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Short Communication

Analysis and Purification of Nkalagu (Nigeria) Limestone and Poultry Eggshells for the Production of Paint Grade Calcium Carbonate

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Abstract. The local limestone (Nkalagu, Nigeria) and poultry eggshells were collected and analysed using gravimetric and spectrophotometric methods. The parameters determined were: moisture content, loss on ignition, impure silica, combined oxides such as CaO, MgO, Fe_2O_3, Na_2O and K_2O. The carbonate contents fell short of that required (> 95%) for paint manufacture. The non-carbonate matters, regarded as impurities, were removed or reduced by chemical processes, which involved acid digestion through carbonation of the resultant filtrates. The purified $CaCO_3$ grades from both these samples were compared with the commercially available grades. The purified grades showed improved whiting and fineness, indicating their usefulness for paints and other $CaCO_3$ applications.

Keywords: limestone, Nigeria (Nkalagu), poultry eggshells, calcium trioxocarbonate, gravimetric limestone analysis, spectrophotometric limestone analysis

Limestone, consisting mainly of Ca and Mg, abounds widely in the earth's crust, most commonly occurring as their carbonates in the rock. Impurities in the limestone include silica, alumina, oxides of Fe, Na, K, and organic matter. Other minor impurities, such as P, Ti, Mn and S may also exist. It is a naturally occurring sedimentary rock, with $CaCO_3$ content greater than 70% (or CaO > 40%). When $CaCO_3$ and $MgCO_3$ occur in approximately equimolar concentrations in the rock, it is called dolomite (Greensmith, 1978).

The naturally occurring limestones, used in the chemical process industries, contain a minimum of 95% carbonate content (Mark *et al*., 1967). Other sources of $CaCO_3$ include chalk, marble, oolite, calcareous marl, corals, pearls and shells. Eggshells of birds are composed mainly of $CaCO_3$ and small quantities of $MgCO_3$, $CaPO_4$, and organic matter (Thorpe and Whiteley, 1949). The most common sources of calcium in poultry rations are ground limestone and marine shells (Card and Nesheim, 1972).

The limestone, eggshells and other sources of $CaCO_3$ are often contaminated with impurities, which can be removed by chemical processes, resulting in the precipitated forms, usually marketed as chalk, whitings, ground limestones, or marble dust containing 96-99% of $CaCO_3$. The precipitated types have finer particle size, best for the hiding power of paints (Ritter, 1963). The industrial production of precipitated $CaCO_3$ is done by different methods, which include carbonation, calcium chloride procedure, or the recovery as a by-product, all starting with the calcination of natural limestones in kilns (Myers and Long, 1975). A different method of limestone purification was developed at Conshohocher by Valley Forge Cement Company. In this method, the froth formed from the lime slurry in cells, mixed with fatty acids and a frothing agent (alcohol), is subjected to a cationic cell separation which then classifies the grains of $CaCO_3$ (Bogue, 1955).

Calcium carbonate belongs to the group of pigments known as "extenders", which mainly add to the bulk and other desirable physical properties of paints with a consequent reduction in the cost of production. They are deficient in both colour and opacity or hiding power (Mark *et al.*, 1968). The types of paints that employ large volumes of extenders are architectural and maintenance finishes, particularly used as interior or flat wall paints where hiding is not as critical as uniform covering (GoodHart-Willcox, 1975).

The limestone and eggshells were, respectively, collected from Nkalagu, Ebonyi State, and Abraka, Delta State, Nigeria. The samples were dried, pulverized and stored. Each sample (1.0 g) was analyzed for the moisture content, loss on ignition, silica, combined oxides, calcium oxide, and magnesium oxide contents gravimetrically, in accordance with standard methods (AOAC, 1970; Palmer, 1965; Bisque, 1961; Vogel, 1954). The Al_2O_3 and Fe_2O_3 contents were determined spectrophotometrically, while the Na_2O and K_2O contents were obtained by flame photometry (Gary, 1980).

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Table 1. Composition of Nkalagu (Nigeria) limestone, poultry eggshells, their purified grades and commercial grade $CaCO_3$

Components	Nkalagu limestone (%)	Poultry eggshells (%)	Purified limestone (%)	Purified eggshells (%)	Commercial grade $CaCO_3$ (%)
Moisture	0.60	0.60	0.50	0.50	0.50
Loss on ignition	37.25	42.51	42.55	43.20	43.11
Impure silica	9.15	0.45	0.20	negligible	1.20
Combined oxides	5.50	2.54	1.10	0.30	0.50
CaO	44.75	50.77	54.90	55.26	53.95
MgO	1.70	1.40	0.35	0.29	0.36
Na_2O	0.35	0.76	0.15	0.17	0.18
K_2O	0.67	0.63	0.32	0.15	0.24
Fe_2O_3	1.56	0.57	0.11	0.08	0.16
Al_2O_3	3.63	0.98	0.66	0.15	0.23

Table 2. Carbonate (CO_3^{2-}) contents of the raw Nkalagu (Nigeria) limestone and poultry eggshells, and after their purification into commercial grades

Sample	Weight of CaO (g)	Weight of MgO (g)	Weight of $CaCO_3$ (g)	Weight of $MgCO_3$ (g)	Total CO_3^{2-} (%)
Nkalagu limestone (raw)	0.4475	0.0170	0.7991	0.0357	83.48
Poultry eggshells (raw)	0.5077	0.0140	0.9066	0.0294	93.60
Nkalagu limestone purified	0.5490	0.0038	0.9804	0.00798	98.84
Eggshell $CaCO_3$ purified	0.5526	0.0029	0.9868	0.00609	99.29
Commercial $CaCO_3$ product	0.5395	0.0036	0.9634	0.00756	97.10

The ground limestone and eggshell samples (1.0 g) were weighed into separate flasks and digested with dilute acid (0.1 M HCl), in accordance with Holderness and Lambert (1982). The resulting solutions were filtered through Whatman filter paper, the residues washed with dil HCl, and slowly added to the filtrates until alkaline. At different pH values, the filtrates, mainly containing $Ca(OH)_2$ solution, were carbonated by passing digestion gas (CO_2), generated *in situ,* from the raw ground samples. The precipitates so formed were collected by filtration and drying. The dried samples were then analysed and compared with the commercial grades of $CaCO_3$.

The quantities of CaO present in the local Nkalagu limestone and eggshell samples were observed to be appreciably high (Table 1). These raw materials are, therefore, useful for industrial production of $CaCO_3$ needed for paint manufacture. The carbonate contents, calculated stoichiometrically from the calcination reaction (Bailer *et al*., 1984; Elsevier, 1964), fell short of that required for paint manufacturing, which is 95% and above (Table 2). During purification, the HCl used for digestion of the raw ground samples produced chlorides of Ca and Mg, which were filtered to obtain acidic filtrates. The filtrates were made alkaline by the addition of ammonia solution. The resultant solution contained mainly $Ca(OH)_2$, as the $Mg(OH)_2$ was relatively insoluble, which was removed partly by filtration before the carbonation process, thus accounting for the low yield of $MgCO_3$ in the purified grades (Table 2).

The calculated percentage of carbonate contents (Table 2) in the purified grades was above 95%, which is adequate for paints and other chemical manufacturing processes. The acid-digestion method of purification gave high yields of precipitate on carbonation. The higher the pH, the higher was the yield (Table 3). When compared with the commercial $CaCO_3$ grade, the purified grade of $CaCO_3$ showed improvement on the fineness and whiting properties, an attribute of significance for the paint and other chemical process industries. These results showed that the characteristics were compa-

Table 3. Precipitated $CaCO_3$ and yields (%) on carbonation at different pH values

Sample	pH of solution	Initial weight (g)	Precipitate on carbonation (g)	Yield (%)
Nkalagu limestone	10	1.0	0.740	74.0
	11	1.0	0.750	75.0
	12	1.0	0.771	77.1
	13	1.0	0.788	78.8
Poultry eggshells	10	1.0	0.765	76.5
	11	1.0	0.799	79.9
	12	1.0	0.820	82.0
	13	1.0	0.846	84.6

rable with the United States grades of $CaCO_3$ (Thorpe and Whiteley, 1946).

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