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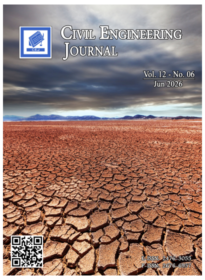

Investigation of the Mechanical Strengths of Concrete with Phosphogypsum from a Fertilizer Plant

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Abstract

The production of phosphoric acid faces a challenge in disposing of its by-product, phosphogypsum (PG). If not properly managed, the PG and its contaminants can leak into soil, causing environmental damage. As there is a large volume of PG that needs to be disposed of, an effective waste management method could be to use it in mass applications such as concrete construction. PG waste is mostly gypsum and can therefore be valorized as a material for concrete production, as cement requires gypsum to control its setting time. Using PG in concrete, particularly at high volume, could result in lower strength. To mitigate this strength reduction, particularly its long-term strength, rice hull ash (RHA) can be used as a supplementary cementitious material. While concrete is the preeminent construction material globally, the production of cement, its main ingredient, accounts for 8% of global carbon emissions annually. It is therefore vital to reduce cement use while maintaining concrete's inherent advantages. This study investigates the use of PG as a partial cement replacement with RHA and evaluates its mechanical properties. Concrete specimens containing 0-15% PG in increments of five were prepared and cured for 28 days. Additional specimens for 5-15% PG were prepared, but each contained 10% RHA. Curing for the PG-RHA-concrete specimens was set at 28 and 90 days. Results showed that at 5% PG, there was no significant decrease in compressive or splitting tensile strength, whereas flexural strength decreased slightly. The overall strength of PG-concrete decreased markedly when the PG content was increased to 10% and 15%. The addition of 10% RHA did not result in a significant improvement in the overall strength of concrete at 28 days of curing for all PG replacement percentages. However, after 90 days of curing, concrete with 5% PG and 10% RHA exhibited mechanical properties similar to those of standard concrete. The 10% and 15% PG specimens modified with RHA also showed significant improvements in their mechanical properties, but they were still not on par with standard concrete. SEM-EDS testing showed significant voids and ettringite in PG-concrete, while PG-RHA-concrete exhibited fewer voids and more C-S-H gel formation. The overall results indicate that RHA can significantly mitigate the negative effects of PG, provided sufficient curing time is allowed.

Keywords: Phosphogypsum; Mechanical Properties; Rice Hull Ash; Nanotechnology; Sustainability.

1. Introduction

Concrete is the most widely produced and utilized construction material globally [1]. The annual global production of concrete continues to increase, reaching 26 billion tons in 2020, up from 11 billion tons in the mid-2000s and "only"

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3 billion tons in 1963 [1, 2]. However, concrete's popularity is associated with increasing environmental costs. Chief among them is the carbon footprint associated with its production, particularly the cement production. More than 70% of the carbon emissions associated with concrete production stem from cement production [3]. Estimates vary, but cement production accounts for 5-8% of global carbon emissions [4, 5] and corresponds to 4 billion tons of cement produced annually [6]. Therefore, it is imperative to find solutions to reduce reliance on cement without sacrificing concrete's natural advantages.

Phosphogypsum (PG) is a by-product of phosphoric acid production through the "wet acid" method (Equation 1) [**7**].

$$Ca_3F(PO_4)_3 + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF \tag{1}$$

PG is mostly gypsum ($CaSO_4{\cdot}2H_2O$). It is estimated that 4.5-5.5 tons of PG are generated per ton of phosphoric acid extracted [8, 9]. Global estimates of PG production range from 100 to 300 million tons [7, 9, 10]. Of these, only 15% is utilized for cement production [9]. The rest are dumped in landfills. However, this poses a problem, as PG and its contaminants (including traces of heavy metals, phosphates, fluorides, etc.) can leach into the soil and cause environmental damage [7]. It is therefore of great interest to find solutions that increase PG utilization to reduce environmental damage. For instance, in the construction industry, one use of PG has been in the production of OPC. Since PG is rich in gypsum, it is often used as an alternative to natural gypsum as a set retarder in OPC production [7]. PG has also shown potential as an effective shrinkage-reducing agent for concrete [11]. For mortars, PG combined with RHA has been shown to enhance early-strength [12]. Even the waste from the PG leachate cleaning can be used as a partial cement replacement in mortars without affecting their properties [13]. In 3D printable concrete, adding 5 - 7.5% PG, in the presence of Ground Granulated Blast Furnace Slag (GGPS), improved mechanical properties [14]. PG can also be used to prepare alternative aggregates for concrete production. It was used as a base to prepare PG recycled aggregates (PGRA) to replace natural aggregates in concrete [15].

PG has also been used as a partial cement replacement [8, 16, 17]. Studies indicate that PG generally reduces concrete strength beyond 10% partial cement replacement, although in some cases, an improvement in strength was observed [18]. Beyond 10% PG, the decrease in concrete strength is much steeper, and so far, PG is not considered a viable partial cement replacement. However, in the presence of excess gypsum, the monosulfate aluminate hydrates in cement paste can revert to ettringites, potentially resulting in lower concrete strength [1]. One possible solution to improve the mechanical properties of PG-concrete is to use pozzolans or supplementary cementitious materials (SCM's) [19]. However, as of this writing, this approach has not been extensively explored for PG-concrete, with fly ash (FA) as the sole binder [17]. In this study, both PG and FA contributed to improvements in concrete mechanical properties by promoting pozzolanic reactions, with PG containing approximately 35% silica and FA approximately 56% silica.

Another SCM that has not been tested on PG-concrete is rice hull ash (RHA), an agricultural by-product. This study was conducted in an area with several rice fields in the vicinity, but no nearby coal power plant. Therefore, it is more appropriate in this study to use RHA as SCM rather than fly ash. RHA consists of around 85-96% silica [20], which is significantly higher than the silica content of FA. This makes RHA a potentially more powerful pozzolan. RHA can be amorphous when combustion temperatures are limited to 500°C–700°C or crystalline when combustion temperatures are greater than 700°C [21]. Amorphous RHA is usually preferred over crystalline RHA since it is more reactive to cement [21]. Amorphous RHA in concrete can result in concrete with higher strength, better durability, and lower cost [22]. The purpose of this study is to evaluate the utility of using PG from a local fertilizer plant. Specifically, this study aims to:

- Determine the mechanical properties, namely the compressive strength, splitting-tensile strength, and flexural strength, of concrete with PG;
- Identify the maximum percentage of PG that can be used as partial cement replacement without detrimental effects on the mechanical properties of concrete; and
- Investigate the extent to which RHA can mitigate the expected drop in the mechanical properties of PG-concrete.

2. Materials and Methods

2.1. Materials

Ordinary Portland cement with a density of 3.05 g/cm^3 was used as the primary binder. Crushed gravel, graded in accordance with ASTM C33, was used as coarse aggregate. The PG was sourced from a fertilizer plant in Leyte, Philippines, while RHA was obtained by burning rice hulls in a combustor from the University of the Philippines Los Baños (UPLB). The PG and RHA were sieved through US sieve no. 100 and their respective densities were determined using the method described in ASTM C188. Further characterization was done by submitting both the PG and RHA to the UPLB Nanotechnology Laboratory for X-ray Diffraction (XRD) analysis. The chemical composition of PG is 93.50% $CaSO_4{\cdot}H_2O$, according to the supplier's specifications, with the remaining 6.5% consisting of free water and trace amounts of chloride and phosphorous. The RHA was submitted to NASAT Labs for X-ray Fluorescence (XRF) spectroscopy to determine its chemical composition. Table 1 summarizes the relevant properties of the materials used. The images of PG and RHA used in this study are shown in Figure 1, while the aggregate gradation curves are shown in Figure 2. Both fine and coarse aggregates are within the specified gradation limits of ASTM C33.

Figure 1. PG (left) and RHA (right) used in this study

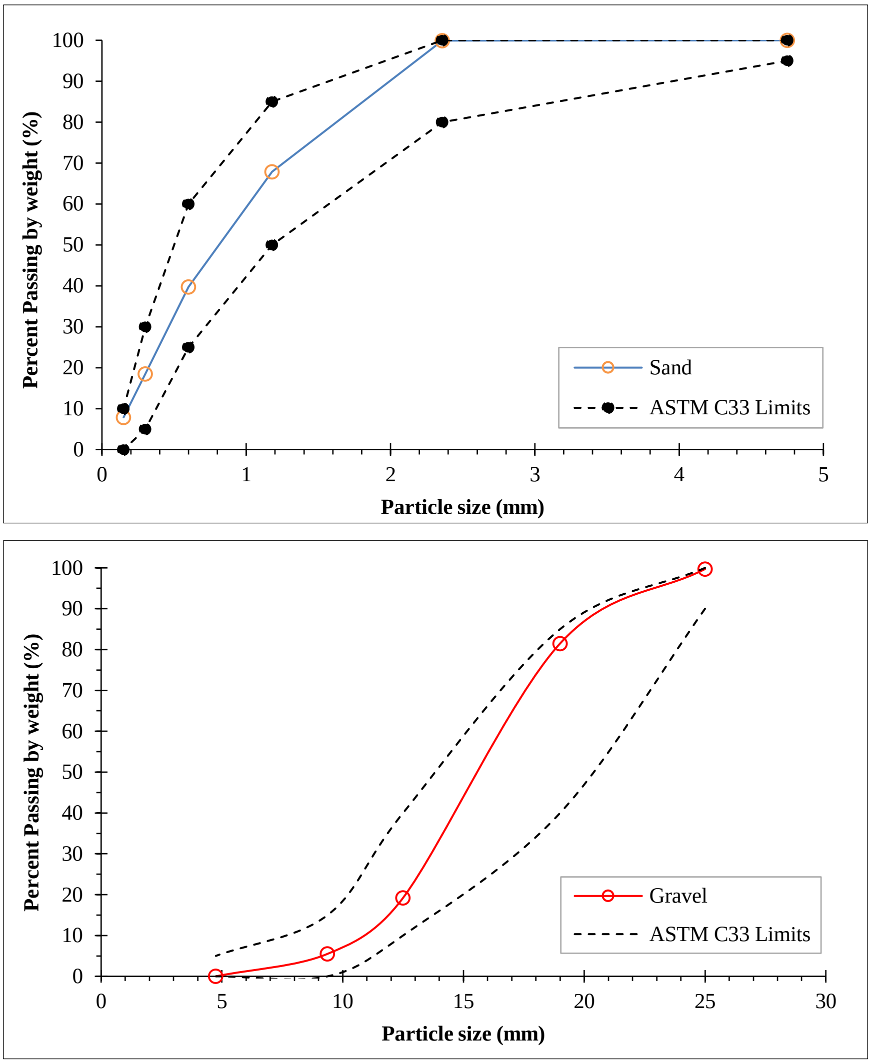

Figure 2. Gradation curves of fine (left) and coarse (right) aggregates

Table 1. Properties of raw materials

Parameter	Sand	Gravel	PG	RHA	Cement
Fineness modulus	2.73	-	-	-	-
S.G.	2.85	2.85	2.32	2.12	3.05
Absorption capacity (%)	1.3	0.78	-	-	-
Dry-rodded unit weight (kg/m^3)	-	1589.44	-	-	-

2.2. Methods

The flowchart showing the methods in this study is shown in Figure 3. Following the determination of raw material basic properties, cement paste, and mortar specimens were initially prepared, cured, and tested, followed by the preparation and evaluation of selected concrete specimens. Initially, cement paste specimens with varying PG as a cement replacement by mass (increments of 5%) were prepared and tested to isolate the effect of PG on cement hydration. Subsequently, mortar specimens of the same PG replacements were investigated to evaluate their performance in the presence of fine aggregates. Based on the results of the cement paste and mortar testing, selected mixtures were used to prepare concrete specimens for further validation as a structural material. In addition, RHA at extended curing was incorporated to mitigate the reduction in strength.

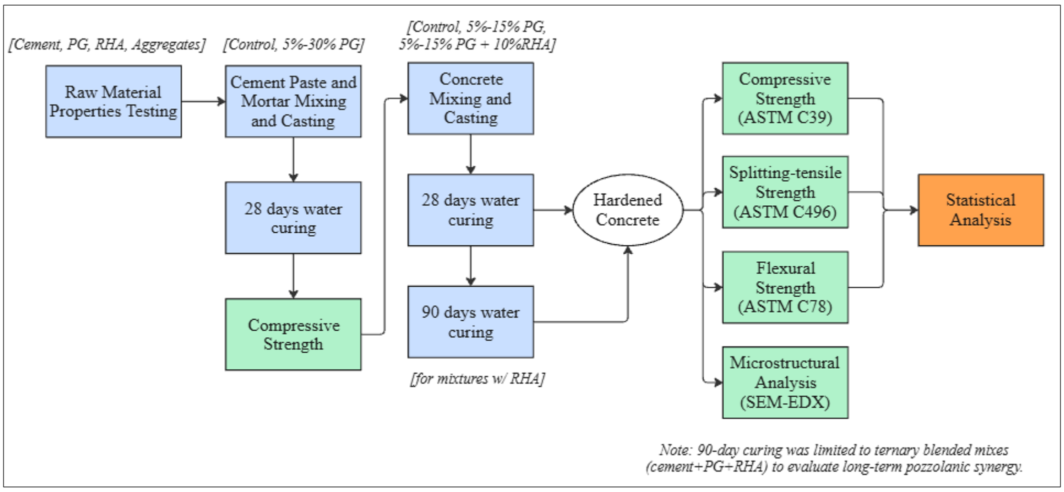

Figure 3. Flowchart of the experimental methodology for cement paste, mortar, and concrete mixtures

The proportions of the mixture for cement paste and mortar cubic specimens with dimensions of 50 mm are shown in Tables 2 and 3. The water curing period was set at 28 days. The percentages of PG as a cement replacement range from 0% to 30% in increments of 5%. Five trials per specimen were prepared. Before testing, the specimens were wiped with a cloth to achieve saturated surface dry (SSD) conditions.

Table 2. Mix proportion per cubic meter for cement paste specimens with PG

Specimen	Water (g)	OPC (g)	PG (g)
Control	588.86	1177.72	0.00
5PG	586.19	1129.42	42.96
10PG	583.72	1084.91	82.53
15PG	581.44	1043.79	119.09
20PG	579.33	1005.67	152.99
25PG	621.78	1044.86	198.70
30PG	294.67	479.85	109.50

Table 3. Mix proportion per cubic meter for mortar specimens with PG

Specimen	Water (kg)	OPC (kg)	PG (kg)	Sand (kg)
Control	319.40	638.70	0.00	1342.90
5PG	319.40	606.80	31.90	1342.90
10PG	319.40	574.90	63.90	1342.90
15PG	319.40	542.90	95.80	1342.90
20PG	319.40	511.00	127.70	1342.90
25PG	319.40	479.10	159.70	1342.90
30PG	319.40	447.10	191.60	1342.90

The concrete mixture was designed in accordance with ACI 211.1, as summarized in Table 4. Concrete was mixed in accordance with ASTM C192. A water-cement (w/c) ratio of 0.50 was set for all mixtures. Before mixing, the proportions of all materials were determined by volume, based on one cubic meter of concrete. Afterward, the materials were weighed and placed in a mixing container. At the start of mixing, the concrete mixer and the pan for catching fresh concrete were moistened with tap water. Then, gravel, sand, and cement were placed into the concrete mixer and rotated for two minutes. For the concrete mix with RHA, the mixing time was extended to 3 minutes. Next, water was added and mixed for another 3 minutes. Afterward, the concrete mix was allowed to rest for 2 minutes before being mixed for an additional 2 minutes.

Table 4. Mix proportion per cubic meter for concrete specimens with PG

Specimen	Water (kg)	Cement (kg)	PG (kg)	RHA (kg)	Gravel (kg)	Sand (kg)	Slump (mm)
Control	205	410	0	0	1009	816	72
5PG	205	390	21	0	1009	810	77
10PG	205	369	41	0	1009	804	76
15PG	205	349	62	0	1009	798	57
5PG10RHA	205	349	21	41	1009	793	46
10PG10RHA	205	328	41	41	1009	787	35
15PG10RHA	205	308	62	41	1009	781	39

After mixing, a slump test was done in accordance with ASTM C143. After the slump test, the fresh concrete was cast by rodding into 100 mm × 200 mm cylindrical molds for compressive and splitting tensile strength testing, and into 100 mm × 100 mm × 400 mm rectangular molds for flexural strength testing. Five trial specimens were prepared for each mechanical test. The percentages of PG replacement used were 5, 10, and 15%, respectively. For RHA, 10% was used. The specimens were left to harden at room temperature for at least 24 hours before being water-cured until the day of testing. Before testing, the specimens were wiped with a cloth to achieve SSD conditions. All mechanical tests were performed using the Shimadzu UH-100A Universal Testing Machine (UTM). Selected specimens were analyzed using a scanning electron microscope (SEM) at the Central Instrumentation Facility, De La Salle University, Biñan.

2.2.1. Compressive Strength Testing of Cement Paste, Mortar, and Concrete Specimens

The specimens were placed individually at the center of the UTM, and the concrete specimens were capped with metal plates with neoprene pads to ensure uniform load distribution. The force (in kN) was recorded at the point of failure. The compressive strength was calculated according to Equation 2.

$$\sigma_c = \frac{P_c}{A_c} \tag{2}$$

where, σ_c is the compressive strength, P_c is also the maximum compressive load applied at the point of failure, and A_c is the cross-sectional area of the cylinder.

2.2.2. Splitting-tensile Strength Testing of Concrete Specimens with PG and PG-RHA

The splitting-tensile strength was performed in accordance with ASTM C496. The splitting-tensile strength was calculated according to Equation 3.

$$\sigma_t = \frac{2P_t}{\pi d L} \tag{3}$$

where, σ_t is the splitting-tensile strength, P_t is the maximum load applied until failure, d is the diameter of the cylindrical specimen, and L is the length of the cylindrical specimen.

2.2.3. Flexural Strength Testing of Concrete Specimens with PG and PG-RHA

Flexural strength testing was performed using a third-point loading setup in accordance with ASTM C78. The flexural strength was calculated according to Equation 4.

$$\sigma_f = \frac{3P_f L}{2bh^2} \tag{4}$$

where, σ_f is the flexural strength, P_f is the cracking load, and b, h, and L are the width, height, and support length of the rectangular specimen.

2.2.4. Statistical Analysis

Statistical analyses were conducted at 95% confidence level ($\alpha = 0.05$). The Shapiro-Wilk test for normality of residuals and Levene's test for homogeneity of variances were evaluated to verify the assumptions for Analysis of Variance (ANOVA). When both assumptions were satisfied, a one-way ANOVA followed by Tukey's post hoc test was performed. When normality was satisfied, but the homogeneity of variances was violated, Welch's ANOVA followed by the Games-Howell test was employed. Statistical significance was evaluated based on p-values. Effect sizes and confidence intervals were not explicitly computed.

3. Results

The concrete specimens were tested after 28 days of curing. For mixtures containing RHA, an additional set of specimens was tested after 90 days of curing, as delayed strength development is expected in concrete with pozzolans.

3.1. Performance Characteristics of PG and RHA

Shown in Figure 4 is the X-ray diffractogram of PG. The major peaks are 11.64°, 20.76°, 23.40°, and 29.12° which are all associated with the crystal structure of $CaSO_4 \cdot H_2O$, the major component of PG [23]. This result further confirms the high purity of PG since no other major peaks associated with other crystalline compounds were detected.

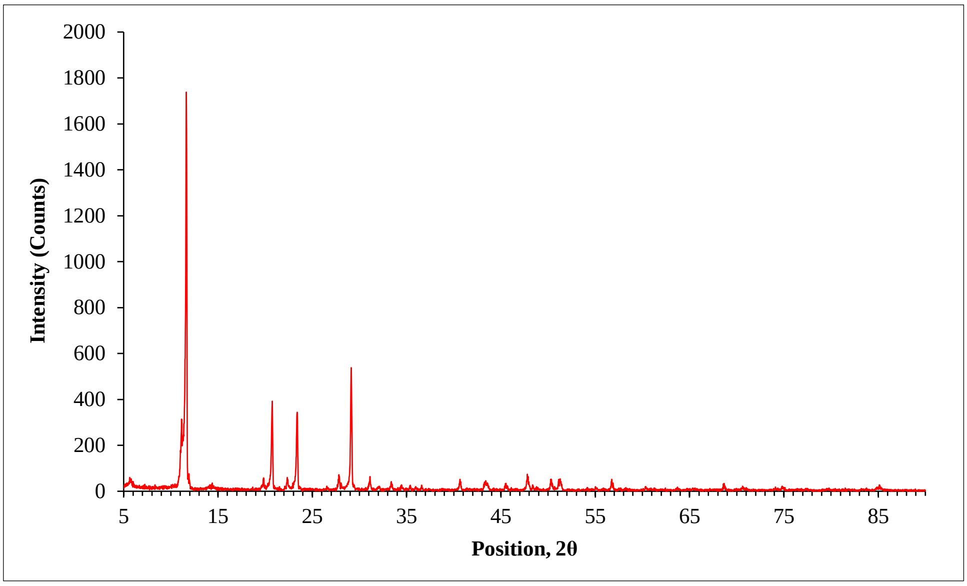

Figure 4. X-ray diffractogram of PG

The performance characteristics of RHA are shown in Table 5 and Figure 5. The RHA was found to be 89.0692% SiO_2, which is well within the expected SiO_2 content range [20]. The major contaminant in RHA is K_2O (5.0044%), which accounts for its gray color. K_2O is known to melt at around 350°C, blanketing the rice hull and causing incomplete combustion [24]. More importantly, the RHA is also amorphous, as indicated by the broad hump at 20-30° characteristic of amorphous silica [25]. This makes it highly likely that RHA will behave as a pozzolan, since, unlike crystalline RHA, its lack of a definite "ordered" structure makes it highly reactive. Concerning the other components of RHA, only chloride is known to have a detrimental effect on concrete quality, but since it is present at very low levels, it is unlikely to induce significant corrosion through chloride ingress.

Table 5. Chemical composition of RHA

Oxide/Element	Percent
SiO_2	89.0692
K_2O	5.0044
Cl	1.2693
P_2O_5	1.9456
CaO	1.1005
Others	1.6107

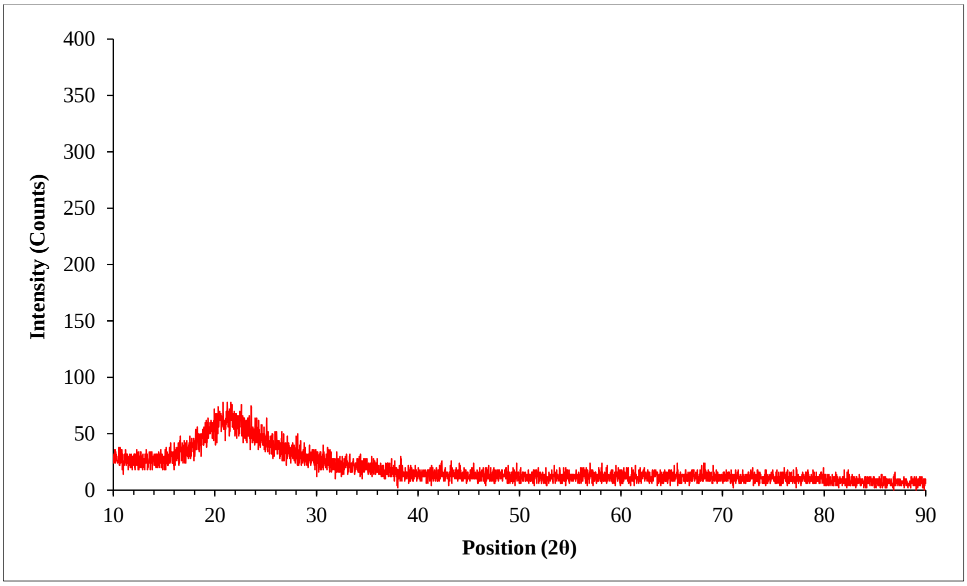

Figure 5. X-ray diffractogram of RHA

3.2. Compressive Strength of Cement Pastes and Mortar Specimens with PG

The compressive strengths of cement paste and mortar specimens are shown in Tables 6 and 7, respectively. The results indicate that for cement paste, up to 10% PG had no significant effect on strength; further additions of PG led to a 43% drop in compressive strength. Compared to cement paste, the mortar specimens have an interfacial transition zone between the cement paste and aggregates, which is considered the weakest link in their microstructure, making them more sensitive to PG replacement. For cement mortars, the maximum PG content that can be used without significant strength reduction is just 5%. At 10% PG, a 53% drop in compressive strength was observed. These results were used to determine the amount of PG in the concrete mix.

Table 6. Compressive strength values of PG-cement paste specimens

Cement Paste Mixture	28-day Compressive Strength, MPa Mean(SD)
Control	18.60 ± 1.84^a
5PG	19.80 ± 1.33^a
10PG	18.56 ± 1.35^a
15PG	10.54 ± 1.19^b
20PG	11.14 ± 1.03^b
25PG	11.31 ± 0.79^b
30PG	11.17 ± 1.44^b

Note: Superscript letters (a and b) indicate the results of the comparison tests. Strength values sharing the same superscript letter are not significantly different.

Table 7. Compressive strength values of PG-mortar specimens

Mortar mixture	28-day Compressive Strength, MPa Mean(SD)
Control	24.05 ± 1.58^a
5PG	25.07 ± 1.05^a
10PG	11.22 ± 1.73^b
15PG	13.33 ± 1.61^b
20PG	13.40 ± 1.36^b
25PG	12.01 ± 1.38^b
30PG	9.41 ± 1.81^c

Note: Superscript letters (a, b, and c) indicate the results of the comparison tests. Strength values sharing the same superscript letter are not significantly different.

3.3. Compressive Strength of Concrete Specimens with PG and RHA

Based on the compressive strength results of cement paste and mortar specimens, only up to 15% PG was considered for the concrete specimens. Too much PG replacement will result in significantly lower concrete strengths. In contrast, the strength reduction for lower replacements could still be mitigated by the inclusion of RHA in the mix and extended curing. The compressive strength of PG-concrete and PG-concrete with RHA is presented in Table 8. Replacing cement with even just 5% PG results in a 11.92% decrease in compressive strength relative to the control at 28 days of curing. However, the statistical analysis indicates that this decrease is insignificant at the 95% confidence level (p-value = 0.29). The addition of 10% RHA resulted in a significant decrease in strength (p-value = 0.0066). But the strength remains well above the minimum compressive strength specified by ACI 318 for structural concrete (17 MPa) and is around the typical strength requirement for normal structural concrete (21 MPa). Some images of the compressed samples are shown in Figure 6, which illustrate the failure patterns of Types 1 to 3 according to ASTM C39. These failure types are well-defined fracture patterns.

Table 8. Compressive strength values of PG-concrete specimens with and without RHA

Concrete specimen	Compressive strength, MPa	
	28 days Mean (SD)	90 days Mean (SD)
Control	29.95 (2.37)^{a}	---
5PG	26.38 (1.61)^{a}	---
5PG10 RHA	21.11 (0.80)^{b}	27.73 (1.14)^{a}
10PG	14.42 (1.59)^{c}	---
10PG10RHA	16.05 (1.18)^{c}	21.36 (0.59)^{b}
15PG	11.64 (2.50)^{d}	---
15PG10RHA	15.22 (0.99)^{d}	19.91 (0.97)^{b}

Note: Superscript letters (a, b, c, and d) indicate the results of the comparison tests. Strength values sharing the same superscript letter are not significantly different.

Figure 6. Sample images of fractured cylindrical samples after compressive strength tests

At 10PG, the compressive strength decreased drastically by 51.85% relative to the control, falling below the minimum threshold of 17 MPa. The addition of RHA appeared to increase the compressive strength values at 28 days curing for 10PG and 15PG. However, statistical analysis (p-value = 0.74 and 0.28) shows that the increases are not significant. Overall, at 28 days of curing, with and without RHA, the concrete specimens, except 5PG, exhibited significantly lower compressive strengths than the control.

At 90 days of curing, there was sufficient time for the RHA to react with the cement hydration products, resulting in a markedly different trend. For 10PG10RHA and 15PG10RHA, the extended curing period yielded significantly higher compressive strength than for 10PG and 15PG. Notably, the compressive strength of 15PG10RHA was comparable to that of 10PG10RHA. For 5PG10RHA, the additional curing allowed it to reach strengths comparable to those of 5PG and the control.

It should be noted that no PG-concrete or standard concrete specimens were tested at 90 days, as PG is not a pozzolan and is not expected to undergo reactions that may improve concrete's mechanical properties. As for standard concrete, it is expected that the mechanical properties at 90 days of curing will, of course, be much better than those of PG-concrete and PG-RHA-concrete, since more cement is present. However, the primary comparison in this study is with standard concrete cured at 28 days. The 90-day curing period was selected because the pozzolanic effect is known to occur much later in the curing stage.

3.4. Flexural Strength of Concrete Specimens with PG and RHA

The flexural strength values are presented in Table 9. Unlike the compressive strength results, the flexural strength significantly decreased (p-value = 0.02) at 5PG. The addition of RHA, combined with 90-day curing, resulted in a flexural strength value statistically similar to that of the control (p-value = 0.14). The decrease in flexural strength was more drastic for 10PG (-46.09%) and 15PG (-43.36%) mixtures. The incorporation of RHA did not improve the flexural strength at 28 days; however, after 90 days of curing, the flexural strengths of 5PG10RHA and 10PG10RHA increased. The increase is particularly notable for 10PG10RHA (+43.48%). A strength increase was also observed for 15PG10RHA, but it was statistically insignificant (p-value = 0.19). Overall, the use of RHA in combination with extended curing resulted in measurable improvements in flexural strength.

Table 9. Flexural strength values of PG-concrete specimens with and without RHA

Concrete specimen	Flexural strength, MPa	
	28 days Mean (SD)	90 days Mean (SD)
Control	5.12 (0.17)^{a}	-
5PG	4.50 (0.20)^{b}	-
5PG10 RHA	3.94 (0.13)^{b}	4.59 (0.44)^{a}
10PG	2.76 (0.21)^{c}	-
10PG10RHA	2.99 (0.12)^{c}	3.96 (0.26)^{b}
15PG	2.90 (0.20)^{c}	-
15PG10RHA	2.75 (0.25)^{c}	3.37 (0.32)^{c}

Note: Superscript letters (a, b, and c) indicate the results of the comparison tests. Strength values sharing the same superscript letter are not significantly different.

3.5. Splitting-tensile Strength of Concrete Specimens with PG and RHA

The splitting-tensile strength values are presented in Table 10. Similar to the compressive strength results, the 5PG had splitting tensile strength comparable to that of the control. At 5PG, the addition of RHA significantly decreased splitting tensile strength at 28-day curing (p-value = 0.0002), but the strength recovered at 90 days, becoming statistically similar to both the control (p-value = 0.13) and 5PG (p-value = 0.99). At 10PG, adding 10RHA resulted in an insignificant decrease in the splitting-tensile strength at 28 days (p-value = 0.93), but the strength recovered at 90-day curing, even surpassing that of 10PG (p-value = 3.25×10-6). At 15PG, the addition of RHA did not produce a significant effect, even at extended curing. The splitting-tensile strength of concrete containing PG remained stable up to 5% replacement. The incorporation of RHA, along with 90-day curing, improved splitting tensile strength, enabling up to 10PG to become statistically similar to the control.

Table 10. Splitting-tensile strength values of PG-concrete specimens with and without RHA

Concrete specimen	Splitting-tensile strength, MPa	
	28 days Mean (SD)	90 days Mean (SD)
Control	2.54 (0.17)^{a}	-
5PG	2.57 (0.15)^{a}	-
5PG10RHA	1.86 (0.19)^{b}	2.40 (0.38)^{a}
10PG	1.74 (0.16)^{b}	-
10PG10RHA	1.32 (0.18)^{b}	2.33 (0.12)^{a}
15PG	1.76 (0.20)^{b}	-
15PG10RHA	1.74 (0.09)^{b}	1.76 (0.05)^{b}

Note: Superscript letters (a and b) indicate the results of the comparison tests. Strength values sharing the same superscript letter are not significantly different.

Overall, the results on the mechanical properties of PG-concrete are generally consistent with the literature on the observed decrease in compressive strength [18]. However, the decrease in strength due to PG cited in the literature occurs at 20% PG or higher. In fact, in some studies, addition of up to 10% PG could even slightly improve compressive strength or have no effect at all [16, 26-29]. At low concentrations, PG can act as a filler, while the sulfate in PG can promote rapid ettringite formation at the early stage of hydration [30]. The filler effect may explain the slight improvement in strength. At the same time, the rapid formation of ettringite, along with reduced cement available due to partial replacement, likely contributes to the drastic decreases in compressive strength at higher PG levels.

4. Discussion

4.1. SEM-EDX of PG and PG-RHA Concrete and Implications on Mechanical Properties

It has been well established that the silica in RHA reduces concrete porosity by densifying the interstitial transition zone (ITZ) between the matrix and the aggregate [22, 31]. Densification occurs through the reaction of silica with portlandite, C-H, to form calcium silicate hydrate (C-S-H) gels, which reduce porosity [32]. In addition to densification, the ITZ width is also reduced [33]. Taken together, these reactions enhance concrete's mechanical properties, especially its compressive strength. Figure 7 shows the SEM images of concrete specimens.

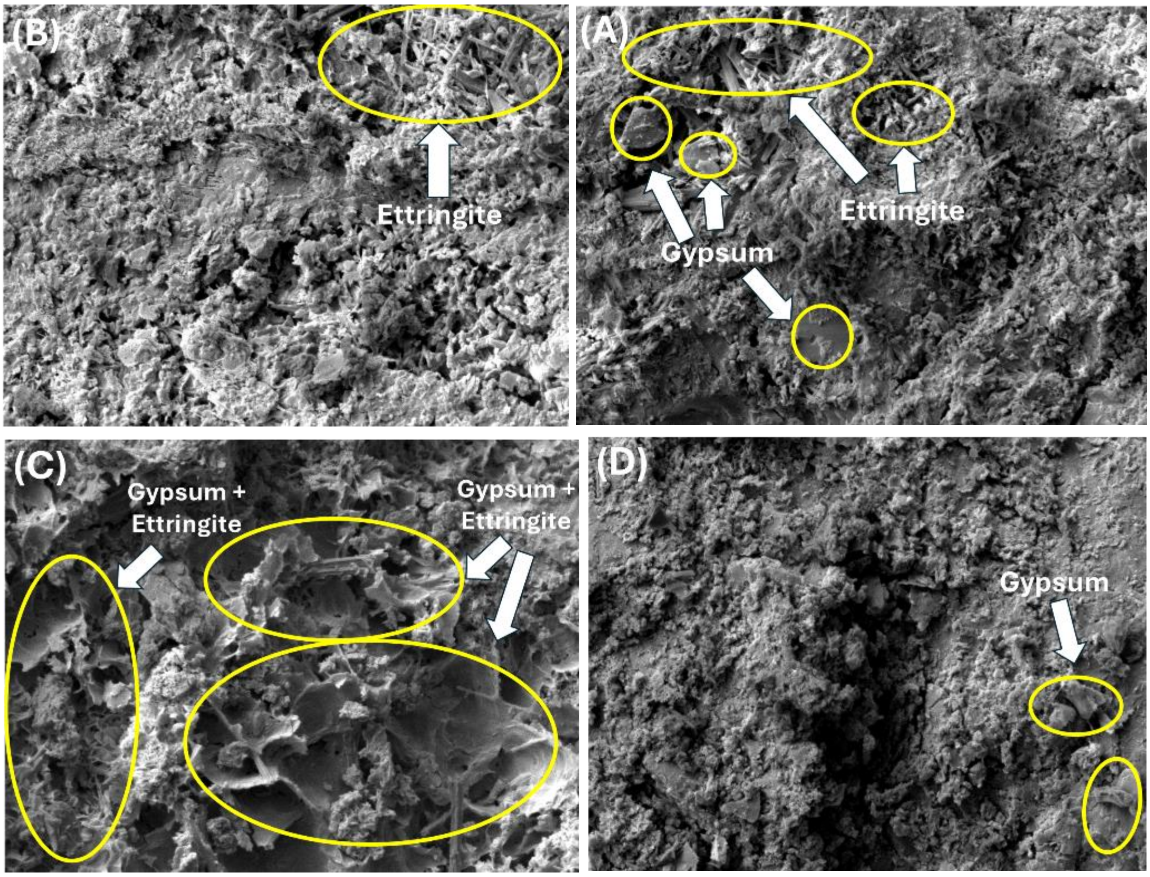

Figure 7. SEM images of PG-concrete and PG-RHA-concrete. Top: (A) –10PG, (B) – 10PG10RHA at 90 days curing; Bottom: (C) –15PG, (D) – 15PG10RHA at 90 days curing. Magnification: 5500x

The SEM images of both 10PG and 15PG show clear ettringite formations as evidenced by the needle-like structures observed. The reaction to form ettringite is given by Equation 5 [34].

$$C_3A + CaSO_4 \cdot 2H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O \quad (5)$$

During the early stages of hydration, gypsum delayed the setting of concrete, and Equation 5 is a natural consequence of this. As a result, the ettringite and portlandite dominate the ITZ during early curing stages, which partially explains why concrete is naturally weak at early ages [1]. However, if too much gypsum is used, as in 10PG and 15PG, excessive ettringite will form, weakening the concrete's strength. This is because its low surface area, coupled with its needle-like shape, makes the ITZ very porous. While the SEM images of 10PG and 15PG do not show the ITZ, the apparent presence of multiple voids due to ettringite indicates reduced C-S-H formation, likely because less cement was initially present.

On the other hand, the SEM results for PG-RHA concrete show clear differences compared with those for PG-concrete. Based on the various mechanical tests conducted on PG-RHA-concrete, it is clear that RHA mitigated the negative effects of excessive PG when sufficient curing time was provided. Based on the SEM images, it can be inferred that the RHA induced a pozzolanic reaction to produce C-S-H, which filled the voids in both 10PG10RHA and 15PG10RHA. The amount of ettringite also seems to have been reduced, as evidenced by the near absence of the needle-like structures. It is known that once the sulfate ions are consumed, ettringite reacts with the remaining C_3A to form AFm hydration products (Equation 6) [1, 35].

$$C_3A + C_3A \cdot 3CaSO_4 \cdot 32H_2O + 22H_2O \rightarrow C_3A \cdot CaSO_4 \cdot 12H_2O \quad (6)$$

This reaction occurs at later stages of curing. Therefore, the authors posit that the improvement in mechanical properties is due to the reduction of ettringite and the production of additional C-S-H gels to fill the voids. The presence of AFm hydration products also has implications for concrete durability, particularly its resistance to chloride ingress [36]. The AFm, along with C-S-H, helps bind chloride ions through a combination of physical adsorption and chemical binding mechanisms [36].

It is also acknowledged that the 90-day curing was limited to PG-RHA concrete mixtures, whereas the control and PG-only mixtures were tested only at 28 days. This limits the extent of long-term comparative assessment across all mixtures. However, the primary focus of this study is to assess the mechanical properties of PG-based concrete and the mitigating effect of RHA at later ages. This focus guided the prioritization of 90-day testing for PG-RHA mixtures to address the study's objective directly.

4.2. Particle Size of RHA and Insights into its Effectiveness as a Pozzolan

Despite improvements in the mechanical properties of PG-RHA-concrete relative to PG-concrete, beyond 5% PG, the mechanical properties do not meet standard concrete requirements. There are two possible and very likely reasons for this. First, there was not enough portlandite available to react with the RHA to produce secondary C-S-H gels. Given the fact that 20-25% less cement was used, this scenario is highly likely. The second reason is more closely related to the nature of the RHA in this study. It was assumed that sieved RHA has a particle size in the tens of micrometers. However, the SEM results revealed that RHA is nano-sized (Figure 8).

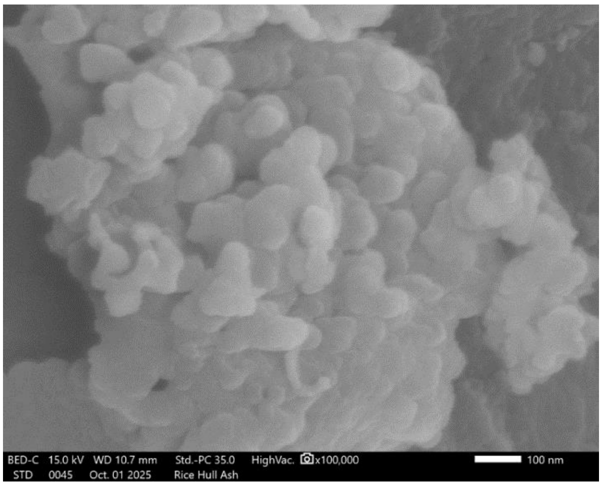

Figure 8. SEM image of RHA. Magnification: 100000x. Individual particle sizes range from 55 to 85 nm

This runs counter to the prevailing narrative in the literature, even into the 2020s, that the RHA is micro-sized [37]. The nano size of the RHA strongly implies a very high surface area. Coupled with its high silica content and amorphous structure (Figure 5), this makes RHA very hydrophilic and more prone to agglomeration than usual, underutilizing its capabilities because the surface area available for the pozzolanic reaction is artificially reduced. It should be noted that studies on nanosilica as a pozzolan recommend a partial cement replacement or additive percentage no higher than 3% [38]. It seems that the same might be true for RHA.

4.3. Relationship of Compressive vs. Flexural and Splitting-tensile Strength

The flexural strength is roughly proportional to the square-root of the compressive strength according to ACI318-25. Shown in Figure 9 is the plot of flexural vs. compressive strength as well as the equation of the line in square-root form. As seen in the graph, for PG-concrete, there is a strong linear relationship between the flexural strength and the square root of the compressive strength. However, it deviates significantly from the equation described in ACI 318-25 by up to 31%. The equation in square-root form between splitting tensile and compressive strength is much closer to ACI318-25 (Figure 10), with a deviation of almost 25%. Nevertheless, for flexural vs. compressive strength, the ACI318-11 standard equation can still be considered realistic for PG-RHA-concrete.

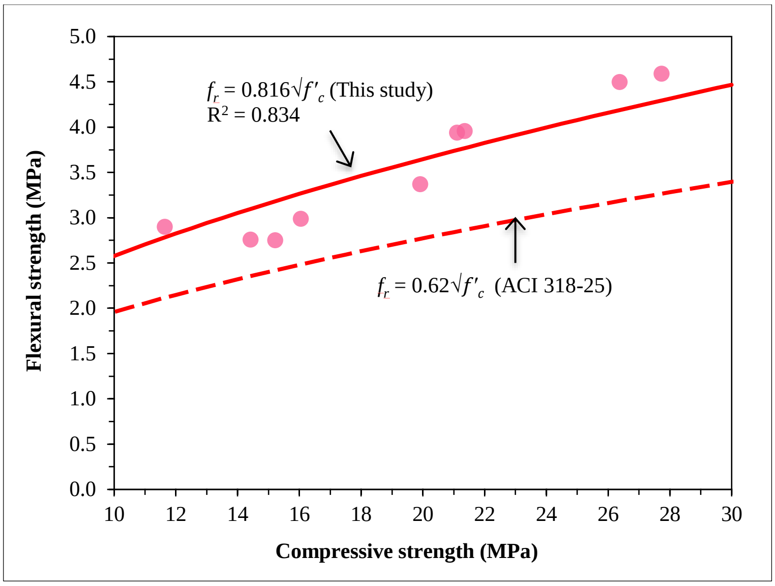

Figure 9. Square-root model of flexural vs compressive strength

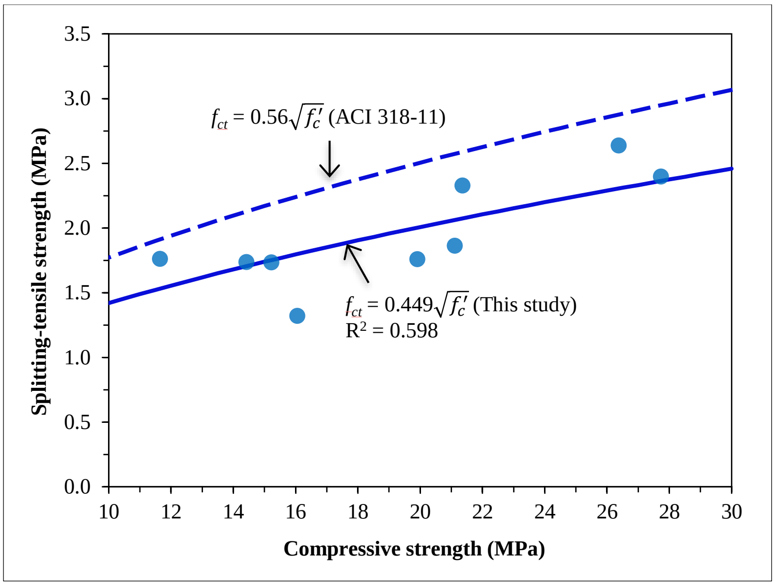

Figure 10. Square-root model of splitting-tensile vs compressive strength

5. Conclusions

To determine if it's feasible to use PG, a waste by-product from a local fertilizer plant, as a partial cement replacement without compromising concrete performance, this study prepared cement paste and mortar specimens with varying PG replacement levels and evaluated their strength. Based on the results from these preliminary analyses, selected mixtures were advanced to concrete specimen preparation and tested for compressive, splitting tensile, and flexural strengths at 28 days. Anticipating potential strength reductions, particularly at high replacement levels, additional PG-concrete mixtures containing 10% RHA were also prepared and tested at 28 and 90 days. Using RHA as a supplementary cementitious material is particularly relevant in countries such as the Philippines, a rice-producing country, where rice hulls are abundant as an agricultural by-product. Based on the mechanical tests done on concrete with PG and RHA, the following insights were derived:

- PG can be used as a partial cement replacement for concrete up to 5%. Beyond 5% PG, pozzolans such as RHA are necessary to mitigate the drastic decrease in mechanical properties of PG-concrete.
- SEM-EDS analysis revealed extensive voids and ettringite crystal formation for PG-concrete at standard curing age. Addition of 10% RHA, along with curing for 90 days, reveals extensive C-S-H gel formation that fills these voids and results in modest to marked improvements in the PG-concrete's mechanical properties, particularly compressive strength, with 5PG10RHA being on par with standard concrete. Less ettringite was also observed at 90 days of curing, indicating that ettringite had broken down into other AFm hydration products.

- SEM analysis of RHA revealed that the individual particles are in the nanoscale range, with reasonable purity. Minor contaminants include K_2O, CaO, and chloride. These contaminants are expected, as no treatment was done on the rice husks before combustion.
- The optimum concrete mix relative to the control is 5PG10RHA cured for 90 days. However, if the basis for the best concrete mix is a compromise among economy, sustainability, and performance, then 10PG10RHA cured for 90 days can be considered.

The key takeaway from this study is that RHA can be reliably used as a pozzolan in tandem with PG to produce a more environmentally friendly concrete. While PG has minimal value for improving mechanical strength, when used in tandem with RHA, it can still be used as a partial cement replacement. The potential utility of PG-RHA-concrete is for concrete structures that do not require immediate usage after concrete placement, such as houses and buildings.

6. Declarations

6.1. Author Contributions

Conceptualization, A.H.O., M.A.B.P., and M.S.M.; methodology, M.S.M., E.A.M.P., Q.K.R.M., I.C.F.S., and K.R.C.O.; software, A.M.M.A. and E.A.M.P.; validation, A.M.M.A., E.K.D.B., and E.A.M.P.; formal analysis, M.S.M., Q.K.R.M., I.C.F.S., and K.R.C.O.; investigation, Q.K.R.M., I.C.F.S., and K.R.C.O.; resources, A.H.O., M.A.B.P., and M.S.M.; data curation, Q.K.R.M., I.C.F.S., K.R.C.O., and E.A.M.P.; writing—original draft preparation, E.A.M.P., E.K.D.B., and A.M.M.A.; writing—review and editing, A.H.O., M.A.B.P, M.S.M., E.A.M.P., E.K.D.B., and A.M.M.A.; visualization, Q.K.R.M., I.C.F.S., K.R.C.O., and E.A.M.P.; supervision, M.S.M. and A.M.M.A.; project administration, A.H.O., M.A.B.P., and M.S.M.; funding acquisition, A.H.O. and M.S.M. All authors have read and agreed to the published version of the manuscript.

6.2. Data Availability Statement

The data presented in this study are available on request from the corresponding author. The data are not publicly available due to restrictions set by the University of the Philippines.

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6.5. Conflicts of Interest

The authors declare no conflict of interest.

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