

## Development of Porcelain Glaze from Recycled Calcium Carbide Waste and Other Local Raw Materials in South Eastern Nigeria.

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### ABSTRACT

Indiscriminate dumping of calcium carbide waste around mechanic garages poses grave risks of ground water contamination through leaching of hazardous contaminants. A quantity of disposed calcium carbide waste was collected from a dump site near a mechanic garage in Afikpo, Ebonyi state of south eastern Nigeria. The calcium carbide waste was soaked and washed with ample amounts of distilled water for seven days, until no more bubbles were released from unreacted carbides. The sample was dried in open air and specimens were taken from the dried sample for x-ray diffraction and x-ray fluorescence analyses. Two batches of calcium oxide glaze were prepared from Nsu clay, potash feldspar and Otammiri river sand. One batch of glaze contained commercial grade CaO, while the other batch contained the processed calcium carbide waste, the amount of which was calculated from stoichiometric relations to obtain the equivalent amount of CaO upon decomposition of the calcium carbide waste during firing. Both glaze samples were used to glaze bisqued porcelain test slabs, which were then glost fired to 1250°C. X-ray diffraction results revealed that the major mineral oxides present in the calcium carbide waste were portlandite Ca(OH)<sub>2</sub>, calcite (CaCO<sub>3</sub>) and rutile (TiO<sub>2</sub>). X-ray fluorescence examination revealed that calcium was the major chemical element present in the calcium carbide waste, up to 69% by weight, with trace amounts of some potentially hazardous metals such as silver, niobium, yttrium and titanium. Comparison of the surfaces of the glost fired porcelain test slabs revealed that the calcium carbide waste yielded substantial amounts of calcium oxide during firing, which enabled the glaze to vitrify properly, just like the glaze containing commercial grade calcium oxide. It was observed that trace amounts of rutile present in the calcium carbide waste produced a matte tendency in the glaze containing calcium carbide waste. These results suggest that calcium carbide can be successfully incorporated in porcelain glazes. It is recommended that improved waste disposal techniques be developed for various end users of calcium carbide in Nigeria, to enable easier collection of recyclable wastes and to prevent ground water contamination.

**KEYWORDS:** Calcium carbide, calcium oxide, porcelain, glaze, x-ray diffraction, x-ray fluorescence, portlandite, calcite, rutile.

### I. INTRODUCTION

One of the factors that affect the profitability of any business enterprise is the cost of raw materials. Processed calcium oxide for glaze production are usually imported in Nigeria, despite the abundance of local alternatives. This adversely affects the sustainability of many ceramic production enterprises in Nigeria. Any process that could convert an otherwise harmful waste, into a useful ceramic raw material, will impart positively on the ceramic industry in Nigeria.

The extensive use of calcium carbide in Nigeria for oxy-acetylene welding results in the indiscriminate disposal of the associated waste product which comprises chiefly of calcium hydroxide, (slaked lime) and possibly trace amounts of some potentially hazardous substances.. This poses serious contamination risks for surface and ground water. However, these risks could be mitigated by exploring possible ways to recycle this waste into useful and harmless products, such as the application of these waste in the production of porcelain glaze.

Porcelain belong to a group of high fired ceramic products composed chiefly of clay, quartz, and feldspar in various proportions. Compared to low and medium fired ceramics, they have superior strength characteristics, such as toughness and durability. They are usually fired at a high temperature, usually above 1260°C, at which the body vitrifies and forms a non-absorbent surface, (Bertollissi 2014).

These properties make porcelain easily the material of choice in many technical applications such as electrical insulation, especially at high voltages, as well as easy clean wall and floor tiles, sinks and W/C fittings. The technical characteristics and in particular mechanical strength of porcelain are closely related to the material porosity. A material with minimum open porosity corresponds to the highest mechanical strength, (Marquez et al 2008).

Many porcelain applications require an impermeable surface; hence the porcelain body is usually covered with appropriate glazing material to eliminate as much as possible, all surface pores, (Lucas 2001). Glazing involves the application of an impervious layer of a glassy substance on a bisque fired body and fusing them through subsequent firing called glost firing. The glaze serves to colour, decorate, or seal the inherent porosity of the bisque fired ware.

Glazes basically consist of a fluxing agent, glass former, (usually silica), viscosity agent, (often alumina), opacifying agents and/or colourants, (Arbuckle, 2007). The fluxes promote partial liquefaction in the clay bodies and other glaze materials. They lower the high melting point of the glass former, usually silica or boron trioxide, (Guarav, 2005).

Common fluxes used in glazes include oxides of lead, sodium, potassium, lithium, calcium, magnesium, barium, zinc, strontium, and manganese, (Greg 1995). Compared to sodium, lithium and potassium fluxes, which are low melting fluxes, calcium oxide is the fluxing agent of choice at medium or high temperatures, for example with porcelain ware which are fired at cone 12 or cone 13. However, most glazes contain some calcium oxide as it increases the durability and hardness of the base glaze, (Fromme 1994).

Calcium oxide is the principal flux in medium and high temperature glazes, beginning its action within the glaze around 1100°C. Below cone 4, calcium oxide is not active. It is a moderate flux in the cone 5-6 range, but a very active one at cone 10, (Hansen 2008)

Calcium oxide is supplied by a number of minerals, chiefly wollastonite, (CaSiO<sub>3</sub>), calcium carbonate, also known as whiting (CaCO<sub>3</sub>), dolomite, (CaCO<sub>3</sub>.MgCO<sub>3</sub>), calcium feldspar, (CaO.Al<sub>2</sub>O<sub>3</sub>.4SiO<sub>2</sub>). The choice of calcium oxide bearing mineral could influence the particular glaze chemistry of the recipe, (Hansen 2008).

Wollastonite is usually the choice raw material for supply of CaO in glazes. However because of its versatile usage in several other industrial applications, it can often be quite expensive. In 2008, price of raw wollastonite was USD 80 – 500 per ton, depending on the country of origin and size and shape of the powder particles, (Virta 2009).

Another potential source of calcium oxide for glaze recipes is the recycled waste from calcium carbide, a chemical compound with the formula CaC<sub>2</sub>. Its main industrial applications include, the production of acetelyne gas, calcium cyanamide, (a nitrogen fertilizer), and in steel making, (Wayne 1996).

Calcium carbide reacts with water to produce acetelyne and calcium hydroxide according to the equation  $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{Ca}(\text{OH})_2$ , (Greenwood et al 1997). This reaction is the basis for the production of acetelyne gas used in oxy-acetelyne welding. The waste by product consists mainly of Ca(OH)<sub>2</sub> (slake lime), and caustic solid substances and are white in appearance when pure, (Joel et al 2014). Slake lime decomposes upon heating to give steam and calcium oxide according to the equation  $\text{Ca}(\text{OH})_2 = \text{CaO} + \text{H}_2\text{O}$ .

Calcium carbide waste is normally dumped at different locations in Nigeria, especially mechanic villages and industries where oxy-acetelyne welding are carried out. Calcium carbide waste is ordinarily disposed via land fill or open dumping which have effect on surface and ground water, arising from the leaching of harmful compounds and alkali to ground and surface water, (Joel et al 2014).

It is therefore desirable to scientifically explore more suitable disposal methods for calcium carbide waste or methods to recycle them into more useful and safe products.

## **II. MATERIALS AND METHODOLOGY**

The calcium carbide waste used for this research was obtained from a dump site near a mechanic garage at Afikpo in Ebonyi state of Nigeria. The calcium carbide waste was soaked in ample distilled water in a clear transparent bucket. The sample was vigorously stirred with a wooden stirrer and bubbles of gas from unreacted carbide were continuously released as the sample was stirred.

Excess water was decanted as well as some organic impurities which floated at the top of the bucket. The sample was allowed to soak for seven days, with the excess water decanted daily and refilled with fresh distilled water until no more bubbles were released from the sample.

The excess water was finally decanted and the wet sample was spread out on a drying mat and allowed to dry in open air for seven days. The dried sample was then ground in a ball mill for six hours and later sieved using a mesh 100 sieve. Some specimen was taken from the sieved sample and scanned on an Empyrean diffractometer, to determine the mineralogical and chemical composition.

Two batches of glaze were prepared, one from a mixture of Nsu clay, Otammiri river sand, potash feldspar and commercial grade calcium oxide, while the other batch contained the processed calcium carbide waste, in place of commercial grade calcium oxide. The amount of calcium carbide waste used to replace commercial grade calcium oxide, was determined from stoichiometry according to the decomposition equation,  $\text{Ca}(\text{OH})_2 = \text{CaO} + \text{H}_2\text{O}$ , i.e approximately 1.3g of calcium carbide waste for each gram of CaO.

Four rectangular porcelain test slabs, measuring 5cm by 10 cm by 0.5cm, were prepared from a mixture of 50% by weight of Nsu clay, 30% by weight of potash feldspar and 20% by weight of Otammiri river sand and marked A1, A2, B1 and B2 respectively. The test slabs were allowed to dry in open air for seven days,

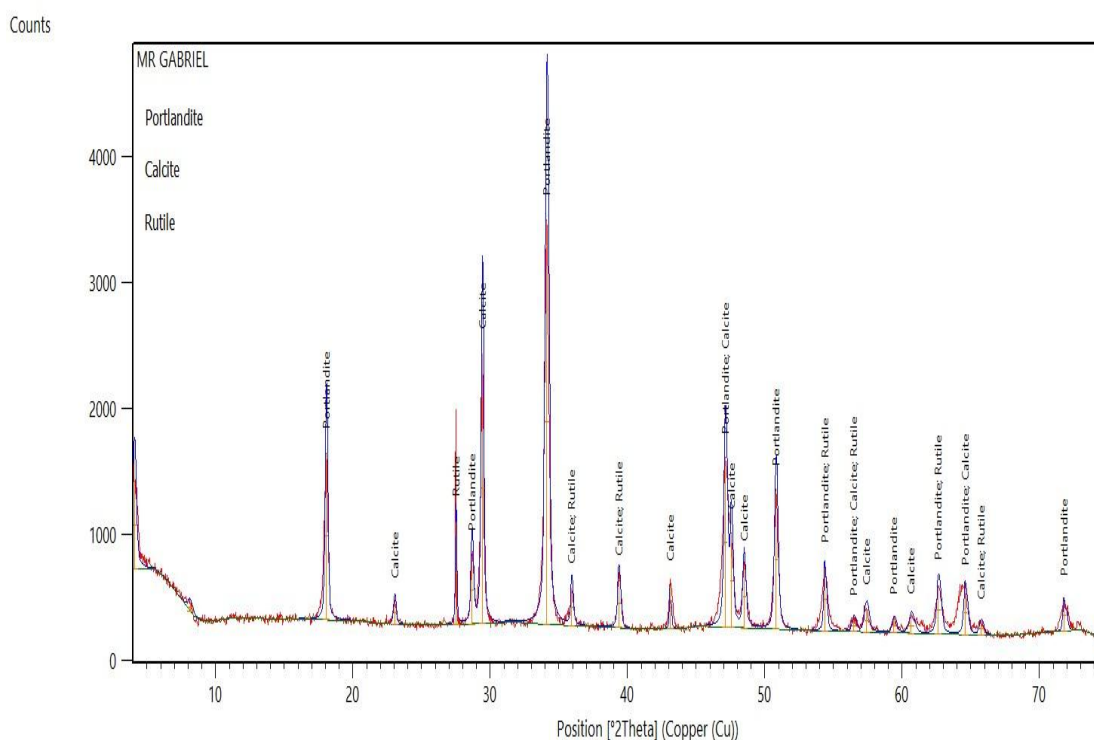
afterwards they were oven dried at 110°C for eight hours. They were then bisque fired up to 950°C in an electric kiln and allowed to soak for two hours.

After cooling, the test slabs were then glazed using the prepared glaze batches. The glaze prepared from commercial grade CaO, was applied on samples A1 and A2, while the glaze prepared from the processed calcium carbide waste was applied on samples B1 and B2. The glaze were applied homogeneously on the samples using a sprayer and the test pieces were allowed to dry.

Afterwards they were fired to a temperature of 1250°C in a gas kiln. After cooling overnight in the kiln, the test pieces were brought out and inspected.

### III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction results of the calcium carbide waste, while table 1 shows the x-ray fluorescence results of the calcium carbide waste.



**Figure 1.** x-ray diffraction pattern generated by the calcium carbide waste sample.

**Table 1:** Results of the x-ray fluorescence analysis of the calcium carbide waste sample.

Element Symbol	Weight Concentration.	Oxide Symbol	Stoichiometric weight Concentration
Ca	69.20	CaO	69.14
Ag	3.39	Ag <sub>2</sub> O	2.60
Y	3.30	Y <sub>2</sub> O <sub>3</sub>	2.99
C	2.97	CO	2.12
Nb	2.85	Nb <sub>2</sub> O <sub>5</sub>	2.91
Si	2.48	SiO <sub>2</sub>	3.79
Ba	2.14	BaO	1.71
Fe	2.03	Fe <sub>2</sub> O <sub>3</sub>	2.07
S	1.82	SO <sub>2</sub>	2.60
Al	1.72	Al <sub>2</sub> O <sub>3</sub>	2.32
K	1.64	K <sub>2</sub> O	1.41
V	1.41	V <sub>2</sub> O <sub>5</sub>	1.80
Cl	1.32	Cl	0.94
Mn	1.02	MnO	0.94

Ti	0.89	TiO <sub>2</sub>	1.06
Mg	0.48	MgO	0.57
P	0.40	P <sub>2</sub> O <sub>5</sub>	0.65
Na	0.25	Na <sub>2</sub> O	0.24
F	0.21	F	0.15

It is evident from the x-ray analysis results, that calcium carbide waste contains remarkable amounts of calcium oxide, as well as trace amounts of other mineral oxides whose presence could impart specific properties to a glaze.

Comparison of the surface of the test slabs shows that the two glaze specimens vitrified properly at the glaze temperature. However, the slight matte tendency observed on the samples B1 and B2 could be attributed to the trace amounts of rutile contained in the calcium carbide waste product. Mamzuder and Mishra (2011) reported that the presence of rutile can cause crystallization, leading to a matte surface.

It was also observed that the trace amounts of rutile contained in the calcium carbide waste imparted better opacity tendencies to samples B. This is in agreement with Fofana et al, who reported that rutile improves opacity and whiteness in calcium containing glazes.

#### IV. CONCLUSION AND RECOMMENDATIONS

From the results discussed above, it can be concluded that calcium carbide waste can yield substantial amounts of calcium oxide. It can also be concluded that this waste product can be successfully incorporated in glaze formulations, especially for high temperature porcelain glazes.

Trace amounts of other oxide minerals, such as rutile, contained in the calcium carbide waste, could impart a range of special properties to such glazes produced from calcium carbide waste, including improved opacity and color development.

It is recommended that improved waste disposal methods be developed for such recyclable wastes, such as calcium carbide waste, especially among artisan users. This will help prevent potential ground water contamination and enable easy collection of wastes for recycling

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