, there is an intersection of interests with regards to the green, sustainable usage of cement and the utilization of chemically compatible waste materials.

The primary chemical phases of Portland cement include dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$ or C_2S in standard cement notation), tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$ or C_3S), tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$ or C_3A), and tetracalcium aluminoferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ or C_4AF). These phases undergo chemical hydration reactions when mixed with water and the resulting hydrates bind the other components together to produce a strong, solid material (Aïtcin, 2000). On average, ordinary Portland cement or OPC is composed of approximately 63 wt.% C_3S and 16 wt.% C_2S with the remainder being C_3A , C_4AF , and other phases such as free CaO . The hydration products of C_3S and C_2S are therefore of primary importance to the properties of Portland cement. The hydration of the C_2S and C_3S phases in cement create a calcium silicate hydrate ($x\text{CaO}\cdot y\text{SiO}_2\cdot z\text{H}_2\text{O}$ or C-S-H) gel, which binds the cement and increases its strength with aging time (Sprung, 2008). Calcium silicate hydrate has an undefined stoichiometry and is usually amorphous when first formed, crystallizing with time. It may be represented theoretically as $3\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$ or $\text{C}_3\text{S}_2\text{H}_3$. The chemical reaction of C_2S with water (H_2O or H) to form $\text{C}_3\text{S}_2\text{H}_3$ is shown in Equation (1) in the standard cement notation. The chemical reaction of C_3S with water to form $\text{C}_3\text{S}_2\text{H}_3$ is shown in Equation (2). In addition to the formation of $\text{C}_3\text{S}_2\text{H}_3$, both reactions also generate calcium hydroxide ($\text{Ca}(\text{OH})_2$ or CH).



Portland cement is produced by the high temperature calcination of natural raw materials, such as limestone, clay, and shale. The output is a calcined cement clinker, which is milled to produce a fine cement powder. A major use of Portland cement is in mortar and concrete, both of which are used in the construction industry. Mortar is a combination of cement, water, and a fine aggregate, such as powdered limestone or sand. Concrete is a combination of cement, water, fine aggregate and coarse aggregate, such as crushed

stone. The use of these aggregates improves the mechanical properties as well as decreases the overall cost of the final mortar and concrete because less of the costlier cement is used. Due to the high demand for mortar and concrete in construction and the sometimes-limited quantities of naturally available aggregates, alternative aggregates have been sought. Several researchers (Rana *et al.*, 2016; Silva *et al.*, 2018) have studied synthetic aggregates, made from various industrial wastes and recycled materials. Though, it's been stated that the use of pozzolan waste materials can be more cost effective when used as cement replacement rather than as aggregate (Paris *et al.*, 2016).

In a mortar or concrete mix, a secondary set of pozzolan reactions can occur between silica (SiO_2 or S) and calcium hydroxide ($\text{Ca}(\text{OH})_2$ or CH) which also results in the formation of calcium silicate hydrate and further contributes to the long-term strength development of the cement. The calcium hydroxide is produced from the prior hydration reactions of C_2S and C_3S , shown in Equations (1) and (2). An example (Appa Rao, 2003) of an important pozzolan reaction between silica and calcium hydroxide, which produces $\text{C}_3\text{S}_2\text{H}_3$, is shown in Equation (3).



Therefore, there is also interest in the use of pozzolans, materials containing chemically reactive silica, in mortar and concrete mixes. Pozzolans can partially replace Portland cement and increase the strength of the concrete (Paris *et al.*, 2016), as well as reduce the cost of the concrete. Pozzolans can come from several different sources, both natural and synthetic, including the ashes produced from organic waste products such as rice husk and sugar cane bagasse (Aprianti, 2017), industrial waste products, such as metal furnace slags (Imbabi *et al.*, 2012), municipal incinerator ashes (Pan *et al.*, 2008) and recycled glass (Du and Tan, 2014; Mohajerani *et al.*, 2017). However, in comparison to the hydration reactions of Portland cement, pozzolan reactions are generally slower to initiate and progress. As such, mortars and concretes blended with pozzolans can take longer to achieve full property development.

Any of the remaining unreacted calcium hydroxide in the cement or pozzolan can be transformed into calcite (CaCO_3 or $\text{C}\bar{\text{C}}$) by a carbonation reaction (Papadakis *et al.*, 1992) with carbon dioxide (CO_2 or $\bar{\text{C}}$) as show in Equation (4).



The carbonation of calcium hydroxide in steel reinforced concrete has been found to lead to corrosion of the steel reinforcements, with an accompanying degradation of the mechanical properties. Although it is often viewed as an undesirable reaction, carbonation may offer some benefits in unreinforced concrete (Šavija and Luković, 2016).

Just as with the aggregates, due to the finite limits of the required natural resources and the potential for reduced cost, as well as now the environmental concerns of greenhouse gas emissions (Imbabi *et al.*, 2012; Paris *et al.*, 2016; Aprianti, 2017), it is desirable to identify supplementary cementitious materials (SCMs), such as pozzolans, as alternatives too or as partial replacements for Portland cement. Bottom ash and fly ash, both of which contain various amounts of silica, calcia (CaO), alumina (Al₂O₃) and ferric oxide (Fe₂O₃), have been studied as cement replacement materials due to their amenable chemistries. Recycled glass that has been pulverized into a powder has also been used to partially replace cement. It should be noted that amorphous silica, such as found in glass, was reported to have a higher pozzolanic reactivity when compared with crystalline forms of silica, such as quartz (Baltakys *et al.*, 2007).

For a Portland cement and pozzolan blend, the pozzolanic reaction typically begins in the later stages of the cement aging process, approximately half a day or longer, after the formation of calcium hydroxide has occurred (Beaudoin and Odler, 2017). In this research, a pozzolanic reaction was designed to begin from the start of the cement aging process, by the direct addition of calcium hydroxide. This research aimed to partially replace Portland cement with a mixture of waste calcium hydroxide and recycled glass powder. A pozzolanic reaction between the waste calcium hydroxide and recycled glass powder was expected to occur, leading to the production of calcium silicate hydrate and setting behavior similar to that of pure Portland cement.

Despite the many investigations of pozzolanic reactions involving waste calcium hydroxide and glass powder separately, there has been limited research (Consoli *et al.*, 2019) on waste calcium hydroxide combined with recycled glass powder as a pozzolanic mixture to partially replace Portland cement. To determine the potential amount of cement that could be replaced, the optimum ratio of waste calcium hydroxide to recycled glass powder was first studied. With the optimum ratio determined, the replacement of Portland cement with increasing amount of waste calcium hydroxide and recycled glass powder in the optimum ratio was

studied through the changes in measured strength and the water absorption values.

Materials and Methods

Materials and Specimen Preparation

Waste calcium hydroxide was obtained from the Thai Acetylene Co., Ltd., in the form of a wet, granular material. This particular type of calcium hydroxide, a waste byproduct from the production of acetylene gas, is often referred to as carbide lime or calcium carbide residue. It was dried in an oven at 105°C for 3 hours, to remove the free water, and screened through a #200 mesh sieve (~75 µm) before use. The recycled glass powder was prepared from discarded green-colored glass drink bottles, which were obtained locally. The bottles were cleaned of any residue, crushed into mm sized pieces and then wet ball milled to produce a powder. The powder was dried in an oven at 105°C for 2 hours and screened through a #270 mesh sieve (~53 µm) before use. A glass powder particle size of 75 µm or less was reported to make it a more reactive pozzolan (Jiang *et al.*, 2019) and also mitigate swelling due to the possible alkali-silica reaction (ASR) (Mohajerani *et al.*, 2017). Portland cement (SCG Portland Cement Type 1) and clean river sand suitable for cement making were both obtained locally.

Pozzolan test specimens were prepared by mixing the calcium hydroxide (CH) and glass powder (GP) in the ratios of (CH/GP) 70/30, 60/40, 50/50, 40/60, and 30/70 by weight. A weight ratio of 0.6/1.0 water to CH/GP powder was used. A reference Portland cement specimen was also made. Table 1 shows the batch compositions of the test specimens. The reference Portland cement is referred to as reference PC and the pozzolan specimens are referred to by their CH/GP ratios of 70/30, 60/40, 50/50, 40/60, and 30/70. The CH/GP powder compositions were mixed with the required water and cast into steel molds, to produce pozzolan test specimen cubes with dimensions of 5x5x5 cm. The test specimens were aged for 14 days under ambient conditions of approximately 28°C and 75% RH.

The batch compositions of Portland cement mortar (PCM) test specimens containing 0, 20, 30 and 40 wt.% of the 60/40 CH/GP pozzolan replacement are shown in Table 2. The PCM specimen containing 100 wt.% PC with 0 wt.% pozzolan is referred to as reference PCM, while the PCM specimens containing 20, 30 and 40 wt.% pozzolan replacing the PC are referred to as PCM20, PCM30 and PCM40, respectively. The composition used 1 part cement to 2.75 parts of sand by weight.

A 0.485/1.0 water to cement weight ratio was used. The cement/sand and water/cement ratios follow the composition outlined in ASTM C311 (ASTM, 2005). The powders were blended, mixed with the required amount of water and cast into steel molds to produce 5x5x5 cm cement specimen cubes. The specimens were aged for 1 day, removed from the mold and submerged in water for the remainder of the aging time. The cement specimens were aged for 3, 7 and 28 days before testing.

Characterization and Testing

The chemical compositions of the starting materials were analyzed using a wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometer (Bruker, Model S4 Explorer). An X-ray diffractometer (XRD) (Bruker, Model D8 Discover) was used for material and test specimen phase identification. The particle size distribution of the milled glass powder was analyzed with a laser diffraction particle size analyzer (Malvern Instruments, Model Mastersizer S). The surface area of the glass powder was determined by the gas sorption technique (Quantachrome, Model Autosorb 1 MP). A thermal analysis of the test specimens up to 800°C was performed by combined thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Perkin Elmer, Model Diamond TG/DTA). The compressive strengths of the test specimens were measured using a universal test machine (UTM) according to ASTM C109 (ASTM, 2007). The water absorption (A) and porosity (P) of the test specimens were determined by the water immersion technique in accordance with ASTM C642 (ASTM, 2006), using Equations (5) and (6), respectively.

$$A (\%) = \left(\frac{W_{\text{sat}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100 \quad (5)$$

$$P (\%) = \left(\frac{W_{\text{sat}} - W_{\text{dry}}}{W_{\text{sat}} - W_{\text{sus}}} \right) \times 100 \quad (6)$$

Where W_{sat} is the specimen saturated weight (g), W_{dry} is the specimen dry weight (g), and W_{sus} is the specimen suspended weight (g).

Results and Discussion

Starting Material Characterization

The chemical composition of the waste calcium hydroxide and recycled glass powder, as determined by XRF, are shown in Table 3. The results are reported as the stoichiometric oxides of the detected elements. The waste calcium hydroxide was found to be composed mainly of calcium and contained minor amounts of silicon and aluminum. As shown in Figure 1, the XRD pattern of the waste calcium hydroxide was matched with the JCPDS patterns of calcium hydroxide ($\text{Ca}(\text{OH})_2$; JCPDS #44-1481) and a minor amount of calcite (CaCO_3 ; JCPDS #5-586). Hydrogen and carbon are typically undetectable by XRF, but they can be identified with XRD if they are part of a crystalline phase, such as calcium hydroxide. The calcite was a result of the calcium hydroxide having been exposed to air, which contains carbon dioxide, as shown in Equation (4). It would be impractical to store the waste calcium hydroxide in an inert atmosphere, so the presence of a minor amount of calcite would be expected. The silicon and aluminum seen in the

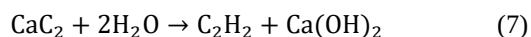
Table 1. Batch compositions of pozzolan specimens made with waste calcium hydroxide and recycled glass powder

Specimen	Calcium Hydroxide		Glass Powder		Water (ml)	Portland Cement (g)
	(wt. %)	(g)	(wt. %)	(g)		
CH/GP Ratio	30/70	30	60	70	140	120
	40/60	40	80	60	120	120
	50/50	50	100	50	100	120
	60/40	60	120	40	80	120
	70/30	70	140	30	60	120
Reference PC	-	-	-	-	140	200

Table 2. Batch compositions of Portland cement mortar specimens with partial cement replacement by the 60/40 pozzolan

Specimen	Replacement Amount (wt. %)	Portland Cement		CH/GP Mix		Sand (g)	Water (ml)
		(wt. %)	(g)	(wt. %)	(g)		
Ref. PCM	0	100	500	-	-	1,375	242
PCM20	20	80	400	20	100	1,375	242
PCM30	30	70	350	30	150	1,375	242
PCM40	40	60	300	40	200	1,375	242

XRF results were not observed in any phases detected by XRD, which indicated that they were contained in very minor amounts. The respective oxides of silicon and aluminum, silica (SiO_2) and alumina (Al_2O_3), are common impurities found in quick lime (CaO) (Kenny and Oates, 2012; Holzrichter *et al.*, 2013). Quicklime is used to make calcium carbide (CaC_2), a raw material for acetylene (C_2H_2) gas production. The production of acetylene gas, shown in Equation (7), generates waste calcium hydroxide, which retains the silica and alumina impurities from the original quicklime.



The composition of the recycled glass powder, Table 3, was found to be mainly composed of silicon dioxide (69.50%), sodium oxide (13.50%) and calcium oxide (11.50%). Minor amounts of alumina, magnesium oxide (MgO) and ferric oxide (Fe_2O_3) were detected, which are also typically found in soda-lime-silicate container glass compositions (Shelby, 2005). The sodium is the alkali element of concern with regards to the alkali-silica reaction (ASR). As previously mentioned, if the glass powder is kept to a small particle size, swelling and cement failure due to ASR can be mitigated. The glass also contains calcium which may contribute to the pozzolanic reaction of the glass powder, however it was not considered in this research. The recycled glass powder was prepared by crushing and wet ball milling. The specific surface area of the milled glass powder was measured as $1.42 \text{ m}^2/\text{g}$. The particle size distribution of the glass powder is shown in Figure 2. The particle size distribution ranged from 1 to $50 \mu\text{m}$, with the average particle size measured as $14.05 \mu\text{m}$. The particle size characteristics of the glass powder used in this research are comparable to glass powders studied by Shao *et al.* (2000) and Wattanapornprom and Stitmannaitum (2015), also for use as a pozzolan for partial cement replacement.

Table 3. Chemical composition of the waste calcium hydroxide and recycled glass powder as analyzed by XRF

Oxide	Calcium Hydroxide (wt.%)	Glass Powder (wt.%)
CaO	83.000	11.500
SiO_2	2.800	69.500
Al_2O_3	0.893	2.200
SO_3	0.195	0.082
Fe_2O_3	0.143	0.599
MgO	0.118	1.220
SrO	0.039	-
Na_2O	-	13.500
K_2O	-	0.553
Cr_2O_3	-	0.337
Total ^a	87.188	99.491

^a Excludes undetectable chemicals

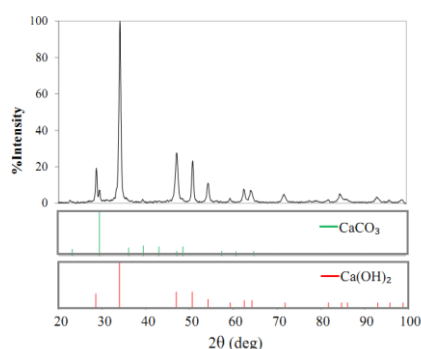


Figure 1. XRD pattern of the prepared waste calcium hydroxide

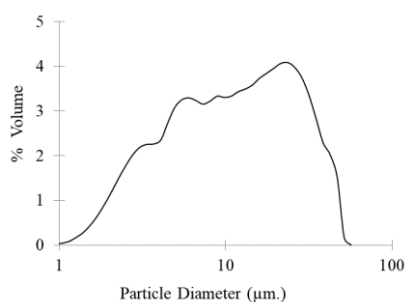


Figure 2. Particle size distribution of the recycled glass powder after sieving

Determination of Calcium Hydroxide and Glass Powder Mixing Ratio

Pozzolan specimens were made with five ratios of waste calcium hydroxide (CH) and recycled glass powder (GP), as shown in Table 1. The pozzolan specimens were aged for 14 days and then analyzed using XRD, TGA and DTA. A reference Portland cement (PC) specimen that was 100 wt.% PC was also made for comparison purposes. Figure 3 shows the collected XRD patterns of the five pozzolan specimens and the reference PC.

The XRD patterns of the pozzolan specimens were all very similar looking. The patterns were matched with the phases of calcium hydroxide (Ca(OH)_2 : JCPDS #44-1481), calcite (CaCO_3 : JCPDS #5-586) and tobermorite ($\text{Ca}_5(\text{Si}_6\text{O}_{16})(\text{OH})_2 \cdot 4\text{H}_2\text{O}$: JCPDS #89-6458), a crystalline form of calcium silicate hydrate. The 30/70, 40/60 and to a lesser extent the 50/50 specimen displayed a characteristic amorphous hump between 20° and 40° 2θ due to the presence of unreacted glass powder. The 60/40 and 70/30 specimens showed no amorphous hump, indicating that the glass powder was potentially fully reacted,

but certainly in a minor amount below the detection limit of XRD. The 70/30 specimen showed the highest peak intensity of calcium hydroxide, as the amount of calcium hydroxide added was more than required to fully react the glass powder. In addition to calcium hydroxide, calcite and tobermorite, several minor phases were also found in the reference PC specimen, which were not detected in the pozzolan specimens. The phases were unidentified, but were likely unhydrated clinker phases such as alite (C_3S) and belite (C_2S) (Zhang and Ye, 2012).

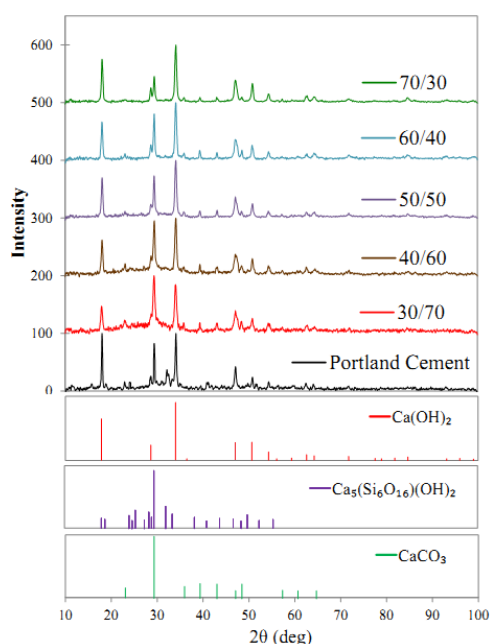


Figure 3. XRD of the reference PC and pozzolan specimens with five ratios of waste calcium hydroxide and recycled glass powder

The TGA curves for the pozzolan specimens are shown in Figure 4. All of the specimens, including the reference PC, exhibited a region of gradual weight loss, followed by two regions of more rapid weight loss. The reference PC sample had the largest percentage of weight loss due to the removal of water mass gained because of the hydration reactions. Based on Equation (3), the theoretical pozzolan reaction between calcium hydroxide and silicon dioxide is water neutral because it consumes no water from the batch, i.e. it is not a hydration reaction. If an assumption is made

that no other phases are generated which result in a mass gain of the pozzolan specimens, then the only weight loss should be due to the removal of free and chemical water and should therefore largely be a function of the calcium hydroxide content, increasing from 30/70 to 70/30 CH/GP. This trend was observed in the TGA results once the calcium hydroxide dehydroxylation temperature of approximately 500°C was reached, with the exception of the 70/30 specimen. The formation of calcite from the calcium hydroxide (see Equation (4)) in the 70/30 sample was responsible for a significant mass gain, due to the replacement of the water (molar mass = 18 g/mol) with heavier carbon dioxide (molar mass = 44 g/mol).

The DTA curves of the pozzolan specimens and the reference PC are shown in Figure 5. For the reference PC specimen, the dehydration of the C-S-H gel occurred with the dehydration of two other hydrated phases, identified as ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$), referred to as AFt and alumina ferrite monosulfate or simply monosulfate ($3\text{CaO}(\text{Al}, \text{Fe})_2\text{O}_3\cdot \text{CaSO}_4\cdot n\text{H}_2\text{O}$), referred to as AFm (Gabrovšek *et al.*, 2006; McCarthy and Dyer, 2017). For the pozzolan specimens, the dehydration of the C-S-H gel occurred with removal of residual free water from the porous structure of the specimens. The DTA curves of the 30/70, 40/60, 50/50 and 60/40 specimens were quite similar up to the calcium hydroxide dehydroxylation temperature of approximately 500°C . Table 4 shows the percentage of mass loss of the pozzolan specimens, due to the removal of residual free water, the dehydration of the C-S-H gel, dehydroxylation of the calcium hydroxide (Portlandite) and decarbonation of the calcium carbonate (calcite). For the 30/70 specimen, which had the lowest starting amount of calcium hydroxide, the remaining amount of calcium hydroxide in the specimen was small, as was the amount of formed calcite. For the 70/30 specimen, which had the highest starting amount of calcium hydroxide, the remaining amount of calcium hydroxide was also small, but the amount of formed calcite was significantly larger. As seen in Table 4, the mass loss due to calcite decarbonation increased with the amount of starting calcium hydroxide content in the pozzolan specimens. This was due to the increased amount of calcium hydroxide that was exposed to carbon dioxide from the air, which is necessary to produce calcite, as seen in Equation (4).

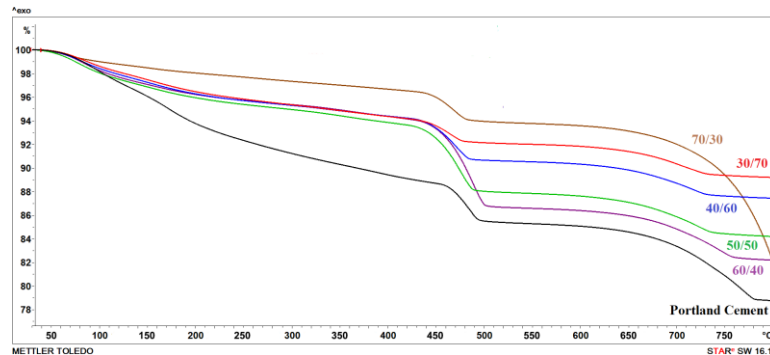


Figure 4. TGA curves of the reference PC and pozzolan specimens with five ratios of waste calcium hydroxide and recycled glass powder

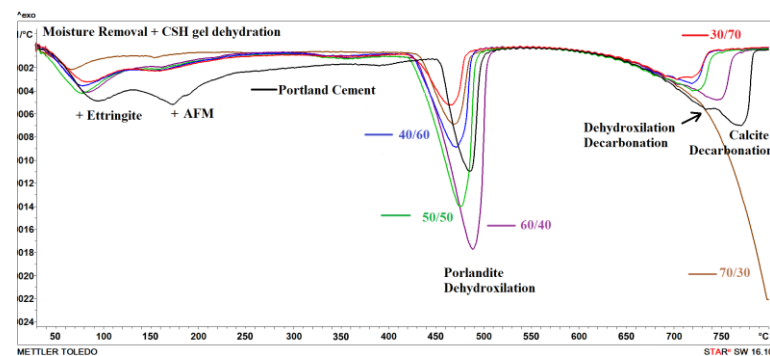


Figure 5. DTA curves of the reference PC and pozzolan specimens with five ratios of waste calcium hydroxide and recycled glass powder

Table 4. Mass loss of the reference PC and pozzolan specimens determined by TGA analysis

Thermal Event	Pozzolan CH/GP Ratio					Ref. PC	Mass Loss (%)
	30/70	40/60	50/50	60/40	70/30		
Free Water Removal	1.41	1.58	1.96	1.75	1.01	1.86	
C-S-H Dehydration	4.45	4.22	4.42	4.13	2.49	9.11*	
Portlandite ($\text{Ca}(\text{OH})_2$) Dehydroxylation	2.11	3.62	5.71	7.49	2.67	3.72	
Calcite (CaCO_3) Decarbonation	2.88	3.16	3.75	4.48	11.83	6.63	
Total Loss	10.84	12.59	15.84	17.85	18.00	21.32	

Considering the amount of C-S-H gel reported in Table 4, the reference PC had the largest amount, however it includes several other hydrated phases, Aft and AFm. The 70/30 specimen had the smallest amount at 2.49 wt. %, while the remaining pozzolan specimens all had similar amounts of approximately 4 wt. %. This result may be related to the total surface area of the glass powder in the pozzolan specimens. For a specimen with a large amount of glass powder, such as the 30/70 specimen, the total surface area of the glass powder was large ($140 \text{ g} \times 1.42 \text{ m}^2/\text{g} = 198.8 \text{ m}^2$) but there was an insufficient amount of calcium hydroxide to fully react with the glass. From Equation (3), the theoretical ideal weight ratio of calcium hydroxide to silicon dioxide was calculated as 65/35, though when accounting

for the glass powder being approximately 70 wt.% silica, the ratio is reduced to 56/44. Therefore, the 30/70, 40/60, 50/50 specimens were calcium hydroxide deficient, while the 60/40 specimen was slightly calcium hydroxide rich and the 70/30 specimen significantly more calcium hydroxide rich. When the CH/GP ratio was increased from 30/70 to 60/40, there was more calcium hydroxide for the pozzolanic reaction but the total surface area of the glass powder decreased from 198.8 m^2 to 113.6 m^2 for 30/70 to 60/40 specimens, respectively. Thus, the amount of C-S-H was not significantly different between 30/70 to 60/40 specimens. The 70/30 specimen likely had reduced C-S-H gel formation because the silica from the glass was the limiting reactant.

It was desirable to select the CH/GP ratio that produced the largest amount of C-S-H gel to act as a pozzolan for partial cement replacement. However, the amounts of C-S-H gel produced were similar in the 30/70, 40/60, 50/50 and 60/40 specimens. The 60/40 ratio was ultimately selected for several reasons. It did not contain a detectable amount of unreacted glass powder, as shown by the XRD results, and with the slight excess of calcium hydroxide as stated above, it would not have to rely on the delayed calcium hydroxide production from the hydration of the PC (Sprung, 2008). In addition, the 60/40 weight ratio is very near to the theoretically ideal weight ratio of 65/35 as shown above, and it did not produce an excessive amount of calcite, as shown by the TGA results.

Partial Cement Replacement with Calcium Hydroxide and Glass Powder

Graphs of the water absorption and apparent porosity values of the Portland cement mortar (PCM) specimens with 0 to 40 wt.% of the 60/40 CH/GP pozzolan, aged for 3 to 28 days, are shown in Figure 6 and Figure 7, respectively. The water absorption (Equation (5)) is the percent of mass change due to water absorption with respect to the sample mass, while the apparent porosity (Equation (6)) is the percent of open porosity with respect to the sample volume. Both results followed the same trend because the water was only absorbed in the open porosity of the specimens. The reference PCM specimen (0 wt.% pozzolan) showed that the water absorption decreased from 6.35 to 5.58 wt.% as it was aged from 3 to 28 days. The amount of water absorption was increased by 1 to 3 wt.% over that of the reference PCM in the PCM20, PCM30 and PCM40 specimens. As previously mentioned, the pozzolanic reaction (Equation (3)) is water neutral. While the batches all contained the same quantity of water, seen in Table 2, the PCM compositions containing the pozzolan (PCM20 to PCM40)

required less water for the reactions than the reference PCM. The excess water in the batch would therefore create the slightly increased amount of porosity and hence increased water absorption seen in the PCM20 to PCM40 specimens. It would be expected that the water absorption would increase with increased pozzolan additions from PCM20 (20 wt.%) to PCM40 (40 wt.%). However, the PCM30 specimen did not follow this trend and has slightly less water absorption than the PCM20 specimen.

The amount of water absorption in the PCM20 to PCM40 specimens also decreased with increased aging time from 3 to 28 days, like the reference PCM. The water absorption decreased with aging time as the hydration products, such as the C-S-H gel, filled the pore space of the PCM specimens. The PCM20 and PCM40 specimens had higher water absorption compared to the PCM30 specimen, which had the most similar value compared with the reference PCM. For the PCM20 specimen, the hydration products would have come mainly from the PC. Also, the 20 wt.% of pozzolan was the smallest addition and therefore the most diluted by the PC and sand, and so it could not react as quickly. For the PCM40 specimen, the PC contributed a smaller portion of the hydration products, while the reaction of the CH/GP pozzolan mixture was still slow due to dilution, thus the water absorption was higher at the early stages of aging. The PCM30 specimen may have had an optimal combination of less pozzolan dilution than PCM20, and more hydration products provided by the PC than PCM40. The compressive strength values of the PCM specimens with 0 to 40 wt.% pozzolan, aged for 3 to 28 days, are shown in Figure 8. The compressive strength of the reference PCM increased from 30.76 to 46.36 MPa for 3 to 28 days of aging. This is above the minimum compressive strength of 35 MPa after 28 days of aging specified in ASTM C311 (ASTM, 2005).

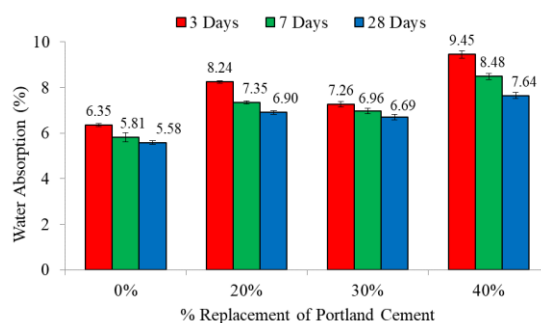


Figure 6. Water absorption of PCM specimens with partial cement replacement by 20 to 40 wt.% of the 60/40 pozzolan. 0% is the reference PCM specimen

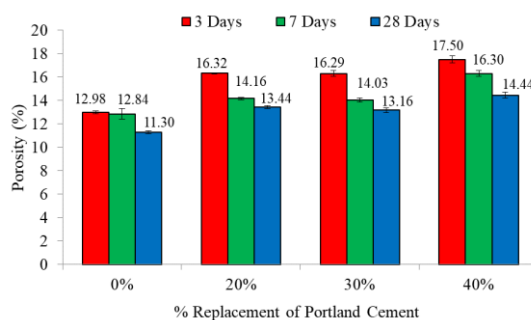


Figure 7. Porosity of PCM specimens with partial cement replacement by 20 to 40 wt.% of the 60/40 pozzolan. 0% is the reference PCM specimen

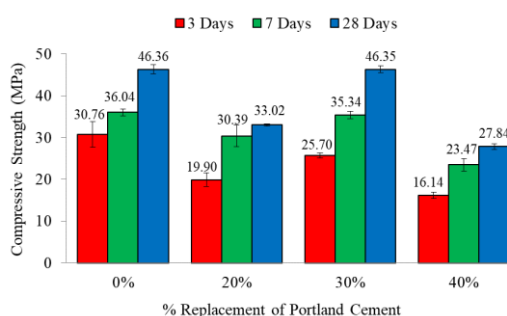


Figure 8. Compressive strength of PCM specimens with partial cement replacement by 20 to 40 wt.% of the 60/40 pozzolan. 0% is the reference PCM specimen

The compressive strengths were significantly reduced in the PCM20 and PCM40 specimens for aging times of 3, 7 and 28 days, over that of the reference PCM. The compressive strengths of the PCM30 specimens were nearly identical to the reference PCM specimens at 7 and 28 days. At 3 days, the PCM30 specimens had a lower compressive strength than the reference PCM specimens, likely due to the slower rate of the pozzolanic reaction.

The compressive strength of a material is directly related to the porosity, with both larger pore size and increased pore content generally predicting a lower strength. The PCM40 specimens had the highest apparent porosity and the lowest compressive strength, followed by the PCM20 specimens. While the porosity contents of PCM20 and PCM30 specimens were similar, the compressive strengths were significantly different at 28 days. If the porosity values were similar, then the significant strength difference is likely due to a compositional difference, such as less C-S-H gel or the presence of a mechanically weaker phase. The increased dilution of the PCM20 specimens could have resulted in the production of less C-S-H gel or the increased carbonation of calcium hydroxide to produce calcite (Equation (4)), which is weaker and may be a contributing factor to the lower strength.

The determination of this was not within the scope of the research and further research would be required for confirmation. Finally, it should be noted that the water to cement ratio was constant for the PCM specimens as well. The different pozzolan contents may require a different water to cement ratio in order to yield comparable strengths to the reference PCM and is an area for further research.

Conclusions

Waste calcium hydroxide from the production of acetylene gas and recycled soda-lime glass powder were used to create a pozzolanic mixture to act as a partial cement replacement. These materials underwent a pozzolanic reaction which resulted in the formation of calcite and a calcium silicate hydrate (C-S-H) gel. Calcite was a result of the carbonation of unreacted calcium hydroxide. From the thermal analysis results, the amounts of the generated C-S-H gel were quite similar for the CH/GP ratios between 30/70 to 60/40. The 60/40 CH/GP ratio was selected to partially replace Portland cement (PC) due to the absence of unreacted glass and minimal excess of calcium hydroxide. The replacement of PC with 30 wt.% of the 60/40 pozzolan showed similar porosity

and near equal compressive strength values to a reference PC after 7 days of aging. The pozzolanic reaction of the waste calcium hydroxide and recycled glass powder was slower in comparison to the hydration of the Portland cement, which reduced the compressive strength properties for the shorter aging time of 3 days. These results suggest that a 60/40 pozzolanic mixture of waste calcium hydroxide and recycled glass powder can function as a partial cement replacement without degradation of the examined properties and without a significant impact on the cement aging process.

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