GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 9, NO.4, SEPTEMBER 2003: 491 - 494
 ISSN 1118-0579

PERIWINKLE (T.FUSCATUS) SHELL AS ALTERNATIVE SOURCE OF LIME FOR GLASS INDUSTRY

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(Received 17 August 2002; Revision accepted 10 June 2003)

ABSTRACT

This research was to conduct a chemical test to ascertain the percentage content and suitability of periwinkle shell wastes for glass industry. Results of the study show that periwinkle shells contain a high percentage (38.4%) of calcium oxide (Ca0). Other important oxides which were also found in substantial percentage were silicon iv oxide (SiO_2): 0.014%; magnesium oxide (MgO) 18.70%; Aluminium trioxide (Al_2O_3): 0.211% and Iron oxide (Fe_2O_3): 0.019%. The result is discussed with particular reference to the glass industry.

KEY WORDS: Periwinkle shells, calcium oxide, mollusc, glass industry.

INTRODUCTION

Nigeria is endowed with abundant natural and mineral resources which have been exploited for useful products for the benefit of mankind. One of these natural endowments is the seashell from which lime otherwise called quick lime or calcium hydroxide, can be obtained (Chang, 1991). Seashells are hard coated coverings of small, soft bodied, sea-animals found on the sea-shore of coastal areas. They belong to the group called Mollusc (Onyekan, 1994). In West Africa, one of the dominant benthic organisms found along its coastal lagoons is the periwinkle (*Tympanotonus fuscatus*). In Nigeria the *T.fuscatus* is restricted to the mangrove swamps and mud flats in high salinity areas of coastal Nigeria (Onyekan, 1984).

This organism is widely eaten for its high protein and mineral content by the coastal peoples of the country. However the empty seashells are thrown away as waste inspite of their valuable lime content. Available evidence (Bajah, 1986) shows that these empty seashells contain a high proportion of calcium oxide (Ca0) which can be converted into lime for industrial use.

In the United State of America for instance, lime ranks among the 50th industrial chemical product, with about £32.3 million annual output (Chang, 1991). As one of the oldest materials known to mankind, it is estimated to contain about 3.4% of the earth's crust by mass and has been used as building material since 1500 BC (Bajah, 1986).

Apart from sea-shells, lime can be obtained from sources such as limestone, calcite, marble (as calcium carbonate), dolomite (as $CaC0_3$) gypsum as ($CaS0_4,2H_20$), and fluorite as (CaF_2). Calcium oxide is one of the basic components of lime. It is an extremely valuable inorganic substance, widely used in industry in the following areas (Bajah, 1986)

(i) It is used as a source of fluxing agent in glass production.
(ii) It is used in water treatment plants to soften hardwater for both domestic and industrial use.
(iii) In the food and pharmaceutical industries, lime is used for preservation and production of drugs, respectively.
(iv) In the agricultural industries, lime is used by farmers to lower the acidic content of the soil for their crops (a process called liming) and also lakes affected by acid rain.
(v) In the medical field, lime in combination with sulphate ($CaS0_4$) is used in producing Plaster of Paris (POP) and when added with water, it forms a plaster of plaster cast which is mostly used in hospitals in supporting the bones of accident victims, to mention just a few (Bajah, 1986).

The inexhaustible uses of calcium oxide (lime). The high content of lime in sea shells which is abundant in the coastal regions of Nigeria as waste, forms the basis of this study. The researcher finds it desirable to carry out a chemical analysis in order to ascertain the percentage content of calcium oxide (lime) in periwinkle seashells, to serve as a source of raw material for Nigeria local industries, and also to generate revenue and employment to her teaming populations.

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MATERIALS AND METHODS

Sampling:

The periwinkle shells were collected randomly from the local markets and from fishermen along the shores of Cross River State estuary by the Atlantic ocean.

Pretreatment and Analysis

40g of the periwinkle shells were pretreated by benificiation (to concentrate materials to be analysed) prior to analysis. All treatment and analysis were according to the recommendations of the Association of Official Analytical Chemist (A.O.A.C. 1975).

The shells of the periwinkles (*Tympanotonus fuscatus*) were used while the flesh was discarded. To purify, samples were washed with warm water and rinsed with distilled water, dried at 110^0C in the oven, homogenised by grinding with algate pestle and mortar and sieved through 120 mm mesh using nylon sieve. The pretreated samples were then analysed for the following: Silica (SiO_2) sexquinoxide (R_2O_3) from trace metal origin, calcium oxide (CaO) magnesium oxide (MgO), ferrous oxide (F_2O_3) and alumina ($A1_2O_3$).

Determination of S_1O_2: 1g of the pretreated sample was acid digested in a porcelain dish after first treating with 20ml of 1:1 HCl, followed by a mixture of 20ml each of concentrated, HCl and HNO_3. The solution was evaporated at 110^0 – 120^0C and further digested with some of concentrated HCl to digest the salt. Then 20ml of water was added, warmed for 10 min and filtered using NO. 41 Whatman filter paper. The solid (precipitate) was washed with 1:100 HCl solution, rinsed with distilled water and ignited to constant weight. The filtrate was diluted to 250 ml, using a volumetric flask and set aside for the determination of other oxides. Percentage SiO_2 was obtained from the residue.

Determination of R_2O_3 was by titrimetric method (Harries, 1975) using 25ml of the filtrate from the above. It was treated with acid solution to an endpoint using methyl-red indicator at constant pH. The % R_2 O_3 was calculated from end point after due precipitation.

Calcium Oxide (CaO) was analysed by boiling on hot plate the filtrate from R_2O_3. fifty percent ammonium oxalate $(NH_4)_2C_2O_4$ was added and stirred and pH kept constant using 1:1 NH_4 OH for 5 min. to form a precipitate and filtered. The precipitate filtrate was stored for analysis of MgO.

While the precipitate was dissolved in 5ml of 1:H_2SO_4 stirred and warmed to 70^0C, CaO was obtained by titrating the solution with 0.1M $KMnO_4$ to a short lived end point. Percentage calcium oxide was then calculated from the end point.

Magnesium oxide (MgO) was determined by treating the filtrate from CaO determination with 15ml of 5% hydroxyquinoline solution and warmed to 70^0C followed by the addition 8ml of 1:1 NH_4OH and stirred for 25 min. and cooled overnight. The precipitate formed was used to calculate the percentage Magnesium oxide (MgO).

Ferrus oxide (Fe_2O_3) was determined from another 1g of the pretreated sample and acid digested in a platinum crucible using a mixture of 1ml, 50% H_2SO_4 and 5ml perchloric acid ($HClO_4$) and heated to complete digestion on a sand bath. The process was repeated until no more fumes were formed.

The residue was dissolved in 10ml of 50% HCl and made up to 250 ml with distilled water. 25ml of the solution was used to determine Fe_2O_3 by titrimetric method and % Fe_2O_3 calculated.

Aluminium trioxide (Al_2O_3) was obtained by the difference between the value of R_2O_3 and Fe_2O_3.

RESULTS AND DISCUSSION

The concentrations of various oxides measured from the sample are shown in Table 1 and depicted in figure 1. Analysis show the highest level of oxides to be from calcium oxide (CaO) with 38.4% of dry weight, second by magnesium oxide with 18.7% and least by silica with 0.014%. It can be concluded from this study therefore that lime and magnesium are found in commercial quantities in periwinkle shell, and could be exploited for their desired uses in glass industries. Most ores do not contain such high concentrations before exploitation is embarked upon (Sell, 1981).

Table 1: Result of the various oxide concentrations from periwinkle (*T.fuscatus*) shell sample

Oxide	Percentage content (%)
Silicia (SiO_2)	0.014
Sexquin Oxide (R_2O_3)	0.23
Calcium Oxide (CaO)	38.40
Magnesium Oxide (MgO)	18.70
Ferrous Oxide (Fe_2O_3)	0.019
Aluminum Oxide ($A1_2O_3$)	0.211

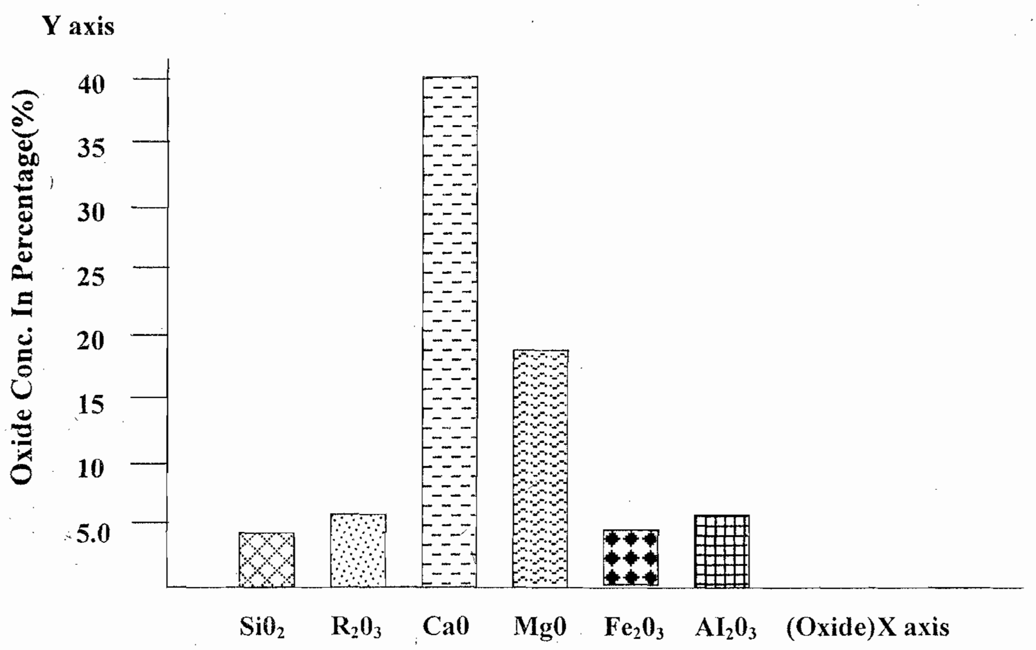

Fig. 1 Shows the Bar Chart distribution of oxides content in Periwinkle shells (*T. Fuscatus*).

This study was motivated by the desire to obtain the percentage of calcium oxide (lime) present in periwinkle shell, which can be utilized by industries especially glass industries, where it is a major raw material for flux. Other industries such as iron and steel, pharmaceutical, medical, agriculture, fertilizer etc. may also utilize calcium from periwinkle shell as raw material.

In the glass manufacturing process, three basic factors are usually considered before a raw material can be used for glass making (Corning Glass works, 1967). These include:

(a) **Purity of raw material**: The raw material must be free from iron oxide (Fe_20_3) and other elements that may bring about unwanted colouration in the final glass product, or the iron oxide percentage must not exceed 0.15% for ordinary glass and 0.01% for optical glass. From Table 1, the periwinkle shell contains a lower percentage of iron oxide (Fe_20_3) which is 0.019%. This is below the specified standard (0.15%) and therefore may be used for glass production.

(b) **The raw material must be capable of yielding the minimum required oxide.** Results from Table 1 shows that, since calcium oxide yielded more than the minimum required concentration of 38.4% which falls between the standard specification for glass manufacturing (30%-60%), the periwinkle therefore can be used for glass production.

(c) **The availability of the raw material, whether it is relatively cheap or abundant.** As earlier stated, periwinkle shells are relatively cheap and abundant in Nigeria especially at the coastal areas as waste material. It therefore may be used as a source of calcium oxide (Ca0) in the commercial production of glass ware.

In Figure 1, the bar chart percentage distribution of the oxide content in periwinkle shell indicates that the percentage of calcium oxide is higher, and the order or trend in oxides content can be represented as Ca0 > Mg0 > R_20_3 > Al_20_3 > Fe_20_3 > $Si0_2$.

Calcium oxide when used in glass batch as fluxing agent, lowers the temperature of the glass melt from 1500°C to 1250°C, while iron oxide when in large amount; produces unwanted colouration in the glass melt.

In conclusion, this research has shown that periwinkle shells, contain a high proportion of calcium oxide coupled with a low iron oxide content and can therefore be utilized as a source of local raw material for glass and other allied industries. This will go a long way saving foreign exchange, increasing revenue generation/employment and accelerate the quest for technological development of Nigeria.

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