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Experimental Investigation of Snail Shell-based Cement Mortar: Mechanical Strength, Durability and Microstructure

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Abstract: Snail shells are the discarded bio-shell waste from restaurants, and oceans creating huge environmental problems for society. Living organisms are harmed when these shells are released. As previously stated, the work focuses primarily on the utilisation of snail shell powder as a raw ingredient in cement mortar. The mechanical and durability features of snail shell-based cement mortar were compared to the nominal mortar in this study. Snail shell powder, ranging from 0% to 35%, was used to partially substitute cement in mortar, with a variation of 5%. XRD (X-Ray Diffraction) was used to determine the chemical composition of both mixes. The mechanical properties of mortar for both mixes were determined using a compressive strength test. The tests on cement mortar viz., Water Absorption, Sorptivity, Acid Durability, and Rapid Chloride Permeability Test (RCP Test) were compared with nominal mortar mix. According to the results of the investigation, the optimum use of snail shell powder is 30%. The durability of both mixes increased by the increase of the snail shell powder. To detect the C-S-H gel formations, microstructural analysis was performed for both mixes.

Keywords: Cement; Snail Shell Powder; Durability Analysis; Water Absorption; XRD & SEM-EDS

1. Introduction

In present days the utilization of cement has been increasing in construction industry. It exhibits an exceptional performance in bonding and strength towards concrete structures. Although cement represents various benefits in concrete structures, but also have negative impacts on the environment [1-3]. Because the manufacturing of cement releases a tremendous quantity of energy. Regardless of energy, a significant amount of Carbon Dioxide (CO2) is released into the environment. Therefore, the reduction in the cement utilization will reduce the CO2 emmission into the environment [4, 5]. The cement industry has been emitting roughly 0.83 kg of CO2 per kg of cement, resulting in a global cement release of 12% by 2020. [5]. Despite the fact that cement releases CO2, it has a brittleness property that causes cracks in concrete constructions. Typically, brittleness of cement composite brought on during formation of hydration products like Calcium Silicate Hydrate Gel (C-S-H Gel), Ettringite (AFt), and Calcium Hydroxide (Ca(OH)2 CH) [3]. In particular, cement composites exhibits high compressive strength but low flexural strength. In general, to enhance the flexural behaviour of cement composite, different types of fibres are included in cement composite [34]. However, the use of fibres were unable to reduce brittleness, it results cracks formation in cement composites structures. So the fibres used in the cement composites could not improve the flexural strength.
To overcome the excess amount of cement usage in construction, alternative waste materials and industrial by-products such as Red Mud, Fly Ash, Ground Granulated Blast Furnace Slag (GGBS), Snail Shells, Clamshells, and Glass can be used by replacing certain quantity of cement in concrete structures. [5-8, 35]. Thorough research was done on cement composites worldwide because cement is the principal constituent in the constructions. Snail shells are the one composite material that shows similar properties to cement. Snail shells can replace cement or aggregates in concrete or mortar composite [9].

Snail shells are the waste product from the restaurants and represents the spherical shape found in the coastal regions. According to the Food and Agriculture of the United Nations (FAO), 16.1 million tons of snail shells are produced annually [15]. Previously, the shells are used with aggregates in the construction works [10]. To the best of my knowledge, using the shells like clams, snails, oysters in the partial or full replacement of cement in concrete production, which reduces the cement usage in concrete constructions. [10, 11]. Some other materials such as GGBS, red mud, silica fume were also utilized to replace cement in the world [5]. In the same manner, agricultural wastes such as sawdust and rice husk ash were employed as admixtures in cement composites in another study [12-14].

The snail shells are dumped as waste material in empty lands due to less waste management. Snail shells possess a pozzolanic nature like cement. In the present work, snail shells were used to replace cement as a cementitious material partially. These are collected from nearby coastal areas belonging to the group of exoskeletons that have rigid and resistance and play a major role in the construction. Due to these shells contains calcium carbonate (CaCO$_3$), which represents the hardness property and shows plenty of potential benefits. It is a more effective and more economical way of getting rid of waste. Incorporating shells in the cement industry will preserve natural resources. The cement mortar obtained from the snail shell powder can be considered a sustainable composite by producing green composites than the conventional constructions [16, 17]. Not many investigations were done on snail shell-based cementitious material in mortar. An added advantage of these discarded shells with cement replacement was assumed. There are various opinions on the usage of snail shells in cement, and their uses were explained by various authors.

Orlando Ketebu et al., (2017) [22] done the work on ashes of snail shells and clamshells are as a replacement of cement due to its pozzolanic properties with a percentage of 0 % to 30 % by weight of cement. The maximum compressive strength obtained at 20 % cement replacement with snail shell ash is 20 MPa, and the strength with clamshells is about 30 MPa at 25 % replacement of cement with clamshells. They described that the compressive strength decreased with an increase of snail and clam shells ash and the optimum percentages of 20 % and 25 % for snail and clamshells.

N. Devendran (2017) [35] worked on Sea Shells are considered in the form of powder, and some of the shells are broken into pieces, used as replacement of coarse aggregates because of their toughness. The maximum compressive strength was obtained at 15% replacement of Cement with Sea Shell powder, and 15% of coarse aggregates are replaced with Sea Shell pieces and is 35.4 MPa compared with nominal concrete of 33.1 MPa.

Syed Talha Zaid et al., (2014) [21] considered the snail shell is in the form of powder and added parts in cement with 0 % to 20 % to acquire the mechanical strength. The compressive strength is maximum at
5% replacement of snail shell powder with cement is 21.42 MPa for 7 days and 31.52 MPa for 28 days and starts to decrease with increasing powder.

Othman et al., (2013) [36] adopted the cockle shells ash for replacement of cement with 0 %, 5 %, 10 %, 15 %, 25 %, and 50 % for a curing period of 7, 28, 90 days, and 120 days. The water to binder ratio is 0.54 adopted for all mixes. The mechanical strengths are maximum at 5 % replacement of and are about 40.28 MPa and decreased from then. Consecutively, the modulus of elasticity increases for 10 % of replacement but is less than 5 % and is 22.2 MPa. Table 1 shows some of the literature on the snail shells incorporated in the constructions.

**Table 1. Experimental Investigation on Snail shell Powder in Cement**

| Name of the Research Reference | Type of shell | Usage in cement composite |
|--------------------------------|---------------|---------------------------|
| Varhen et al., 2017 [18]       | Peruvian scallop | Replacement of F.A.       |
| Lalitha and Raju, 2014 [19]    | Scallop shells  | Replacement of C.A.       |
| Kumar et al., 2016 [20]        | Shells of cockle| Replacement of C.A.       |
| Syed Talha Zaid et al., 2014 [21]| Snail shells Ash| Partial Replacement of Cement |
| Orlando Ketebu et al., 2017 [22]| Mollusc and Clams shells Admixtures | Replacement of Cement and F.A. |

As per the literature, there is necessary to estimate the extended life behaviour of snail shells in cement replacements. The present work was executed on distinctive mechanical, durability and microstructural properties to fill this research gap. In the present study, snail shell powder (SSP) is used by the replacement of cement for the formation of pozzolanic activity. In this, snail shell powder is replaced with cement partially with ranges of 0%, 5%, 10%, 15%, 20%, 25%, 30%, and 35% by weight of cement used.

2. Materials and Methods

2.1 Materials

Ordinary Portland cement of 53 grade is used in the present work from KCP Cements, Guntur, Andhra Pradesh, confirmed with ASTM C 150-19 [23]. The snail shell powder is confirmed with ASTM C 618-08 [24]. The preliminary tests were done on the cement and snail shell powder of specific gravity, fineness, and specific surface area. The specific gravity for cement and snail shell powder was 3.16 and 2.41. Fineness for both the materials is 5%, and the specific surface area of cement and snail shell powder is 331 m²/kg, 19,000 m²/kg. The fine aggregates of size 2.36 mm are considered and confirmed with BIS, IS 383-2016 [25].

2.2 Snail Shell Powder Preparation

Snail shell powder is used in the present work, which is extracted by grinding the snail shells which were considered. The following points represents the process of snail shell production.

a. Firstly, snail shells are collected from Bapatla Coastal Area, Guntur, Andhra Pradesh, free from organic matter.

b. Wash them with clean water until the constituents like flesh in the shells were free and keep them under sunlight until dry.
c. Grind the shells into powder, sieve the powder in 90µm and keep the powder in an air-tight container.

XRD analysis is presented in Fig. 1. The major constituent of snail shell powder is Aragonite (CaCO$_3$) with a high dominion of 20 = 26° and 33°. Quartz (SiO$_2$) is the second principle constituent of snail shell, observed at various ranges of 2θ (46, 48, 53, and 58°). The significant peaks of cement observed in cement are Portlandite (18°), Quartz (24, 28°), Alite (31, 33°), and Belite (35, 36°), other constituents observed at various ranges of 2θ presented in Fig. 1. The chemical composition of cement and snail shell powder is shown in Table 2.

Table 2 Chemical composition of Pozzolans

| Chemical Constituent | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO  | MgO  | K$_2$O | Na$_2$O | SO$_3$ | TiO$_2$ | P$_2$O$_5$ | Mn$_2$O$_3$ | LOI |
|----------------------|--------|-------------|------------|------|------|-------|--------|-------|--------|-----------|------------|-----|
| Cement               | 64.12  | 4.95        | 3.18       | 65.89| 1.8  | 1.02  | 0.61   | 1.95  | -      | -         | -          | 0.35|
| Snail shell powder   | 33.52  | 4.78        | 3.17       | 54.89| 1.10 | 0.98  | 0.25   | 0.03  | 0.12   | 0.21      | 0.02       | 1.42 |

Fig. 1. XRD Analysis of Snail shell powder

2.3 Calculations of Mix

The mix proportion of cement composite mortar is 1:3:0.42, confirmed with I.S.: 2250-1981 [26]. Therefore, in that one portion Represents (OPC+SSP), three portions of Fine aggregates and 0.42 of Water/ Cement ratio is required. Table 3 represents the mix calculations needed in the present study.
Table 3. Required Mix Calculations

| Sample Mix | Cement | Snail Shell Powder (SSP) | Fine Aggregates | Water Required |
|------------|--------|-------------------------|----------------|----------------|
| C0S        | 300    | -                       | 450            | 150            |
| C5S        | 285    | 15                      | 450            | 150            |
| C10S       | 270    | 30                      | 450            | 150            |
| C15S       | 255    | 45                      | 450            | 150            |
| C20S       | 240    | 60                      | 450            | 150            |
| C25S       | 225    | 75                      | 450            | 150            |
| C30S       | 210    | 90                      | 450            | 150            |
| C35S       | 195    | 105                     | 450            | 150            |

2.4 Compressive Strength Test

The compressibility test is performed on the mortar specimens of size 70.6 mm*70.6 mm*70.6 mm, confirmed with I.S.: 516-2013 [27]. Then, the samples were casted and kept in the water bath for 28 days for the hydration process as stated by I.S.: 9013-1978 [28]. Fig.2 shows the compressive strength test setup.

![Compressive Strength Test](image)

2.5 Water Absorption Test

A water absorption test was conducted on the specimens which were cured for 28 days in water. Then, taken out the samples and kept in the oven for 72 hrs at a temperature of 100°C, which is confirmed with I.S:1199 (1959) [29]. Discard the samples from the oven after 72 hrs and weigh them. Note the oven-dry weight of samples and note it as $W_1$. Later keep the specimens in a water bath for 24 hrs to know the wet weight and report it as $W_2$. By using equation 1, water absorption has been calculated and is represented in "%.

$$W.A \ (Water \ Absorption) \ (%) = \frac{W_2-W_1}{W_1} \times 100$$

Where, $W_1$=Weight of Oven Dried Sample, $W_2$=Wet Weight of Mortar Sample
2.6 Sorptivity Test

A water penetration value is evaluated using Sorptivity in a prescribed time and confirmed with ASTM C 1585-20 [30]. The disc of 50mm thickness and 100mm of diameter is considered for the test. A non-absorbent coat like silica gel is applied on all disc surfaces except the surface exposed to the water surface. Figure 3 represents the setup of the Sorptivity test. First, the penetration of water from the exposure is determined concerning time. Then, the Sorptivity values are calculated by using equation 2.

\[ S = \frac{i}{\sqrt{t}} \]  

Where \( S \)=Sorptivity (mm/min0.5), \( i = \frac{\nabla W}{A \cdot d} \), \( \nabla W \)=Weight of samples concerning time, \( d \)=density of water, \( t \)=Elapsed time in minutes, and \( A \)=area of the disc.

![Fig 3. Sorptivity test setup](image)

2.7 Rapid Chloride Permeability Test

RCP Test was conducted to determine the electrical conductivity of the Cement + SSP composite mortar as per ASTM C1202-12 [31]. The discs are prepared with sizes of 50mm height and 100mm diameter. The specimens are placed between the reservoirs of RCP Test cells filled with 3% of NaCl and 0.3M NaOH, and these were used as negative and positive terminals. Fig 4 represents the setup of RCP Test samples. The flow of electricity between the two reservoirs can determine by Coulombs of equation 3.

\[ RCP T = 900 \times 10^{-3} \left( (I_0 + I_{360}) + 2(I_{60} + I_{90} + I_{120} + I_{150} + I_{180} + I_{210} + I_{240} + I_{270} + I_{300} + I_{330}) \right) \]  

Eq. 3
2.8 Acid Durability Test

2.8.1 Mass Loss

The casted and water cured samples of size 70.6mm*70.6mm*70.6 mm are taken and kept in the oven for 72 hours at a temperature of 100°C to avoid moisture from specimens. Thereafter, take out the samples from the oven and note the mass of samples as \( W_o \). Subsequently, prepare an acid solution of 5% concentrated \( \text{H}_2\text{SO}_4 \) with a pH of 0.3 which is maintained constant until the end of the test. Immersed samples in the acid solution for about 28 days. Finally, remove the samples from acid, keep them under running water, and take mass as \( W_a \). The percentage loss of mass gives the durability under acid solution and is calculated using equation 4.

\[
A = \frac{W_o - W_a}{W_o} \times 100
\]

Where \( W_o = \) Mass of oven samples, \( W_a = \) Mass of Acid Samples

2.8.2 Dimension Loss

Dimension loss is also a factor in the durability analysis. Edges of specimens are marked as \( L_1, L_2, L_3, \) and \( L_4 \) and measured diagonals lengths as \( L_1, L_4 \) and \( L_2, L_3 \). Dimensions of samples were determined before placing them in an acid bath. Remove all samples from the acid bath after 28 days, keep them under the running water, and measure the diagonals. The loss of dimensions gives durability. Figure 5 represents the setup of dimension measurements.
2.9 Microstructural Studies

Scanning Electronic Microscopy (SEM) analysis is conducted to analyze the morphological behaviour of mortar samples. The samples are collected from the mortar of 10mm*10mm*5mm, which are smooth surfaces. Energy-dispersive spectroscopy (EDS) analysis is also conducted on the same samples to know the compositions of elements constituted in the samples. Moreover, the X-Ray diffraction (XRD) analysis was performed on the powder sample of 90µm and analyzed in X’Pert High Score software.

3 Results and Discussions

3.1 Compressive Strength

The mix proportion of materials are represented in table 3 with various proportions of snail shell powder in place of cement. From the compressive strength test, the maximum strength of 25.279 MPa and 38.89 MPa is obtained for C30S at 7 days and 28 days of curing and observes the decrement in strength from then presented in Fig 6. It has been observed that the strength increased up to 72% of C30S for 7 days and 28 days compared to C0S. Due to the high specific surface area of snail shells, which represents the increased strength properties when mied with cement composites. Due to this, the pores in the mortar are refilled with snail shell powder particles and trapped the air.

Moreover, the portlandite, silicates and aluminates in snail shell powder accelerate the hydration process and gain strength at an early age than nominal mixes. The formation of C-S-H gel in the hydration process increases the strength of snail shell-based cement mortar [21, 22]. SEM images reveal the reason behind the increment of strength is the formation of Ettringite. The Ettringite helps to improve the hydration process and reduce shrinkage.

![Fig 5. Dimensions Measurements](image-url)
3.2 Water Absorption Test

The water absorption values of all the samples decrease with an increase of the snail shell powder is observed in Fig 7. The water absorption values of mix samples reduced from 8.29 - 3.53 and 5.12 - 2.5 for 7 & 28 days of curing and increased from C35S. The value of water absorption has reduced due to curing and the size of the shell powder [33]. The fineness and specific surface area of shell powder also play a significant role in water absorption because the finer particles settle on the pores and decrease the voids.

3.3 Sorptivity Test

Absorption of water through capillary suction determined for 28 days water cured samples and is presented in Fig 8. The absorption of water called Sorptivity is decreasing along with the increasing of snail shell powder. The Sorptivity values decrease from 0.58194 mm/min$^{0.5}$ for C0S to 0.10912 mm/min$^{0.5}$ for C30S and increase from then. The capillary action decreases with increasing snail shell powder due to its higher specific surface area. Voids that are formed due to sand particles are filled with snail shell powder and forms dense structures. The pozzolanic reaction developed in mortar is due to the filling
nature of voids with snail shell powder. The Sorptivity values decrease with the increase of snail shell powder in mortar because voids, pores, and cracks are filled with powder. The bars in Fig 8 represent the capillary action distribution in decremental order of frequency, with a cumulative line on a secondary axis as a percentage of the total capillary action.

![Fig 8. Sorptivity for Different mixes](image)

3.4 Rapid Chloride Permeability Test

In the present work, the passage of chloride ions to the SSP cement composite has been investigated for samples of a curing period of 28 days. Fig 9 represents the passage of charge in the SSP cement composite at a respective time. The passage of coulombs has been reduced from 580 Coulombs of C0S SSP to 99 Coulombs for C30S SSP. The passage of current is decreased with an increase of snail shell powder in cement. It is because the pores in the composite are filled with fine snail shell powder. The decreasing of coulomb starts from 35% (C35S) replacement, decreasing the pozzolanic nature and less formation of C-S-H gels. A

![Fig 9. RCP Test values for mixes](image)
The RCP Test values are correlated with the values which are presented in table 5. These values are confirmed with ASTM C1202-12 [31]. According to table 4, the lesser the permeability values lesser the charge passage (coulomb), and the higher the resistivity.

**Table 4.** Correlated Values for RCPT [30]

| Charge (Coulombs) | Chloride Permeability |
|-------------------|-----------------------|
| >4000             | High Permeable        |
| 2000-4000         | Moderate              |
| 1000-2000         | Low                   |
| 100-1000          | Very Low              |
| <100              | Negligible            |

3.5 Acid Durability Analysis

3.5.1 Mass Loss and Dimension Loss

The mass and dimension loss due to the immersion of all specimens in 5 % of H$_2$SO$_4$ are presented in table 5. It is clearly evident that C30S has less loss of mass and dimension like 10 and 1.8 and increases from then. The loss is decreasing from C5S is due to the incorporation of snail shell powder in place of cement and forms a dense structure. This decrease of loss is continuous up to C30S and starts increasing from then. On the other hand, the loss is increasing from C35S due to increasing of snail shell powder and forms a loose structure.

**Table 5: Mass loss and Dimension loss of Mix samples**

| Sample  | C0S  | C5S  | C10S | C15S | C20S | C25S | C30S | C35S |
|---------|------|------|------|------|------|------|------|------|
| Loss of Mass (%) | 25.9 | 18.2 | 17.0 | 16.5 | 15.4 | 14.1 | 10.0 | 12.6 |
| Loss of Dimension (%) | 15.3 | 12.4 | 11.8 | 7.6  | 5.9  | 4.7  | 1.8  | 4.1  |

3.6 Microstructural analysis

3.6.1 X-Ray Diffraction Analysis

XRD analysis is performed on the mixes to identify the mineral phases. Fig 10 represents the XRD of snail shell cement mortar with various replacements. Quartz, Portlandite, and Ettringite were observed from the analysis. Ca (OH)$_2$ (Portlandite) has the property to uphold the solutions releases during the hydration process and improve the formation of C-S-H gel. Ettringite $[\text{Ca}_3\text{Al}_2(\text{OH})_6(\text{SO}_4)_3\cdot26\text{H}_2\text{O}]$ is the major complex structure that helps for the formation of C-S-H gel. The present study stated that a higher amount of Ettringite and Portlandite were observed for the C30S mix.
3.6.2 SEM & EDS Analysis

SEM analysis is performed on different mixes to know the morphological behaviour. EDS test is to understand the compositions of elements in the mixes. Fig 11a-h represents the SEM images of snail shell cement mortar. It was observed from the SEM Analysis and the formed structure is dense. It is because the finer particles in snail shell powder occupy the pores results in less porosity. Fig 9a-h represents the energy dispersive spectroscopy of all the mixes. The Calcium/Silica (Ca/Si) ratio ranges from 0.8-2.5, proving the formation of C-S-H gel in mixes [32, 33]. The results show that at 30%, cement replacement with snail shell (C30S) has a lesser Ca/Si ratio. It states that the lower the Ca/Si ratio, the higher the formation of C-S-H gel and vice versa.
Energy Dispersive Spectroscopy graph shows that the energy peaks that overlap the elements. The elements like O, Al, Ca, Si, and S were observed, and the energy spots were observed from SEM images. Table 6 represents the atomic weights of the elements detected from EDS. The elements from Fig 12a-h are responsible for the formation of C-S-H gel during the hydration process.
4. Conclusions

The following conclusions were drawn purely from the investigations done on snail shell powder-based cement mortar-like microstructural analysis and durability properties.

- Snail shell powder is composed of a high amount of calcium and silica. This results in greater strength at a primitive time than nominal mortar mix.
- All mixes have greater strength improvement with an age of curing, but C30S has observed more strength than all mixes. The strength improvement is because of the high alkaline nature of snail shell powder that accelerates pozzolanic activity between cementitious materials.
- Pores, cracks, and voids in mortar are sealed with snail shell powder during the hydration process. And also, C-S-H gel formed in the hydration process resulting in a dense structure in mortar. The effectiveness of snail shell powder mortar has been identified in Sorptivity, Water Absorption and RCP Test.
- In C30S mix sample shows less amount of Ca/Si ratio resulting from achieving greater strength.
- SEM images show the dense structure, leading to more strength than the nominal mortar mix.
- Microstructural analysis was disclosed that the formation of Ettringite results in C-S-H gel formation than the nominal mix.
- The values obtained from all experiments prove that the snail shell powder mortar can replace nominal mortar in all Civil Engineering Aspects.
This research highlights the usage of snail shell powder mortar, and further research has been developed in constructional fields by considering some aspects.

(i) The snail shell powder will lead to sustainable By-products as a cementitious material that releases less CO\textsubscript{2} than a nominal mortar.

(ii) It lessens the use of cement in all civil engineering constructions.

(iii) 30\% replacement of snail shell powder-based mortar can be recommended from the results.

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Conflicts of Interest

None

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Figure 1

XRD Analysis of Snail shell powder
Figure 2

Compressive Strength Test
Figure 3

Sorptivity test setup
Figure 4

Setup of RCP Test
Figure 5

Dimensions Measurements
Figure 6
Compressive Strength for Different mixes

| Mix  | 7 Days | 28 Days |
|------|--------|---------|
| C0S  | 7.241  | 11.14   |
| C5S  | 11.655 | 17.93   |
| C10S | 14.203 | 21.85   |
| C15S | 15.854 | 24.39   |
| C20S | 20.87  | 32.1    |
| C25S | 23.19  | 35.68   |
| C30S | 25.279 | 38.89   |
| C35S | 23.953 | 36.85   |

Figure 7
Water Absorption for different mixes

| Mix  | 7 Days | 28 Days |
|------|--------|---------|
| C0S  | 8.29   | 5.12    |
| C5S  | 7.6    | 4.17    |
| C10S | 7.21   | 3.77    |
| C15S | 6.27   | 3.55    |
| C20S | 5.94   | 2.89    |
| C25S | 4.38   | 2.9     |
| C30S | 3.55   | 2.5     |
| C35S | 4.39   | 3.9     |

Figure 8
Sorptivity for Different mixes

Figure 9

RCP Test values for mixes
Figure 10

XRD Analysis of mixes
Figure 11

SEM images of a.C0S, b.C5S, c.C10S, d.C15S, e.C20S, f.C25S, g.C30S, and h.C35S
Figure 12

EDS images of a.C0S, b.C5S, c.C10S, d.C15S, e.C20S, f.C25S, g.C30S, and h.C35S