THE EFFECT OF WALNUT SHELL ASH ON THE PROPERTIES OF CEMENT PASTE AND MORTAR: A STUDY ON PARTIAL REPLACEMENT OF CEMENT

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1. INTRODUCTION

As the world's population grows and urban areas expand, there is an increasing need for construction and building materials. This trend is driving the need for more housing, commercial buildings, and infrastructure projects. Consequently, there has been an increase in the need for materials like cement, steel, wood, and other building products. For centuries, natural materials have been utilized in building construction as a customary practice. However, the expanding demand for building and construction materials has raised concerns about the environmental impact of their extraction and production processes. Natural materials such as wood, stone, and clay are extracted from the earth and processed, which can lead to increased Carbon dioxide (CO₂) emissions. This not only contributes to climate change, but also has a negative impact on local ecosystems and wildlife. Furthermore, the use of natural materials also requires large amounts of energy to extract, transport, and process, which can further contribute to CO₂ emissions.

Concrete is a material found everywhere in society, and it holds the title of being the most extensively utilized human-made item on a global scale. It is widely employed in the construction of structures, such as buildings, bridges, roads, and various other types of infrastructure (Farfan, Fasihi and Breyer, 2019). The primary binding component in concrete is cement, which constitutes roughly 13% of the weight of concrete (Griffiths et al., 2023). In terms of volume, cement typically makes up around 10-15% of a concrete product (Duchesne, 2021). In today's world, cement and concrete are considered to be among the most significant industrial products, with concrete being the second most consumed material in the world by mass, after water. The annual consumption of concrete is estimated to be around 30 billion tonnes, resulting in a per capita production that surpasses all other materials (Monteiro et al., 2017). The environmental impact of cement and concrete production is significant. In 2019, the production, transportation, usage, and demolition of these materials accounted for approximately 9-10% of global energy-related CO₂ emissions, which included carbonate decomposition, fuel combustion, and electricity usage (Griffiths et al., 2023). Cement production was responsible for 77% of the total emissions, while the remaining emissions were mainly attributed to the transport of aggregates for concrete (around 8%), equipment operation for concrete placement on-site (around 8%), and other related activities (around 7%).

As a step towards an eco-friendly future, scientists are investigating ways to incorporate materials that are left over from industrial processes or discarded as waste are being considered for use in concrete, as a means of creating "green" concrete. Incorporation of different supplementary cementitious materials, including Fly ash (Khatib, 2008; Ghanem et al., 2019), slag (Khatib, 2014) and silica fume (Wild, Sabir and Khatib, 1995) has already been implemented in the construction materials. Adding industrial by-products into construction materials offers a cost-effective solution as an alternative to cement, while preserving the mechanical and durability properties of the materials. Nonetheless, there are concerns that the availability of these industrial by-products will decrease in the future, and may not be readily accessible in all regions, particularly in developing countries (Paul et al., 2019). Agriculture is a crucial aspect of human existence, providing the necessary resources to sustain life. With the world population projected to reach 9.7 billion by 2050, the need for increased agricultural production has become more imperative than ever (FAO and OECD, 2019). The disposal of agricultural waste often involves burning or burying, which can lead to negative environmental impacts like pollution and contamination (Karade, 2010). Agricultural activities yield significant quantities of waste materials, such as sugarcane bagasse, rice husk, jute fiber, coconut husk, and cotton stalk, nutshells etc. Asia, on an annual basis, is responsible for the generation of a staggering 4.4 billion tonnes of solid wastes (Spain, 2004). These agricultural by-products present an opportunity for reuse as sustainable construction materials, offering a viable solution not only to pollution concerns but also to the challenges of landfills and the high costs associated with traditional building materials. The combined effects of population growth, urbanization, and technological advancements leading to improved standards of living have contributed to a substantial increase in the volume and diversity of solid waste generated across industrial, domestic, and agricultural sectors (Pappu et al., 2007).
The construction industry has shown an increasing interest in utilizing agro-wastes as a substitute for cement and aggregate. In the pursuit of mitigating environmental pollution and preserving valuable raw materials, researchers have dedicated significant efforts to the development of diverse building materials derived from agricultural wastes. This approach aims to reduce reliance on traditional resources while offering sustainable alternatives. Already, a multitude of agricultural wastes have found applications in the production of bricks and concrete, serving as replacements for clay, aggregate, sand, and cement. Examples of agro-wastes that have been utilized as replacements for cement include Phragmites australis (M.; Khatib et al., 2022; Khatib, ElKhatib, Elkordi, et al., 2023; Khatib, ElKhatib, Sonebi, et al., 2023; Ramadan et al., 2023), bamboo (J. Khatib et al., 2022), rice husk ash (Ramasamy, 2012), saw dust ash (Ikponmwosa et al., 2020) and sugarcane bagasse ash (Jahanzaib Khalil, Aslam and Ahmad, 2021).

Every year, the nut industry generates a staggering number of by-products, with millions of tons discarded globally (Stefanowski, Curling and Ormondroyd, 2017). However, research has shown that these residues can be utilized in various forms to create sustainable building materials (Hamada et al., 2020; Mo et al., 2020; Sujatha and Balakrishnan, 2021a). Different types of nut shells have been tested and found suitable for use in concrete and mortars, as substitutes for cement and aggregate such as cashew nut shell ash (Thirumurugan et al., 2018), coconut shell (Sujatha and Balakrishnan, 2021b), argan nut shell (Akhzouz et al., 2021) and walnut shells (Kamal et al., 2017).

The walnut tree is prevalent across the expansive Asian region, spanning from the Balkans to China (Potter et al., 2002). Its cultivation in Europe dates to as early as 1000 BCE, and it subsequently spread to Mediterranean regions (Martínez et al., 2010). Notably, China, USA, and Iran emerged as the leading walnut producers. In 2019, the world saw an abundance of walnuts with a bountiful harvest of over 3.7 million tons, making it the second most produced nut, following closely behind almonds (Chudhary et al., 2020). The walnut industry generates a considerable number of by-products in the form of shells, which are often disposed in landfills or burned. The shells of walnuts account for 67% of the fruit’s overall weight and are composed mainly of cellulose, hemicellulose, and lignin (Cañellas et al., 1992). Walnut shells have been the subject of various investigations as a potential resource in multiple fields, including the production of particle board (Gürü, Atar and Yıldırım, 2008), MDF panels (Da Silva et al., 2017) and as aggregate replacement in concrete (Cheng, Liu and Chen, 2017; Venkatesan et al., 2021).

The objective of this study is to investigate the impact of varying amounts of walnut shell ash (WSA) used in lieu of cement on cement paste’s consistency and setting time. The study also aims to evaluate the influence of incorporating WSA on key mortar properties such as compressive strength, ultrasonic pulse velocity (UPV), water absorption, and drying shrinkage.

2. EXPERIMENTAL STUDY

2.1 Materials

The cement used in this study was identified as type II Portland limestone cement PA-L 42.5, characterized by a specific gravity of 3.1 and a Blaine fineness of 4060 cm²/g. The walnut shells were burned, resulting in the production of WSA with a specific gravity of 2.5. The WSA was then sieved through a 300 µm sieve size. Table 1 and Table 2 provides the chemical composition of the cement and WSA respectively. The sand used had a maximum particle size of 4.75 mm, specific gravity of 2.65, water absorption 1.41 % and fineness modulus of 2.8.
Table 1. Chemical Composition of Cement

<table>
<thead>
<tr>
<th>Components</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>18.98</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.17</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.59</td>
</tr>
<tr>
<td>CaO</td>
<td>63.27</td>
</tr>
<tr>
<td>MgO</td>
<td>1.06</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.52</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.33</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.33</td>
</tr>
<tr>
<td>Cl*</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>LOI**</td>
<td>6.37</td>
</tr>
</tbody>
</table>

Table 2. Chemical Composition of WSA

<table>
<thead>
<tr>
<th>Components</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>3.63</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.92</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.83</td>
</tr>
<tr>
<td>CaO</td>
<td>24.77</td>
</tr>
<tr>
<td>MgO</td>
<td>3.31</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.82</td>
</tr>
<tr>
<td>K₂O</td>
<td>32.31</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>3.74</td>
</tr>
<tr>
<td>Cl*</td>
<td>1.07</td>
</tr>
<tr>
<td>Na₂Oeq</td>
<td>21.19</td>
</tr>
<tr>
<td>LOI**</td>
<td>26.89</td>
</tr>
</tbody>
</table>

2.2 Mix Proportions:

To investigate the effects of WSA on cement paste and mortar, various mixtures were prepared with different WSA contents. Four paste mixes P₀, P₅, P₁₀ and P₁₅ were created, with one serving as the control (P₀) and the other three mixes incorporating 5%, 10%, and 15% WSA as a replacement for cement. The water required for each paste mixture was determined through consistency test. Additionally, four mortar mixes M₀, M₅, M₁₀ and M₁₅ were formulated using a ratio of 1:2.25:0.55 for cement, sand, and water, respectively. These proportions of materials were selected based on initial trial mixes to achieve adequate workability. In these mortar mixes, the cement content was replaced by WSA at levels of 5%, 10%, and 15%. Table 3 provides an overview of the different paste and mortar mixes used in the study.
### Table 3. Mix Proportions of Paste and Mortar

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Quantity (kg/m³)</th>
<th>W/C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement</td>
<td>WSA</td>
</tr>
<tr>
<td>P₀</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>P₅</td>
<td>475</td>
<td>25</td>
</tr>
<tr>
<td>P₁₀</td>
<td>450</td>
<td>50</td>
</tr>
<tr>
<td>P₁₅</td>
<td>425</td>
<td>75</td>
</tr>
<tr>
<td>M₀</td>
<td>1300</td>
<td>0</td>
</tr>
<tr>
<td>M₅</td>
<td>1235</td>
<td>65</td>
</tr>
<tr>
<td>M₁₀</td>
<td>1170</td>
<td>130</td>
</tr>
<tr>
<td>M₁₅</td>
<td>1105</td>
<td>195</td>
</tr>
</tbody>
</table>

#### 2.3 Samples Preparation and Test Procedure:

To carry out the testing, 10 cubes of dimension 50×50×50 mm were casted for each mix of the mortar, while two-layer compaction was done in metal cube with surface dressing and levelling according to ASTM C109 (ASTM C 109, 2020). 8 cubes were subjected to compressive strength testing and UPV at 1, 7, 28, and 56 days, while the remaining 2 cubes were used to determine water absorption at 28 days. After 24 hours, all the cubes except the ones that will be tested at day 1, are immersed in lime water in storage tank. To determine the drying shrinkage of mortar, three samples were prepared for each mix. The samples were casted in molds with dimensions of 25mm x 25mm x 285mm. After 24 hours, the samples were taken out of the molds and prepared for shrinkage measurements. Two demec points were applied on opposite sides of the samples at 200 mm. The samples were then tested for drying shrinkage in accordance with the guidelines set by ASTM C157 (ASTM C 157, 2017b). Finally, the samples were placed in a constant temperature environment at 25°C.

The determination of normal consistency was conducted using the Vicat Apparatus in accordance with (ASTM C 187, 2016). The setting time was carried as per ASTM C 191 (ASTM C 191, 2021). The UPV test was conducted according to ASTM C 597 (ASTM C 597, 2023). The compressive strength of the cube specimens at 1, 7, 28, and 56 days, was conducted as per ASTM C 109 (ASTM C 109, 2020). Drying shrinkage of the mortar was carried out in accordance with the guidelines outlined in ASTM C 157 (ASTM C 157, 2017a).

#### 2.4 Results and Discussion:

##### 2.4.1 Normal Consistency:

Figure 1 shows the water requirements for achieving consistency in control (0% WSA) and WSA-blended cement pastes. The incorporation of WSA led to a notable rise in the water required for standard consistency, with a 30% increase being observed. The consistency of the control paste (0% WSA) was 30%, while that of the pastes containing 5%, 10%, and 15% WSA was 33.6%, 37%, and 39%, respectively. The rise in water demand can be explained by the larger specific surface area of WSA particles. Similar findings have been reported for agricultural waste ashes used in cement paste preparation (Singh and Rai, 2000; Al-Akhras and Abdulwahid, 2010). Mixing natural or synthetic pozzolans with larger particles than OPC can reduce its consistency (Hossain, 2003). Also, due to its lower specific gravity compared to cement, WSA requires a greater volume to replace the same mass of cement. The greater volume of WSA needed to substitute cement necessitates the addition of more water to achieve similar consistency levels for varying WSA ratios in the mix. Consequently, the total volume expands, necessitating additional water to create a paste with comparable consistency.
2.4.2 Setting Time:

As shown in Figure 2, it is apparent that an increase in the proportion of WSA in blended cement results in a decrease in both the initial and final setting time of cement pastes. The use of 5% WSA led to a substantial reduction of 92% and 52% in the initial and final setting time, respectively. At higher levels of WSA replacement, the final setting time decreased, but the initial setting time remained constant at 5%, 10%, and 15% replacement. By incorporating 15% WSA, the initial and final setting time of cement were reduced by 91.28% and 70.76%, respectively. Various studies have demonstrated that high alkali content can lead to a shorter induction period, a larger primary heat release, and faster deceleration of hydration (Kumar et al., 2012; Ma and Qian, 2018). Similar results were observed in studies that used Hazelnut Shell ash (Baran, Gökçe and Durmaz, 2020a) and Cashew Nutshell Ash (Balasubramanya et al., 2023) as cement replacements. Alkaline accelerator admixtures cause extremely fast setting rather than alkali-free accelerators (Paglia et al., 2001). In this study, the introduction of WSA, which is an alkaline accelerator, resulted in a higher reduction in the setting time of OPC. Coconut shell ash having less amount of alkali oxides results in the retardation of setting time of OPC (Utsev and Taku, 2012).
2.4.3 Ultrasonic Pulse Velocity (UPV):

UPV measurements were taken on all samples with varying WSA proportions after 1, 7, 28, and 56 days as shown in Figure 3. The UPV values for the control mix is higher than that of WSA-based blended mortar which shows a dense and compact structure. However, at day 1 all the specimens exhibit a low UPV less than 3 km/s which shows poor quality. The UPV values for the WSA-based blended mortar were found to be between 3 and 3.5 km/s at days 7, 28, and 56, indicating a satisfactory quality level. In contrast, the UPV values for the control mix were between 3.5 and 4 km/s at the same time intervals, indicating good to very good quality. In general, the UPV of the mortar increased as the curing age was extended, owing to the hydration process. However, the addition of a higher proportion of WSA may have contributed to the reduction in UPV. In general, the UPV of the mortar increased as the curing age was extended, owing to the hydration process. However, the addition of a higher proportion of WSA may have contributed to the reduction in UPV by increasing the porosity of the mortar. This is because the WSA particles may have occupied the spaces between the cement particles, leading to an increase in the voids in the mortar. The presence of more voids in the mortar may have led to a reduction in the UPV. Similar results were found by using cashew nutshell ash as a replacement of cement in mortar (Manjunath et al., 2023a).

![Fig.3: UPV for Mortar with Different WSA Contents](image)

2.4.4 Compressive Strength:

Figure 4 shows the results of the compressive strength at all ages. The results show that the introduction of WSA led to a reduction in the compressive strength of the cement mortars at 1, 7, 28, and 56 days. Specifically, the compressive strength at 28 days decreased by 11%, 22.6%, and 53.2% for M5, M10, and M15 mixes, respectively, compared to the control mix. At 56 days, the control mix had a compressive strength of 37.2 MPa, whereas the WSA blended mortar had compressive strengths of 28, 24, and 14 MPa for M5, M10, and M15 mixes, respectively. After a curing period of 28 days, the cement mortar incorporating WSA displayed a certain level of strength development, though still inferior to the control mix. The compressive strength of mix M0 increased...
by 45% in comparison to its 28-day compressive strength after 56 days of curing. In contrast, mixtures M5, M10, and M15 exhibited only slight increases of 9.5%, 8.9% and 2.2%, respectively, in their compressive strength at the same age. Several studies have demonstrated that incorporating various types of ash, such as bambara nutshell ash, cashew nutshell ash, and hazelnut shell ash, into cement mortars can lead to a decrease in compressive strength (Baran, Gökçe and Durmaz, 2020b; Alaneme and Mbadike, 2021; Manjunath et al., 2023a). In addition, the high content of alkali oxide in WSA can also cause a reduction in compressive strength. This trend has been observed in similar studies using biomass ash with high alkali oxide content, such as corn stalk ash and corn cob ash (Shakouri et al., 2020; Li et al., 2021).

Fig. 4: Compressive of Mortar with Different WSA Contents

2.4.5 Drying Shrinkage:

In Figure 5, the behavior of mortar shrinkage is demonstrated under air-cured conditions, with varying levels of WSA included in the mixture. Mortar with WSA exhibit more drying shrinkage than that of control. At 14 days of dry curing, samples with 5, 10 and 15% with WSA have showed drying shrinkage of -1135.2, -1492.53 and -1362.84 µm/m respectively, which is much higher than that of control with 802.89 µm/m. After 28 days, the mortar containing 10% WSA exhibited the highest drying shrinkage with a value of -1962.79 µm/m, while the control mix had a drying shrinkage of -804.56 µm/m. At 90 days, the drying shrinkage values for M0, M5, M10, and M15 were -1971.48, -2473.91, -3833.84 and -3743.77µm/m, respectively.

Furthermore, the mass loss of the specimens was measured at different ages, and the results are presented in Figure 6. The WSA-blended mortar displayed greater mass loss at later ages compared to the control mortar. At 28 days, the mass loss for M0 was 2.06%, while M5, M10, and M15 exhibited mass losses of 2.72%, 2.343%, and 2.88%, respectively. Similarly, at 90 days, M15 demonstrated the highest mass loss with 3.63%, whereas M0 had a mass loss of 2.18%.

The relationship between drying shrinkage and water evaporation in specimens exposed to the environment is a widely recognized phenomenon. The extent of shrinkage is known to be influenced by the amount of water present during the drying process. Our observations indicate that the mass loss
of specimens increased with time, which may be attributed to the evaporation of excess water present in the pores of the mortar. The greater mass loss observed in WSA blended mortar compared to cement mortar suggests a higher amount of extra water present in the pores of the former. In certain research studies, it was suggested that the rise in drying shrinkage could be attributed to elevated capillary stress and reduced disjoining pressure (Beltzung, Research and 2005, 2005; Sant et al., 2012). Alternatively, it could be due to the heightened porosity of the microstructure caused by the increase in alkali content (Sant et al., 2012). It is possible that all these explanations contribute to the phenomenon observed in the current study.

2.4.6 Water Absorption:

Figure 7 depicts the water absorption results of various mortars with differing contents of WSA. It was observed that all dried samples exhibited a significant surge in water absorption within the first four hours of immersion, with the maximum value of 12.75% observed for the 10 WSA content, while the minimum value was 7.8% for the 0 WSA content. After 48 hours of immersion, the water absorption values for the mortar samples were 8.7%, 11.7%, 12.8%, and 13.15% for 0 WSA, 5 WSA, 15 WSA, and 10 WSA contents, respectively. The percentage increase in water absorption, correlated to the control mortar, was found to be 25.6%, 32%, and 33.8% for 5 WSA, 15
WSA, and 10 WSA contents, respectively. One of the key factors influencing the water absorption of mortar samples is the formation of the pore system (Xiong et al., 2021). An explanation for this observation is that the excessive WSA content results in a shortage of calcium hydroxide, which is required for the reaction, ultimately leading to the formation of pores in the mixture. These pores, in turn, enhance the water absorption capacity of the mortar samples. Similar results were shown with Cashew Nut Shell Ash (Manjunath et al., 2023b) and Pistachio shell ash (Tekin, Dirikolu and Gökçe, 2021).

3. CONCLUSIONS

By examining the performance of WSA as a replacement of cement in paste and mortar, this study has drawn several conclusions from the experimental findings. Based on the test results of the blended cement containing WSA, the following can be concluded:

1- The addition of WSA to cement paste increases the consistency water demand. And as the WSA content increased, the initial and final setting times decreased. For 15% WSA, the initial and final setting times reduced by 91.28% and 70.76%, respectively, compared to the control mix.

2- UPV values exhibit a proportional decrease corresponding to the increase in the content of WSA at 5%, 10%, and 15%. Nevertheless, the use of WSA in mortar production still yields acceptable UPV values of around 3-3.5 km/s, indicating a satisfactory quality of the resulting mortar.

3- The addition of WSA to the mortar resulted in a reduction of compressive strength by 11%, 22.6%, and 53.2% for 5%, 10%, and 15% WSA, respectively, after 28 days. Moreover, the development of strength in WSA blended mortar after 28 days was minimal.

4- WSA blended mortar demonstrated greater drying shrinkage compared to the control group at all ages, with 10% WSA exhibiting the highest shrinkage after 56 days.

5- Mortar containing 10% WSA shows the highest water absorption after 28 days of curing, at 13.15%, which is 33.8% higher than the control mix.

There is a need for extensive research to enhance WSA efficacy and properties, especially in terms of reactivity, hydration, microstructure, and durability. Currently, literature mainly focuses on WSA's effects on mortar and paste properties, but its potential in structural concrete remains unexplored. It is also crucial to investigate whether the higher alkali content of WSA leads to alkali-silica reaction. Interestingly, WSA's high alkali content may make it a replacement for...
commercial alkaline activators in geopolymer concrete and mortar. Therefore, further research is required in this area.

REFERENCES:
- FAO and OECD (2019) *Background Notes on Sustainable, Productive and Resilient Agro-Food Systems*.