

UTILIZING THE WASTE SNAIL SHELL AS A SOURCE OF CAO IN WHITEWARES

Md. Minhajul Islam¹, Abdullah Al Mahmood², Md. Bodiul Islam³ and Md. Manwar Hossain⁴

^{1,2,3,4}Department of Glass and Ceramic Engineering, Rajshahi University of Engineering & Technology, Kazla, Rajshahi-6204, Bangladesh.

ABSTRACT

Environmental and financial concerns have driven the use of substitute raw materials in ceramic manufacture become popular. The primary goal of this study is, using naturally wasted snail shell (calcined at 1000°C for 24 hours) as a source of conventional Calcium Oxide and feldspar in manufacturing whitewares. In ceramics body, they improve mechanical qualities, minimize firing temperature and promote to vitrification. By utilizing the calcined snail shell, this will reduce the cost of raw materials and depletion of natural sources. The renewable waste snail shell, mostly consisted of calcium carbonate (CaCO₃), feldspars with trace elements amounts of magnesium. This work replaced CaO at 0%, 8.00 and 18.78% substitution levels by processing waste snail shells into a fine powder and including different amounts into typical whiteware's compositions such as porcelain. Thorough characterization was done assessing their mechanical and chemical compositions by measuring important parameters including bulk density, and flexural strength, EDX and XRD help to evaluate how substitution affects on material's performance.

INTRODUCTION

The major component of snail-shell is CaCO₃, collected from ponds, river, lake from different local areas. The majority of a snail's shell contains calcium carbonate, and snails are abundant in nature. Here, they have been successfully used to create hydroxyapatite (HAp) nanorods using a quick and easy microwave irradiation process using EDTA as a chelating agent [1]. The most famous crystalline form of calcium phosphate is hydroxyapatite, or Ca₁₀(PO₄)₆(OH)₂, HAp. This mineral is present in large amounts in vertebrates and teeth [2]. Seashells consist of 98% CaCO₃, 0.79% MgCO₃, and 0.15% SrCO₃ [3]. The seashell waste exhibits a significant calcium content, serving as a source for CO₂ absorption [4]. Kaplan (1998) states that seashells are primarily composed of CaCO₃, with 95–99% of their composition being CaCO₃ [5]. However, when subjected to a specific heating temperature, they yield a singular metal oxide, CaO. According to Kwon et al. (2004), seashell waste serves as an effective reagent for the removal of phosphorus from wastewater [6]. Various regions of Thailand are home to mussels, cockles, and scallops. Shell waste is a major byproduct of the processing of shellfish such as mussels, cockles, and scallops, which are produced in vast quantities [3]. Limestone and dolomite are non-renewable resources from which calcium oxide is extracted. Because of its current widespread use, the resources needed to create CaO are dwindling. Commercial CaO is also more costly and has a high production cost. Instead of using CaO derived from non-renewable resources, a variety of renewable CaO alternatives are being considered. One renewable material resource is calcium oxide, and eggshells are considered a source for its production [7], [8]. There have been numerous papers on CaO catalyzed transesterification utilizing laboratory grade, and it is clear that CaO is a promising heterogeneous catalyst among those currently utilized in transesterification. The compound is inexpensive, found naturally (in limestone, for example), and can be sourced from some renewable sources (waste material made of calcium carbonate, CaCO₃ [9]. The catalyst made from used shells not only recycles the waste but also paves the way for renewable catalysts. Making use of these trash items does more than only saves money on the catalyst and encourages a procedure that is kind on the environment. These shells can potentially be used in other significant organic reactions that are catalyzed by bases, which will increase the value of the waste they produce [10]. Dolomite used for refractory purpose should be firm and compact with uniform texture including very low amounts of iron, silica, alumina etc. This is due to these contaminants adversely influence the refractoriness of dolomite refractories [11]. Researchers are interested in studying the biocompatibility and mechanical qualities of synthetic HA, which is synthesized from different waste sources. In order to make better use of the waste materials, researchers have found a

way to incorporate them into the synthesized HA as a source of calcium. Many types of waste materials are being utilized in research, such as sea shells [12] egg shells [13], animal bones [14], and fruit waste extracts [15]. CaCO_3 has the ability to substitute metal and ceramic in implantations and shares many characteristics with human bone, making it an important material in orthopedy applications [16]. To a large extent, the exceptional characteristics displayed by nanoparticles (NPs) are responsible for this advancement. This material has unique characteristics compared to its bulk form, such as a larger surface area to volume ratio, smaller particle size, different shape, charge, and magnetic properties. Nanoparticles (NPs) show improved chemical efficacy and practicability at lower temperatures, which has led to novel research and applications in areas including electronics, materials science, medicine, and more [17].

Using the thermal decomposition method, this study was synthesised Snail-ash to check the mechanical and physical properties of whitewares with XRD and EDS characterization. Then it was compared the effects of adding Snail-ash to whitewares with and without the substitution of CaO with bone ash. The substantial study that was conducted to test the qualities of whiteware yielded valuable insights.

MATERIALS AND METHODS

Specifically, one batch composition was made for CaO, while two other batches were made for snail Ash. The components used in this project were sourced from the Nano-synthesis facility at RUET's Department of GCE. Among the elements contained in potash feldspar are Potassium (K), network modifier of glass or ceramics component reduces the maturing temperature as well as single cation Sodium (Na), Aluminium (Al) is the intermediate molecules modify crystal structure, Quartz (SiO_2) gives main strength and structure, Oxygen (O), and many more. After collecting snails from various ponds, rivers, and lakes, they were processed with a ball mill for five hours. Kaolinite is a source of aluminium silicate minerals, whereas quartz offers silica [18]. Firstly, carboxymethyl cellulose (CMC) was utilized for binding they were removed at sintering process. XRD and EDX for materials characterization to make sure we looked at the mechanical, physical, and chemical qualities of the whiteware samples snail ash added to them. While the thick paste was at room temperature, the UTM machine (UH64200) delivered a compressive force of 14 N/mm². Under that pressure, the sample was maintained. A 35 mm width and 75 mm length made up the mould. Because of the documented success of conventional bar- making procedures such compression moulding in the creation of abrasive materials, these methods were employed to manufacture the abrasive bar[19].

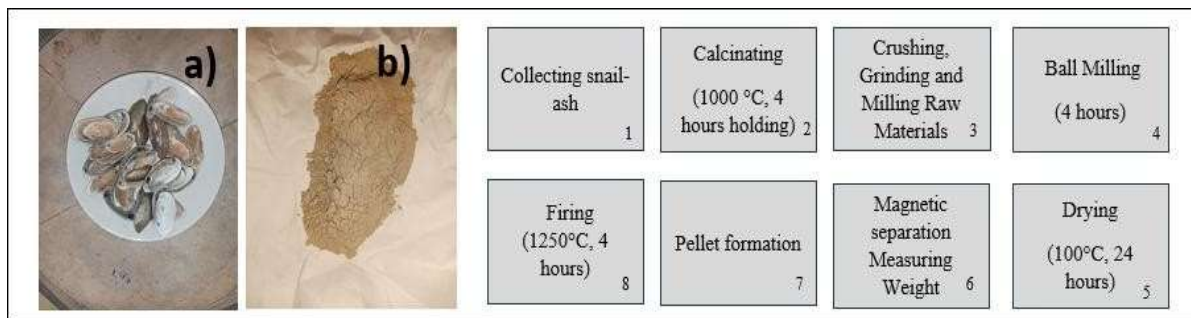


Figure 1 Preparation of Whiteware body .

Figure 1 shows the process of producing whiteware sample a) calcined snail ash and b) grinded powder of calcined snail another (1 to 8 describes the whole process of making samples).

MECHANICAL PROPERTIES

Impact Strength

The 'Izod Impact Tester' was used to evaluate impact strength in the lab. The standard calculation for calculating impact strength is as follows: the ASTM specimen dimensions are 64 x 12.7 x 3.2 mm. The Impact strength was tested by using Izod Impact Testing machine,

$$S = \frac{12I}{t^2} \quad (1)$$

Compressive Strength

The resistance to size reduction under compressive stress is known as the compressive strength of a material. The fact that the materials can withstand substantial loads is another proof of their strength. One way to measure compressive strength is via a UTM, or universal testing machine. Finding the compressive strength of a sample begins with measuring its diameter and thickness. The two compressive plates were used to position the specimen. A force was applied to the specimen by means of the movable head. There were multiple measurements taken of the load and the contractions that went along with it. The specimen fell as a result of the application of load. All of the components were linked to a graph-generating program, and the compressive strength was determined by the UTM (HUT106) through this formula based on the graph. Compressive strength in MPa or N/mm² [19], [20]

P: Applied load or force at failure (in N or kN)

A: Cross-sectional area of the specimen (in mm² or m²)

$$\text{Compressive Strength} = \frac{P}{A} \quad (2)$$

Bending Strength (MOR)

The 'Three Point Bending Tester' was used to conduct the MOR test in accordance with the ASTM D-790M standard test procedure in the laboratory. The bending strength was determined using the formula:

$$MOR = \frac{3FL}{2bd^2} \quad (3)$$

Vickers Hardness Test

Hardness refers to the strength or impermeability of the substance. To find the Vickers hardness, the ASTM E384 standard approach was used. We found the average of the two diagonals by measuring their lengths. After that, the testing sample was hit with the required square base pyramid-shaped diamond indenter for the exact time of the impact utilizing Struers Duramin-1, and the test force (load) F was delivered to it. The object's hardness was calculated using these parameters.

$$HV = \frac{1.854F}{D^2} \quad (4)$$

HV: The Vickers hardness

F: The applied load in kilograms-force

D²: The area of the indentation in square millimeters.

Density Measurement

The amount of mass contained in a specific volume is called its density. The mass-to-volume ratio is the standard definition. Dividing the mass of an object by its volume yields its density. Multiplying the length, breadth, and thickness of an object yields its volume. The ASTM C 559 standard process is a reliable way to evaluate dry bulk density.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \quad (5)$$

Porosity Measurement

Whitewares suffer from excessive porosity when heated to a point when HAp turns liquid and fills the interior gap. Porosity measurement was performed using the following equation:

$$\text{Porosity (\%)} = \frac{\text{Soaked weight} - \text{Dry weight}}{\text{Soaked weight} - \text{Suspended weight}} \times 100 \quad (6)$$

Percentage Firing Shrinkage

$$\text{Firing Shrinkage (\%)} = \frac{\text{Initial dimension} - \text{Fired dimension}}{\text{Initial dimension}} \times 100 \quad (7)$$

RESULTS AND DISCUSSION

Insulating ramming mass made of refractory raw materials from Nigeria, with mica and calcium aluminate as pore formers, can line melting furnaces and ceramic kilns. The sample containing with different composition was tested and data analyzed with the above equation.

Table 1 Mechanical and Physical analysis

Tests	CaO	Snail-ash	Snail-ash
	18.78 gm	10.78 and CaO 8.00 gm	18.78
Impact Strength (J/cm ²)	1.12	1.15	1.20
Bending Strength (MPa)	68.04	70.09	71.23
Porosity	3.08	2.21	1.06
Density (g/m ³)	1.32	1.45	1.55
Percent Firing Shrinkage (%)	0.25	0.29	0.35
Micro-hardness	499	517	535
Compressive Strength (kN/cm ²)	18.57	19.05	20.31

The samples yielded values ranging from 1.37 to 3.95 KN/cm². These numbers are excellent since they exceed expectations [11]. The following properties were seen to change as the proportion of additives increased: density, hardness, MOR, apparent porosity, Table 1. describes different mechanical data and result sheet. When tested for efflorescence, every single brick sample fell within the permissible range that is, between slight and moderate [21] . The apparent porosity decreases as the firing or sintering temperature increases the vitrification process, which takes place at high temperatures and causes the particles to fuse into a cohesive body with glassy phase, is responsible for the lowering of porosity. Pores constrict during this procedure [22]. Other raw materials were same the main variation was in percentage of CaO and snail ash. For finding the effects of snail ash in whitewares body with respect to CaO, snail ash was taken larger amount, for having HAp some properties changes dramatically, if snail ash was taken in small amount in preparing whitewares samples the properties may be changed slightly. According to the results, out of all the minerals in the clay sample, kaolinite contains the most. The results of this investigation indicate that the clay sampled is kaolin. The clay mineral found in Baddegi primarily consists of quartz, with trace quantities of kaolinite, illite, and rutile. According to the results, out of all the minerals found in the clay sample, quartz contains the most.

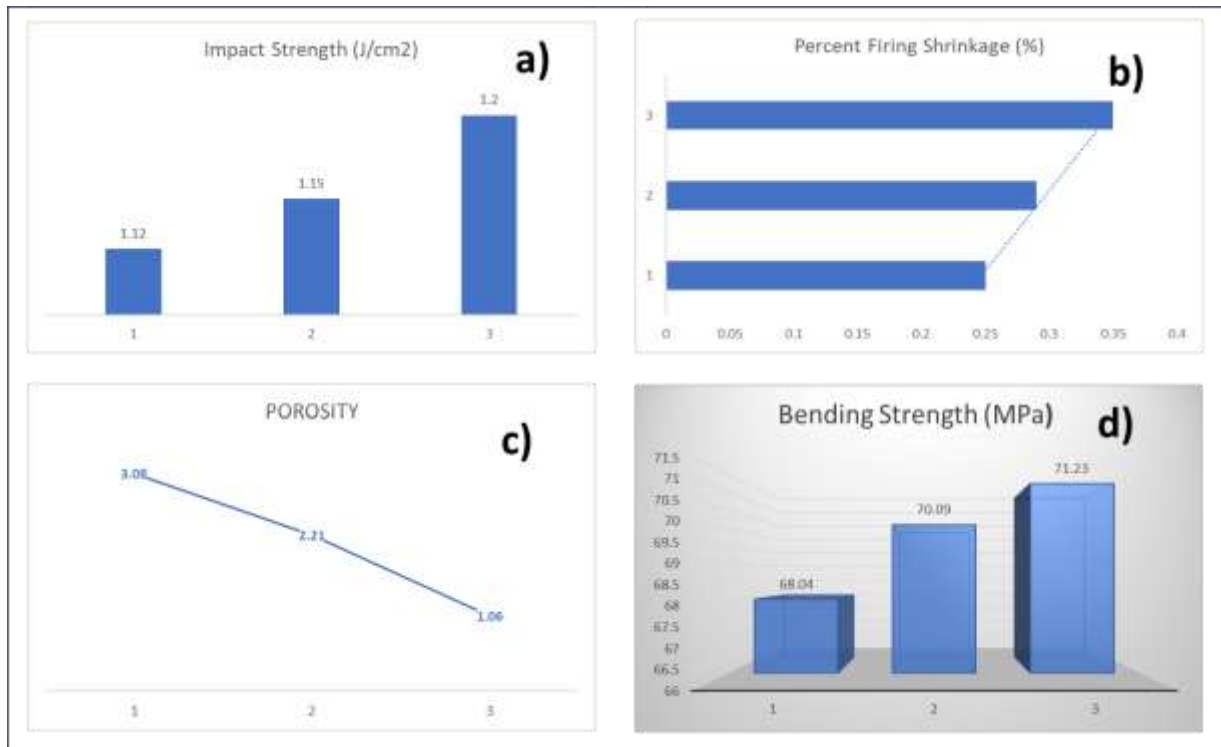


Figure 3 a) Impact strength, b) firing shrinkage, c) porosity and d) bending strength of whiteware Samples containing with, sample 1. CaO(18.78 g), 2.snail(10.78 g)+ CaO(8.00g) and 3. snail(18.78 g) The results of the analysis indicate that the clay that was tested is ball clay. All three samples have a water absorption rate that is above average; nevertheless, a brick with a rate below 7% will perform better. protection from freezing. Bricks' water resistance is proportional to their porosity [23].

XRD Characterization

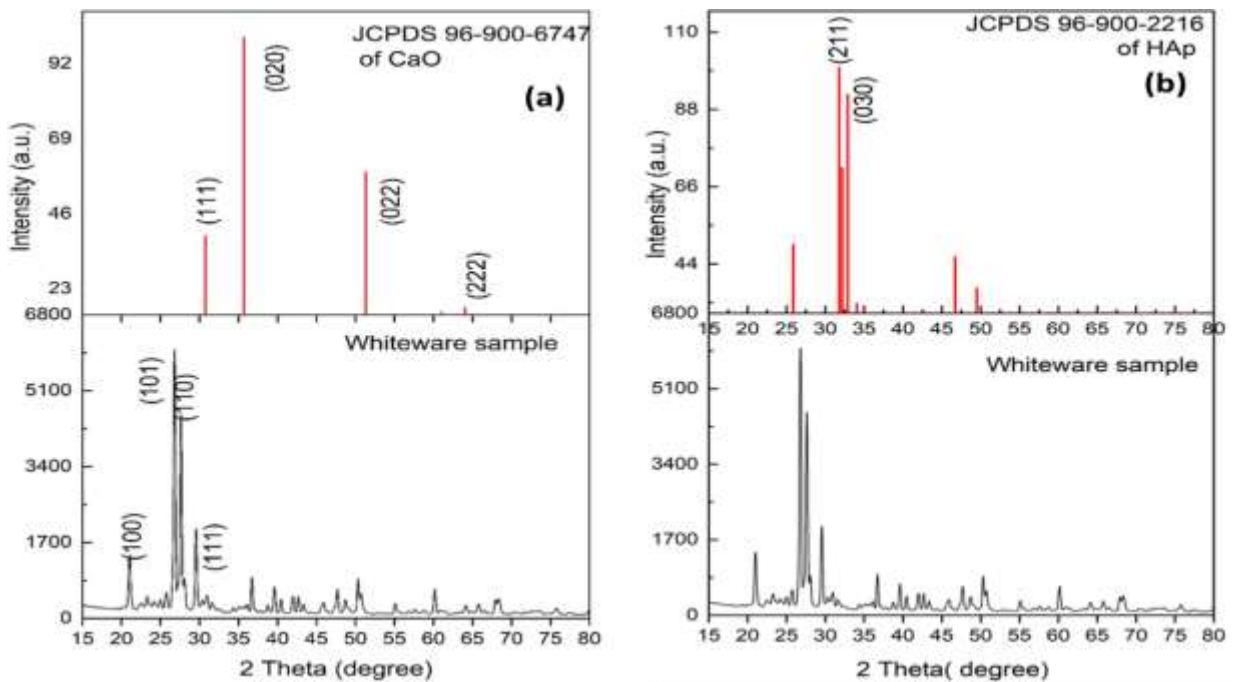


Figure 4 XRD of whiteware Samples Containing snail-ash.

A thorough crystallization of the calcined material occurred during heat treatment, as shown by strong XRD reflections with (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) orientations [24]. Above Figure 3 shows the presence of CaO and HAp. Calcium oxide is the most abundant mineral component. The concentration of CaO in the catalysts generated from discarded mussel, cockle, and scallop shells is 98.37 wt.%, 99.17 wt.%, and 97.53 wt.%, respectively [3]. The specific surface areas may be greater, though, if the aggregates and grains were smaller. It seems to reason that the particle size is proportional to the surface area, given that all samples are either less porous or completely nonporous [25]

$Al_2O_3 \cdot 2SiO_2$ (Metakaolin) + CaO (Lime) \rightarrow $CaAl_2Si_2O_8$ (Anorthite), Phase changes of materials[26]. Adsorbent 48 (315) had the maximum intensity, and the peak of HAP occurred at 31.9 degrees [27]. Due to the fact that fine clay particles enhance the sintering kinetics and promote particle cohesion, samples with 3, 6, 9, and 12% snail shell extra fall within the range (Folorunso and Bello, 2021). On the other hand, samples with 0% snail shell addition were somewhat closer to the range, and samples with 15% snail shell addition crumbled during the test. Moreover, the range in bulk densities could be explained by the voids that arise when organic materials (such as snail shells) are burned off from the bricks during the fire process. Since this organic matter is typically not evenly distributed, the variation exists. According to Folorunso and Bello (2021) [25], Folorunso (2015) [25], and Folorunso [21] particle size and the forming pressure are other factors to consider. The results also showed that the composition with 12% snail shell addition had the highest porosity, while the one without additions had the lowest porosity of 23.90%. Unfortunately, for 15% wt. %, the sample crumbled during the test, thus the apparent porosity was 0%. Snail shells with apparent porosities between 0% and 6% fell within the permissible range of 10% to 30%, as recommended for refractory bricks [28]. However, snail shells with apparent porosities between 9% and 12% did not meet this recommendation. Additionally, the sample was insoluble at 15% snail shell addition [23]. characterized and evaluated chosen kaolin clay deposits in Nigeria for furnace lining application, and Akinwande [28] used clay from the banks of the river Benue in Makurdi as a medium-duty refractory material. In order to calculate thermal shock resistance, a prior work by [29] employed the following principle: Results were classified as "outstanding" for TSRs with 30 or more cycles, "good" for 25– 30 cycles, "fair" for 20–25 cycles, "acceptable" for 15-20 cycles, "poor" for 10-15 cycles, and "extremely poor" for less than 10 cycles. Consequently, it is determined that refractory works lining materials containing snail shell (ranging from 9% to 12% by weight) will produce an acceptable product. All three of the snail shell addition levels 3%, 6%, and 15%—prove to be viable. But zero percent snail shell is not going to cut it. As porosity increases, the strength of clay-based ceramic structures often decreases. Values between 1.43 and 2.47 KN/cm² were obtained for the samples. Since the readings are within the acceptable range of 1– 15 KN/Cm², we can proceed [11]

Table 2 XRD of Both Whiteware samples

Elements	References	2 Theta[deg]	Crystallographic Planes (hkl)
Quartz	JCPDS	26.69	(1 0 0)
	96-101-1177	20.91	(1 0 1)
CaO	JCPDS	35.67	(0 2 0)
	96-900-6747	30.76	(1 1 1)
HAp	JCPDS	31.78	(2 1 1)
	96-900-2216	32.92	(0 3 0)

EDX Characterization

The EDX spectrum (Fig. 3) reveals the large peaks for Si, Al, O, and lesser peaks for K, Ca, and P. These observations match with the expected composition of whitewares, which typically comprise kaolin, quartz, and feldspar[18]. Porcelain has a significantly lower densification temperature, which is likely due to its lower melting point and higher glass content. Most of the shrinkage happens because of the liquid phase sintering. The standard stoichiometric comparison between calcium and phosphate is 1.67, which is widely recognised [30]. According to the results of this study, the extracted HAp had a Ca/P ratio of 1.849 at 800°C, 1.718 at 900°C, and 1.81 at 1,000°C, indicating that the Ca/P ratio was excessive for sintering at high temperatures to introduce β -tricalcium phosphate (β -TCP) [7].

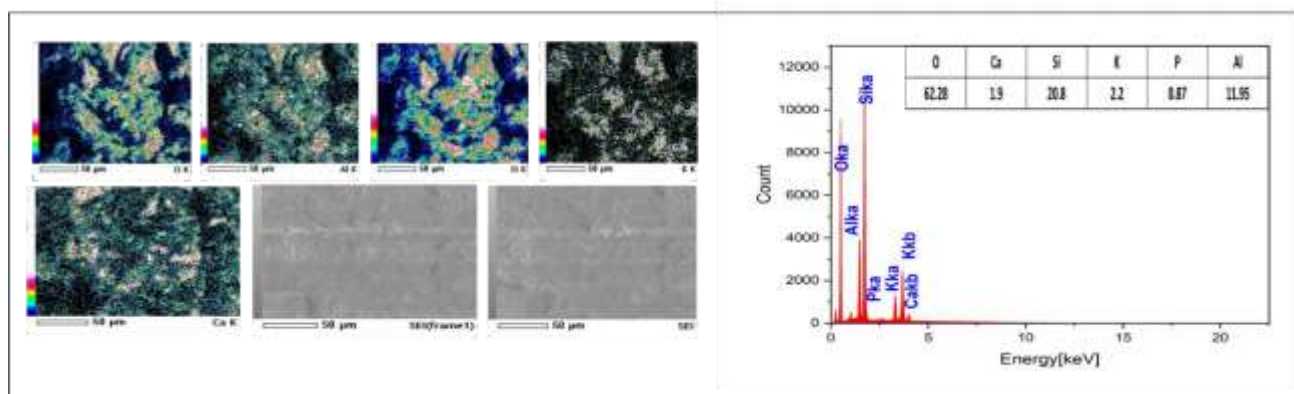


Figure 4 EDX of the sample containing CaO.

The element of CaO and HAp was confirmed using EDX analysis. The sample that contained bone ash had phosphorus, an ingredient of HAp. The sample's primary crystalline phases, as revealed by the EDX pattern, were glassy phase embedded anorthite and quartz. Figure.4 shows that fine crystalline anorthite grains form a glassy ring around sub-angular quartz grains. The anorthite phase has formed, and the EDX patterns show that there is residual quartz. The results of the XRD analysis corroborate this conclusion.

CONCLUSIONS

Calcined snail ash serves a purpose by exhibiting mechanical and chemical qualities comparable to, or even superior to, those of CaO, even when only a trace quantity of apatite compound is present. The impact strengths of the samples containing 1.12 J/ cm² of CaO and 1.15 J/ cm² of CaO completely substituted with snail ash were 1.20 and 18.78 grammes, respectively. as well as bending strengths of 68.04 MPa, 70.09 MPa, and 71.23 MPa. Porosity, shrinkage, and density are further characteristics. In this study, EDX and XRD confirmed the presence of the Apatite element, and the results showed that the element melted before other materials with a high melting point, improved the melting properties for the formation of liquid phases, and made the samples more dense. An effective waste management strategy and a valuable source of pure HAp can be achieved by making use of snail ash.

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Declaration of competing interest

The writers of this paper affirm that they are free from any ties or financial conflicts of interest that may have seemed to impact their work.

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