

Synthesis and Characterization of Precipitated Calcium Carbonate from Biogenic Waste

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Abstract—Calcium carbonate is widely used as a filler material in many manufacturing industries such as paints, plastics, ceramics, as well as for cosmetics and medical purposes. In this work precipitated calcium carbonate was synthesized by calcination of chicken eggshells. The optimum calcination temperature and calcination time were investigated. Similarly, the dissolution time of the quick lime and the alkalinity of the co-generated NaOH - a by-product from the process were also studied. The chemical structure of the synthesized PCC was also verified. The results indicate optimum calcination temperature of 720°C, the calcination time of 3.5 hours and optimum dissolution time of 8.5 minutes. Tests for NaOH produced from the alkalinity analysis showed average concentrations of the NaOH produced were 0.9903M, 0.7417M, 0.3629M and approximately 0.0000M for the first filter, the first wash, second wash and third wash respectively. The precipitated calcium carbonate produced showed the calcite structure.

Keywords — precipitated calcium carbonate, sodium hydroxide, eggshell, calcination temperature, calcination time, calcite

I. INTRODUCTION

Rapid population growth across the globe, and Nigeria in particular, has led to extensive production and consumption of poultry products which has made the poultry industry emerged as one of the most commercialized and fast-expanding segments of the Nigerian agricultural sector. For example, the consumption of poultry and eggs is projected to rise by 200% between 2010 and 2020 in sub-Saharan Africa [1]. Eggshell (ES) which forms the outer crust of an egg is a non-edible component with very limited use and value, and therefore largely disposed as waste. The indiscriminate disposal of ES can cause serious pollution problems in the environment. The rise in waste disposal costs due to increase in landfill taxes coupled with growing environmental concerns necessitates efforts to find possible techniques that would transform waste eggshells into valuable product. More also, such technologies will give financial benefits to the competitive egg processing industries and help them alleviate the high disposal costs as well as ease their

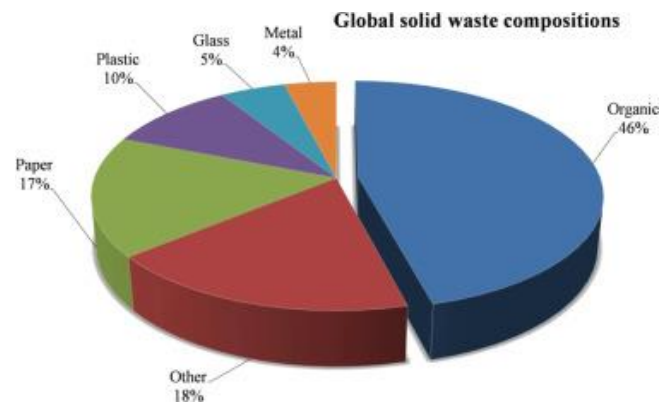


Fig.1.Global solid waste composition [2]

environmental burden. Eggshell is also a major constituent of domestic wastes, food processing industries and restaurants. Fig. 1 illustrates the global solid wastes distribution by type. The bulk of which comes from organic sources that ES form part of.

Recently, the global demand for calcareous products such as precipitated calcium carbonate (PCC) is on the increase. PCC in particular has received significant attention in recent years owing to its extensive applications in the areas of papermaking, rubber, plastics, paints, pharmaceuticals, cosmetics, health and dietary, building, oil recovery, agriculture, environmental control, etc. Moreover, several workers have investigated the production of PCC from various sources [3-5].

Consequently, natural biogenic waste materials such as the eggshells are being exploited as substitute raw materials for the production of calcareous products. This is primarily due to their biodegradability, lower price and abundance compared to the synthetic materials.

Eggshells and other biogenic materials are vital reserves of many bioactive compounds with high economic potentials that can be harnessed. Eggshells whether from hen, duck, bird, goose, partridge bird etc., have a very significant calcium carbonate (CaCO_3) content ranging from 94-95% in the form of calcite; and 5-6% inorganic materials such as magnesium [6].



Fig.2. (a) Fresh eggshells (b) Yolk membrane

In this regard, chicken eggshell presents a potent form of renewable resources which can reduce the overreliance on calcium carbonate filler from non-renewable calcium carbonate sources. The desirability to produce more calcium carbonate from such alternative sources cannot be overemphasized [5]. Thus, the use of eggshell to generate calcium carbonate in commercial application will present a useful means to beneficiate eggshell wastes in very cost-effective manner [7]. In this work, eggshell from domestic wastes was used as a base raw material to produce precipitated calcium carbonate (PCC). Fig. 2 (a) and (b) show raw eggshell and the peeled yolk membrane from fowl eggs respectively.

II. PCC SYNTHESIS

Precipitated calcium carbonate is currently produced via three different processes; the lime soda process, the calcium chloride process and the carbonation process.

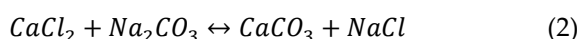
A. The Lime Soda Process

In the lime soda process, calcium hydroxide is reacted with sodium carbonate to produce sodium hydroxide solution, from which calcium carbonate is precipitated. This process is commonly used by alkali manufacturers, for whom sodium hydroxide recovery is the main objective, and often the coarse PCC produced is only a by-product according to the reaction illustrated in equation 1. This is the process adapted in this work.



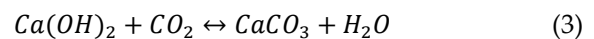
B. The Calcium Chloride Process

In the calcium chloride process, calcium hydroxide is reacted with ammonium chloride, forming ammonia gas and calcium chloride solution. After purification, this solution is reacted with sodium carbonate to form calcium carbonate precipitate and sodium chloride solution as illustrated in equation 2. This process is the simplest but requires a low-cost source of calcium chloride to be economical. Therefore, it is usually conducted in a satellite facility adjacent to a Solvay process soda ash plant.



C. The Calcium Chloride Process

The carbonation process is the most widely used process, in which the base raw material is burned in a lime kiln at the designed temperature where it decomposes (calcines) into calcium oxide (CaO) and carbon dioxide. The dry CaO is slaked (hydrated) with water at temperature of 30–50°C, producing a Ca(OH)₂ slurry. The slurry production starts with sending stored lime to a slaker tank, which is stirred by a high shear mixing agitator, after which water at the desired temperature is added and the slurry is formed. The slurry contains undissolved calcium hydroxide, calcium ions (Ca²⁺) and hydroxide ions (OH⁻). The calcium ion concentration in the slurry is dependent on the solvent solubility limit, which decreases as the temperature increases. Before carbonation, the process slurry is screened to remove impurities originating from the limestone. The slurry is then fed to a three-phase stirred tank reactor, either at atmospheric pressure or pressurized, where it reacts with CO₂ gas to yield calcium carbonate precipitate as represented in equation 3.



III. METHODOLOGY

A. Materials

Fresh chicken eggshells were obtained from K. P. Restaurant, Maiduguri, Borno State, Nigeria. Commercial grades of sodium tri-oxo-carbonate IV, ferrous ammonium sulfate and cobalt nitrate solutions were bought from a local store in Maiduguri Metropolis, whereas distilled water, phenolphthalein solution, sodium hydroxide solution, nitric acid and hydrochloric acid were obtained from the Department of Chemical Engineering and the Department of Chemistry laboratories, University of Maiduguri.

B. Methods

1) Heat Treatment

The eggshells were washed thoroughly with hot water and the membranes were manually removed. The shells were then crushed into small pieces using mortar and pestle as shown in Fig. 3 after which samples were calcined by heat treatment to transform the eggshells to CaO [8]. The chemical stoichiometry for the reaction is as illustrated in equation (4).



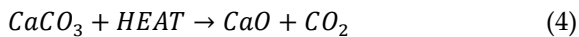
Fig.3.Crushed eggshells



Fig.4.Calcined eggshells until turned white at various temperatures



Fig.5.Calcined eggshells at various temperatures for 1 hour.



Six (6) batches weighing 20g each of the pretreated eggshells were drawn and labeled *A1*, *B1*, *C1*, *D1*, *E1* and *F1* respectively. The identified samples were calcined at temperatures of 400°C, 500°C, 600°C, 700°C, 800°C and 900°C respectively. Each sample was calcined separately until the eggshells turned white and the calcination time and weight of sample were recorded. Fig. 4 shows the heat-treated samples.

Another set of six (6) batches labeled as *A2*, *B2*, *C2*, *D2*, *E2* and *F2* weighing 20g each of the pretreated eggshells was prepared. The samples were calcined at respective temperatures of 400°C, 50 °C, 60 °C, 700°C, 800°C and 900°C for a period of 1 hour (see Fig. 5); the weighed of the samples were recorded and the change in colour of the samples was observed.

The calcium oxide (CaO) generated in the heat treatment step for all samples were grinded to fine powder and sieved to a particle size of < 75 microns using mesh size BSS 120.

2) Lime Slaking

The calcined CaO was slaked using distilled water in the mole ratio of 1:3, the chemical reaction is illustrated by equation 5.

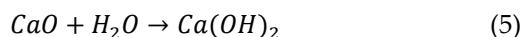


Fig. 6 illustrates the complete experimental process flow chart.

3) Quick Lime Dissolution Test

The CaO from the heat-treated samples were subjected to a dissolution test to determine the optimum dissolution time. For each sample, 10g of the CaO was measured and dissolved in 20ml of distilled water with vigorous shaking at 100rpm and 20°C, the dissolution time was recorded after uniform solution was obtained. The pH of the sample was also recorded using a portable pH meter.

4) PCC synthesis from the Lime Soda Process

The lime-soda process (ASTME 291-09) was adopted; 10g of Ca(OH)₂ was added to 50ml of distilled water and was stirred for 5 minutes. Similarly, 15g of Na₂CO₃ was added to 50ml of distilled water and added to Ca(OH)₂ solution, the mixture was allowed to stir at 900rpm for 60 minutes at temperature of 25°C. The product calcium carbonate slurry (see equation 1) from the lime-soda step was separated using a simple filtration. The residue (CaCO₃) was washed 3 times with 100ml of distilled water, and titred using sulfuric acid with phenolphthalein indicator. The procedure was conducted on all the filtrates to check for traces of sodium hydroxide. The CaCO₃ samples were dried at 100°C for 2 hours until constant mass of the sample was obtained.

C. Characterization

The method of MD. Shahinoor Islam [9] was adopted to characterize the produced PCC derived from samples *A1*, *B1*, *C1*, *D1*, *E1*, and *F1*.



Fig.6. Process flow diagram for PCC production

1) *Determination of Crystal Structure PCC*

For each sample, 2g of the PCC was dispensed into a conical flask; 100ml of distilled water was added and stirred thoroughly to form a homogeneous solution after which 1g of ferrous ammonium sulfate was added to the solution. The mixture was stirred vigorously for about 5 minutes and the color change of the solution was observed.

2) *Analysis of Sodium Hydroxide Solution*

For each sample, 2g of the PCC was dispensed into a conical flask; 100ml of distilled water was added and stirred thoroughly to form a homogeneous caustic solution. 25 ml of the caustic solution was measured into a burette. 25ml of 1.0 N sulfuric acid was measured in a conical flask and 2-3 drops of phenolphthalein was added to the sample solution. The solution was titrated against the caustic solution until colour change from colorless to pink was observed.

IV. RESULTS AND DISCUSSION

Table 4.1 shows the analysis of the mass of samples A1, B1, C1, D1, E1 and F1 before and after complete calcination at various temperatures. The time taken for complete calcination of the sample at the respective temperatures were also presented.

A. *Effect of Calcination Temperature on Mass Loss*

The effect of calcination temperature on the mass loss of the calcined eggshell is shown in Table I and Fig. 7. The mass loss increases significantly with increased calcination temperature at low calcination temperatures. The observed loss in mass, more than treble between 400-550°C. However, the mass loss increases rather slightly with increased calcination temperatures for calcination temperatures higher than 600°C.

The optimum calcination temperature of 720°C was observed, beyond which no appreciable loss in mass was observed.

At the optimum temperature, the eggshells have completely turned white indicating complete calcination to CaO. The eggshells transit initially to black prior to attainment of the optimum temperature (see Fig. 4 and 5). The corresponding percentage loss in weight of the sample at the optimum temperature was 9.6%. Increasing the calcination temperature beyond the optimum by 25% only yielded about 4% increase in loss in mass. The optimum calcination temperature observed is lower than the calcination temperature of 900°C required for the complete calcination of duck eggshells reported in previous works [8 and 10]. In another work [5] the optimum calcination temperature for fowl eggs was determined to be around 1300°C which was considered extremely high.

Calcining the eggshells for a set time of 1 hour at various temperatures (samples A2, B2, C2, D2, E2 and F2) yield the resultant CaO that was only partially calcined. Some of the flakes were observed as a mixture of white, black and ash colours (see Fig. 5). This is probably due to partial burning of the eggshells, because of too short the period of exposure of the shells to the heating source regardless of temperature for all temperatures investigated. This indicates that only eggshells on the sample's periphery were calcined adequately.

B. *Effects of Calcination Time*

Fig. 8 illustrates how calcination temperature affects calcination time. The higher the calcination temperature the faster the calcination process and the shorter is the time required for complete calcination. The optimum calcination time was about 3.5 hours.

From the dissolution test (see Table II and Fig 9), the optimum dissolution time was 8.5 minutes at a pH of 12.5. It could be seen that the pH increases with increase in the dissolution time, but plateaued after the optimum dissolution time and the corresponding pH increase of 12.5 was selected as the optimum dissolution pH. The pH corresponds to that of CaO dissolution obtained from the calcination of limestone reported in [11].

TABLE I. RESIDUAL MASS OF SAMPLES AFTER COMPLETE CALCINATION

Sample	Temperature(°C)	Time of Calcination (h)	Initial Mass, Mo(g)	Final Mass, MF(g)	Percent Weight Loss (%)
A1	400	8	20	19.50	2.50
B1	500	7	20	18.60	7.00
C1	600	5.5	20	18.26	8.70
D1	700	4	20	18.10	9.50
E1	800	3	20	18.09	9.55
F1	900	3	20	18.09	9.55

TABLE II. QUICK LIME DISSOLUTION TEST: PH OF DISSOLVED SAMPLES* AT VARIOUS

Dissolution time (min)	0	2.5	5.0	7.5	10.0	12.5	15.0
Solution p.H	10.00	11.40	12.31	12.45	12.50	12.50	12.50

*(CaO = 10g; Water = 20ml; Temperature = 20°C Normality = 1.0 mol/dm³; Mixing Speed – 100rpm)

C. Determination of PCC Crystal Structure

Precipitated calcium carbonate exists in two distinct crystal structures; namely aragonite and calcite. When ferrous ammonium sulfate is added to a solution of PCC, the color change depends on the prevailing crystal structure. If the color of the solution changed to green, the PCC structure is aragonite; while color change to yellow indicates calcite structure.

In this work (see section III, C), the color change of the solution observed was yellow, confirming the calcite structure of the synthesized PCC.

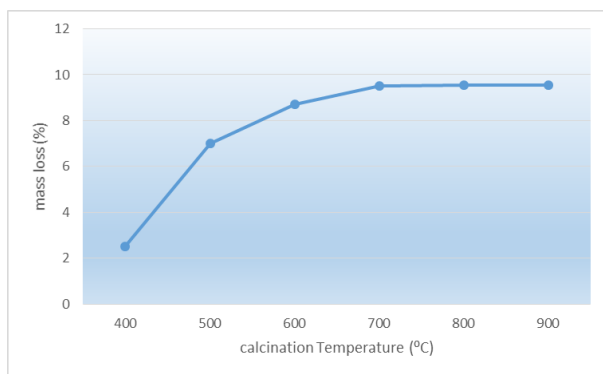


Fig.7. Effect of calcination temperature on mass loss of eggshells

D. Analysis of Sodium Hydroxide Solution

The amount of NaOH generated as a co-product in the lime soda process of PCC manufacture was determined by titrating after the filtration, and subsequently the first, second and third washing respectively.

From Table III, it can be seen that the average concentrations of NaOH of PCC samples were 0.9903M, 0.7417M, 0.3629M and approximately 0.0000 for the first filter, first washing, second washing and third washing respectively. The concentrations agreed with the ASTM standard. The required number of washes was also found to be three (3), because after the third wash the concentration of NaOH was observed to be approximately zero.

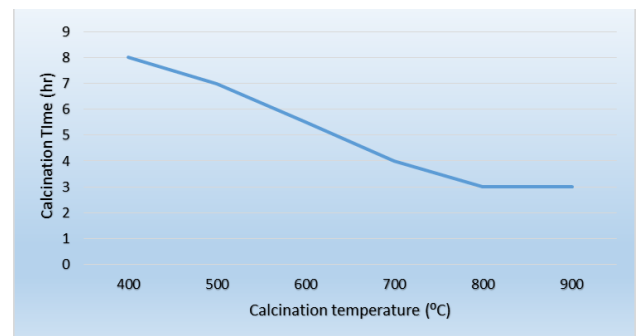


Fig.8. Calcination times of eggshells at various temperatures

TABLE III. ALKALINITY TEST FOR RESIDUAL NaOH IN SAMPLE

SAMPLE	CONCENTRATION OF NaOH (M)			
	1 ST FILTER	1 ST WASH	2 ND WASH	3 RD WASH
A1	1.0085	0.7136	0.3571	0.0000
B1	0.9868	0.6726	0.3676	0.0000
C1	0.9947	0.7198	0.3788	0.0000
D1	0.9535	0.7583	0.3472	0.0000
E1	0.9387	0.7854	0.3846	0.0000
F1	0.9793	0.8004	0.3425	0.0000

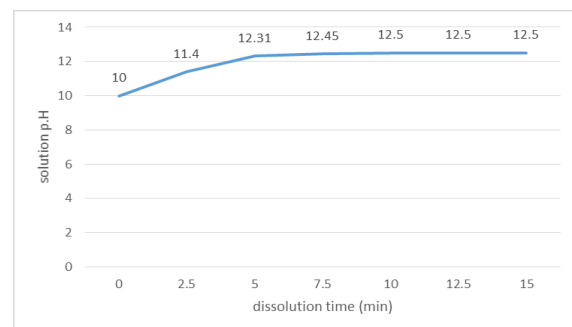


Fig.9. pH of dissolved quicklime at various dissolution times

V. CONCLUSIONS

Precipitated calcium carbonate (PCC) was successfully synthesized from biogenic waste i.e. chicken eggshells using the lime soda process. Sodium hydroxide or caustic soda was yielded as a desirable by-product. The results show the optimum calcination temperature and calcination time for chicken eggshell as 720°C and 3.5 hours respectively. The quicklime dissolution test investigation shows optimum dissolution time of 8.5 minutes with a corresponding pH of 12.5. The results also highlighted strong influence of calcination temperature on the mass loss of eggshell samples for all calcination temperatures lower than the optimum temperature.

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