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Ceramic Properties of Mud Volcanoes Effluent

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The ceramic properties of the effluent of the Piparo mud volcano in central Trinidad have been investigated in relation to chemistry, mineralogy and fired physical and mechanical properties. X-ray diffractometry (XRD) and differential thermal analysis (DTA) revealed that mineralogically the high-plasticity effluent is essentially a kaolinitic clay. However, some quartz, mica and potash feldspar were also detected. Chemically, the organic matter was found to be 2.2% while the SiO_2, Al_2O_3 and Fe_2O_3 content amounted to 55.2, 16.6 and 6.5% respectively. Loss on ignition (LOI) at 1000°C amounted to 14%. Testbars fired in the temperature range 800°C - 1000°C for 4 hrs exhibited the "black core" phenomenon. In addition, bloating occurred at 1000°C. However, specimens fired at and below 950°C where no bloating was evident, exhibited modulus of rupture and fracture toughness values in the range 6 - 19 MPa and 0.4 - 0.7 $MNm^{-3/2}$ respectively, depending on temperature. Based on data previously reported for the effluent of The Devil's Woodyard mud volcano[1], the Piparo effluent is of similar chemical and mineralogical character and exhibit comparable fired properties.

1. Introduction

For many years, mud volcanoes have been active on the island of Trinidad in the eastern Caribbean. Further, exclusive to the south and central regions, some tend to be small and occur in remote forested areas, while others are relatively large and readily accessible. For example, the tassiks of The Devil's Woodyard and the Piparo volcanoes, the two largest on the island, currently measure some 95m and 250m across respectively.

Historically, The Devil's Woodyard is recorded to have first erupted in 1852, with other major eruptions occurring in 1888 - 1889, 1906, 1942, 1969, 1988 and again as late as May 1995. Further, since the 1995 eruption non-explosive, low-level activity has persisted at The Devil's Woodyard where mud in the form of a slurry continues to ooze slowly from a number of sporadic vents close to the centre of the tassik. Consequently, over a period of time an estimated 20,000 - 50,000 tonnes of the grey, fine-particle size, sun-baked effluent now form a mound at the site. On the other hand, in a single first eruption at Piparo in February 1997, an estimated 300,000 tonnes of mud were brought to the surface.

Furthermore, recent studies[1,2] have established that The Devil's Woodyard effluent is essentially a high-plasticity, low-temperature vitrifying kaolinic clay. Consequently, given the importance and wide usage of kaolinite as base raw material for many silicate ceramics, its ceramic properties have been investigated[1]. Arising from this, indications are that potentially, high-strength, high-toughness products are possible from The Devil's Woodyard mud at a much lower firing temperature compared with the firing most other Trinidad ceramic clays to equivalent strength and toughness. This study reports on a similar study, involving the chemistry, mineralogy and fired characteristics of the Piparo mud volcano effluent. A comparison of results is also made with The Devil's Woodyard effluent.

2. Experimental

2.1 Chemistry and Mineralogy

Dark grey, moist, malleable and highly plastic, the samples collected for the study were taken at various points of the volcano tassik on the day of the eruption. After air-drying at room temperature, these were crushed and ground and sieved

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through a 500 μm mesh size sieve. Equal portions by weight of the <500 μm fractions from the various collection points were then batched to give one representative sample. Particle size distribution (obtained by wet sieve analysis) for this is shown in **Figure 1**.

Chemically, the oxides content was determined by standard analytical methods involving fusing with sodium hydroxide followed by spectrophotometry analysis[3,4] while the organic matter content was quantified by the potassium dichromate oxidation method[5]. X-ray diffractometry (XRD) and differential thermal analysis (DTA) were used to characterise the mineralogy. For the XRD study, CuKα radiation was used in a Rigaku diffractometer operated at 40kV and 20mA. Similarly, DTA was done over the temperature range 75 - 1000°C at a heating rate of 10°C/min. Calcined alumina was used as standard.

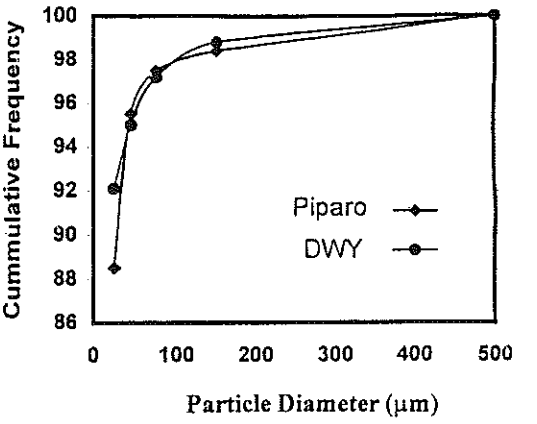

FIGURE 1: *Particle Size Distribution in the <500 μm Fraction of the Mud used in the Experiments*

2.2 Fired Characteristics

Testbars of square cross-section, 1.2 x 1.2 cm were fabricated by extrusion of a plastic, hand-worked dough of the powdered mud with water (17.8%) under a hydraulic pressure of ~2MPa through a PVC die. Subsequently, the bars were air-dried at room temperature (typically 27 - 30°C and relative humidity 80%) and the linear drying shrinkage determined using vernier calipers. Firing was then carried out at five different temperatures in the range 800 - 1000°C in an electric furnace at a heating rate of 10°C/min and for a soaking time of 4hrs.

The modulus of rupture (MOR) of both green and fired specimens was determined in three-point bend loading using a specimen span of 2.5cm. The specimen width and depth depended on the degree of shrinkage at the various firing temperatures. Similarly, the fracture toughness of the fired specimens was determined on the basis of the critical stress intensity factor K_{IC} (ref. 6) in three-point bend loading using single-edge, notched bars. Again the specimen span was 2.5 cm, while the notch depth, a, was such that $0.45 < a/w < 0.55$, where w is the specimen width. For both the MOR and the K_{IC}, average values were taken over 10 specimens.

3. Results and Discussion

Included for comparison in each Table and Figure of this section is equivalent data previously reported for The Devil's Woodyard (DWY) mud.

3.1 Chemistry and Mineralogy

An organic matter content of 2.2% was determined for the mud. This represents a value significantly higher than the <0.1 - 1% typical of most Trinidad ceramic clays[7] but about the same as the 2.1% of The Devil's Woodyard mud[2]. However, in terms of ceramic properties, the relatively high values exhibited by the mud from the two volcanoes (attributed to an abundance of lignitic matter mixed in with the mud at both tassiks[2]) are not expected to be overtly problematic since organic matter normally burns out at relatively low temperatures during firing.

Table 1 shows that in terms of oxides content, the Piparo mud is not too dissimilar to The Devil's Woodyard mud. Similarly, both exhibit comparable loss on ignition.

Regarding mineralogy, **Figures 2** and **3** show the XRD and DTA profiles respectively, obtained from the mud. As with The Devil's Woodyard mud, the clay mineral kaolinite features prominently in the XRD profile of the Piparo mud, with some quartz, mica, potash feldspar and calcite also detected. Similarly, the DTA profile of **Figure 3** seems to confirm that like the Devil's Woodyard mud, the Piparo mud is essentially a kaolinitic clay. Further, the relatively high organic matter content of the mud previously mentioned is reflected in the strong exothermic peaks (representing decomposition of organic matter) seen between ~125°C and ~400°C of the DTA profile. Such exotherms,

TABLE 1: *Wt.% Oxides Content and Loss on Ignition (LOI) of the Piparo Mud. Included for comparison is corresponding Data for The Devil's Woodyard Mud.*

Analysis	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	TiO_2	LOI
Piparo	55.2	16.6	6.5	2.2	1.1	0.1	0.2	0.4	14.0
The Devil's Woodyard	53.7	17.6	6.1	1.8	1.9	0.4	0.5	0.2	13.2

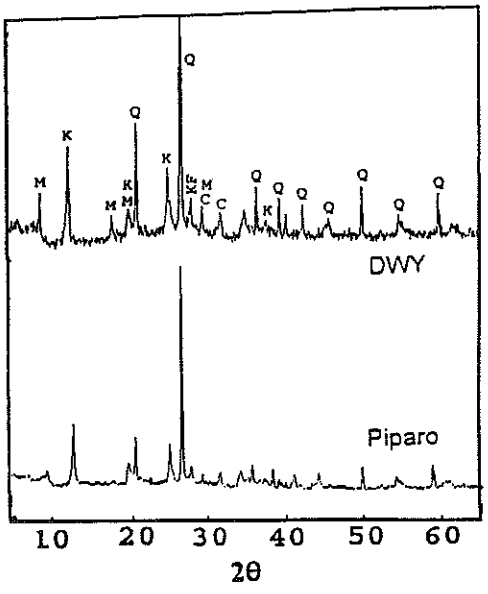

FIGURE 2: *XRD Profiles of the Piparo and The Devil's Woodyard Mud (K, Kaolinite; M, Mica; Q, Quartz; C, Calcite; KF, Potash Feldspar)*

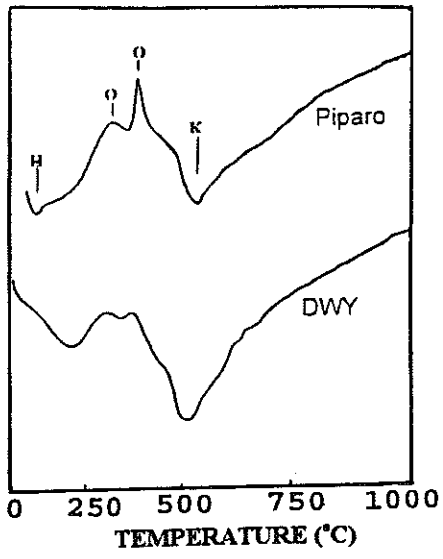

FIGURE 3: *DTA Profiles of the Piparo and The Devil's Woodyard Mud*

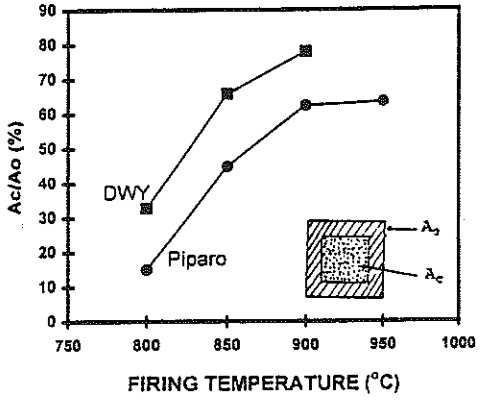

FIGURE 4: *Variation in A_c/A_o as a Function of Firing Temperature, where A_c is the Cross-sectional Area of the Black Core and A_o that of the Fired Bars*

reported[8] to be typical of metal-organic complexes involving Si, Al and Fe, disappear from the DTA profiles once the organic matter is removed prior to analysis. However, the high organic matter content coupled with a high clay mineral content is believed to be predominantly responsible for the high LOI (14%) of the mud. This is so since the LOI of natural clays is normally mainly due to the decomposition of organic matter, dehydroxylation of clay minerals and decomposition of carbonates. However, specific to the mud, contribution from the decomposition of carbonates is expected to be minimal since no carbonated decomposition peak (expected in the vicinity 800 - 900°C) appeared in the DTA profile (**Figure 3**) and the calcite peaks detected by XRD (**Figure 2**) are weak, suggesting a low carbonates content.

3.2 Drying Shrinkage and Green Strength

Mean linear drying shrinkage of the testbars amounted to 5.7%, a value of the order of 2% lower than the 8.2% previously reported[1] for The Devil's Woodyard mud. Similarly, the Piparo mud specimens exhibited a mean green strength of 1.9MPa, a value superior to both the 1.1MPa reported for The Devil's Woodyard mud[1] and the 0.1 - 0.7MPa typical of other Trinidad ceramic clays[9].

3.3 Fired Characteristics

3.2.1 General

At the temperatures studied, the testbars fired brown to reddish-brown. Further, similar to the bvehaviour reported for The Devil's Woodyard mud, the Piparo mud testbars exhibited the central black core phenomenon, whereby the interior fired black at all the temperatures studied. Firing at

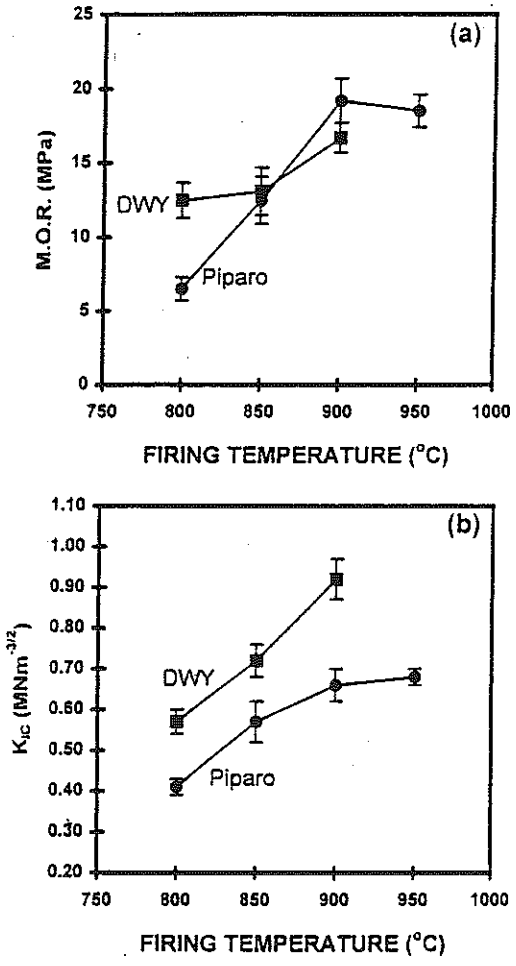

FIGURE 5: *(a) MOR and (b) K_{IC} as a Function of Firing Temperature*

1000°C resulted also in bloating of the testbars (compared with testbars from The Devil's Woodyard effluent which bloated at and above 950°C). Nevertheless, on firing at and below 950°C, the black core was observed to be symmetrical in cross-section, with the area fraction increasing with increasing firing temperature (**Figure4**), as was the case reported for The Devil's Woodyard mud[1]. However, while the trend in increase is similar for both the Piparo and The Devil's Woodyard mud (**Figure 4**), at corresponding firing temperatures, the cross-sectional area occupied by the black core is smaller in the Piparo testbars.

As suggested previously for The Devil's Woodyard mud[1], both the bloating of the Piparo testbars at 1000°C and the black core formation, even at a temperature as low as 800°C, suggests advanced early vitrification of the mud. This is so since bloating is mainly due to the trapping of gases from volatiles and gas-evolving reactions, such as the decomposition of iron pyrite, by a molten vitrified phase and their subsequent expansion. Similarly, the formation of the black core is related to early vitrification slowing down the diffusion of oxygen into the interior to effect oxidation of free carbon, present from carbonised organic matter, and sulphides resulting from the decomposition of iron pyrite. In effect, strong local reducing conditions prevail and ferrous iron is formed.

3.2.2 Mechanical and Physical Properties

Because of bloating of the testbars at 1000°C, mechanical and physical properties were measured only for firing temperatures up to 950°C. **Figure 5 (a)** shows that between 800 and 900°C, the MOR of the testbars increases almost linearly with increasing firing temperature. However, firing at 950°C appears not to have effected further increase in strength compared with firing at 900°C. This could possibly reflect the onset of bloating on firing in the vicinity of 950°C. Nevertheless, while the strength of the Piparo mud is substantially lower than that of The Devil's Woodyard mud on firing at 800°C, comparable values are exhibited for firing temperatures of 850 and 900°C.

As with the MOR, **Figure 5 (b)** shows that the K_{IC} of the mud also increases firing temperature, tending to level off towards the higher end of the firing temperature range. However, at corresponding firing temperatures, the values tend to be lower than values reported for The Devil's Woodyard mud, although better than $0.4MNm_{-3/2}$ over the firing temperature range. Nevertheless, the important point of note is that MOR and K_{IC} values of the magnitude exhibited by the mud are only possible for most other Trinidad ceramic clays on firing to temperatures in excess of 1050°C[9].

Commensurate with the MOR and K_{IC} increasing with increasing firing temperature, **Figures 6 (a)** and **6 (b)** show that the apparent porosity and water absorption decrease while the bulk density (**Figure 6 (c)**) and linear firing shrinkage (**Figure 6 (d)**) tend to increase as the firing temperature is raised. However, the decrease in porosity and the increase in shrinkage between 850°C and 900°C is quite sharp compared with between 800°C and 850°C. This would suggest that advanced vitrification of the mud occurs only above 850°C.

4. Conclusions

In terms of mineralogical character, the Piparo volcano mud is, like The Devil's Woodyard mud, essentially a high-plasticity low-temperature vitrifying kaolinitic clay.

Compared with most Trinidad ceramic clays, the green strength of the mud is significantly superior. However, the organic matter content, the loss on ignition and the drying shrinkage are comparatively high.

As with The Devil's Woodyard mud, the Piparo mud testbars exhibited the central black core phenomenon at all

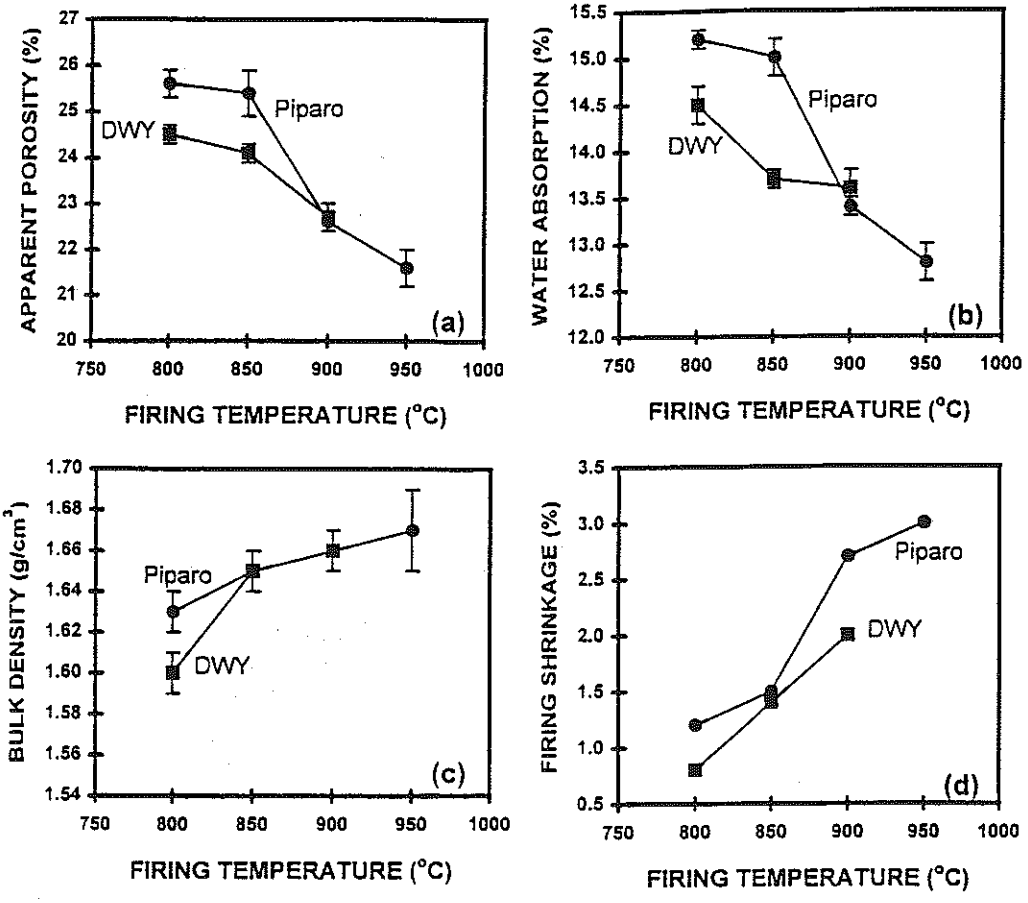

FIGURE 6: *(a) Apparent Porosity, (b) Water Absorption, (c) Bulk Density and (d) Linear Firing Shrinkage as a Function of Firing Temperature*

the firing temperatures studied. Bloating also occurred on firing at 1000°C, compared with testbars from The Devil's Woodyard mud which bloated at and above 950°C.

On firing in the temperature range 800 - 950°C where no bloating was evident, the Piparo mud testbars developed strength and toughness achievable in most other Trinidad clays only on firing to temperatures in excess of about 1050°C. Hence, as with The Devil's Woodyard mud, implications are that high-strength products are possible from the Piparo mud at a lower firing cost compared with firing most other Trinidad clays to equivalent strength and toughness. However, because of the relatively high-drying shrinkage, batching with other clay(s) of low plasticity and/ or "non-plastics" may be necessary for prospective commercial products.

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