

CERAMIC CHARACTERISTICS OF THE WHITE-BURNING VALENCIA CLAY OF TRINIDAD

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ABSTRACT

The ceramic potential and application scope of the white-burning, low-shrinkage Valencia clay of Trinidad have been investigated on the basis of chemistry, mineralogy and fired characteristics. Standard analytical chemical methods show that in addition to the major oxides SiO_2 and Al_2O_3 , the clay contains minor amounts of MgO and TiO_2 and as low an Fe_2O_3 content as 0.3%. While x-ray diffractometry (XRD) and differential thermal analysis (DTA) show the clay to be kaolinitic, the deposit also contains some quartz, mica, potash feldspar and calcite. On firing, significant vitrification of the clay commences only above $1,000^\circ\text{C}$. This, in part, leads to relatively low shrinkage and high porosity in the temperature range $900^\circ\text{C} - 1,100^\circ\text{C}$ where many ceramic bodies are usually fired. However, the corresponding strength and toughness are sufficiently high to render the clay potentially suitable for a range of ceramic products. Further, as a potential component in certain refractories and as a shrinkage-reducing agent when blended with high-shrinkage clays, the high porosity and low shrinkage are desirable.

1.0 INTRODUCTION

Of the vast deposits of clays throughout the Caribbean, only minor quantities are currently mined for ceramic and refractory applications. Further, these applications are mainly confined to traditional pottery and coarse-finished structural products such as building blocks, floor tiles and wall tiles. However, recent investigation

of samples from several deposits in Trinidad has established certain outstanding characteristics of many, indicative of potentially diverse and viable large-scale commercial exploitation¹⁻⁵. Of considerable interest in this respect are the white-burning and near white-burning clays of the Valencia deposit to the north-east of the island. High in quartz and mica content, these low plasticity kaolinitic clays exhibit significantly lower drying and firing shrinkage than most other Trinidad clays². In addition, compared to other Trinidad clays, they are of low iron, organic matter and water-soluble salts¹.

Consequently, as part of wider study of the non-metal minerals of the region, the ceramic potential and application scope of the Valencia clays have been studied. This paper reports on the chemistry, mineralogy and fired physical and mechanical characteristics (in the temperature range $900^\circ\text{C} - 1,400^\circ\text{C}$) of the white-burning variant.

2.0 EXPERIMENTAL

2.1 The Raw Material

While a learned study of the geology, the extent and the commercial viability of the Valencia clay deposit is outside the scope of this work, a representative sample from a major quarry Works in the area was studied. After drying at room temperature, equal weights of samples collected from various locations inside the quarry were mechanically ground, mixed together and the fraction of the whole passing through

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a 500 μm sieve mesh used in the experiments. Particle size distribution (obtained by standard wet sieve analysis) in this fraction is shown in Table 1.

The oxides content of the clay was determined by standard analytical chemical methods involving fusing with sodium hydroxide followed by photospectrometry analyses ^{5-8, 6,7}. As part of the procedure, the loss on ignition (LOI), at 1,000°C, was also determined. Similarly, while the soluble sulphate and soluble phosphate were determined photospectrometrically, the organic matter content was quantified by the potassium

PARTICLE SIZE (μm)	500	150	75	45	25
CUMULATIVE FREQUENCY	100	97.5	91.6	83.1	70.9

Table 1: Particle Size Distribution in the Starting Powder

dichromate oxidation method. Determination of free alumina involved digestion with sodium hydroxide and calcination at 1,200°C.

Both x-ray diffractometry (XRD) and differential thermal analysis (DTA) were used to investigate the mineralogy of the clay. In the case of XRD, $\text{CuK}\alpha$ radiation was used in a Rigaku diffractometer operated at 40kV and 20mA. DTA was carried out in the temperature range 75°C - 1,000°C using both the as-mined bulk clay and the separated 2 μm clay mineral fraction (obtained by standard sedimentation procedure based on Stoke's law). No reference standard was used and the heating rate was 10°C/min.

Quantitatively, the clay/non-clay mineral ratio was determined based on the method of comparing the dehydroxylation weight loss from the bulk clay with that from the separated 2 μm fraction.

2.2 Physical and Mechanical Properties

To investigate the physical and mechanical properties of the clay, rectangular testbars (10.7 x 1.3 x 1.3cm) were fabricated from a hand-worked plastic dough of the clay with water (18%). Moulding was done in a metal mould at a pressure of 2MPa applied in a hydraulic press. On removal of the bars from the mould and drying at room temperature (typically 25°C - 30°C and relative humidity 80%), drying shrinkage was determined using vernier calipers. Firing of the testbars

(at a heating rate of 10°C/min and for a soaking time of 4hrs) was subsequently done in the temperature range 900°C - 1,400°C in an electric furnace.

On cooling and removal of the samples from the furnace, fired shrinkage was determined, again using vernier calipers. Apparent porosity, water absorption and bulk density were determined gravimetrically using a method based on Archimedes principle. This involved weighing samples of portion of the testbars dry followed by vacuum-impregnation with water and a subsequent determination of a "wet" and "suspended" (in water) weight.

The flexural strength (modulus of rupture - MOR) of the fired samples was determined in three-point bend loading in a Griffin tensometer. The specimen span used was 2.5cm while the width and depth depended on the

degree of drying and firing shrinkage. Fracture toughness measurements (based on the critical stress intensity factor, K_{IC} , concept ⁸⁻⁹) were also done in three-point bend loading using single-edge notched beam specimens. A loading span of 2.5cm was used and the notch depth "a" was such that $0.45 < a/w < 0.55$, a necessary requirement for valid K_{IC} values (w is the specimen depth). For compressive strength measurements, specimens of rectangular cross-section and typical aspect ratio 1.3 were used. As with the MOR and K_{IC} , average values were taken over five or more specimens for each firing temperature.

Finally, scanning electron microscopy (SEM) was used to study the microstructure of the fired specimens as revealed in fractured section.

3.0 RESULT AND DISCUSSION

3.1 Chemistry

While Table 2 shows the oxides content and loss on ignition of the clay, Table 3 shows the organic matter, free alumina and soluble salts content. As can be seen from Table 2, the SiO_2 and Al_2O_3 content of the clay amounted to 74% and 17% respectively while the Fe_2O_3 content was as low as 0.3%. This low Fe_2O_3 content accounts for the clay burning white, as compared to high- Fe_2O_3 clays which generally burn brownish to red. Of the other oxides, only MgO (4.1%) is present to any significant amount.

SAMPLE	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	LOI
Valencia	74.0	17.0	0.3	-	4.1	-	-	0.7	3.9
Cocoloco	66.3	14.1	4.1	-	4.1	-	-	1.6	9.8
La Brea	58.0	17.8	5.4	-	3.8	0.1	0.5	0.8	13.7
Caparo	73.0	11.0	4.5	-	3.9	-	-	0.6	7.0
Flanigin Town	71.0	13.5	1.5	-	3.8	0.1	-	1.1	9.1
Mayo	58.5	14.8	5.0	2.0	4.6	0.1	0.2	1.0	13.8

Table 2: Oxides Composition and Loss on Ignition of the Clay. Included for Comparison is the Composition of Some Clay samples taken from other Locations in Trinidad

Table 2 shows that the loss on ignition at 1,000°C is of the order of 4%. Compared to values of the order of 6 - 14% reported for some other Trinidad clays¹, this value is low and is most likely indicative of a combination of low organic matter content (Table 3) and relatively low clay mineral content. This is so since the loss on ignition results predominantly from combustion of organic matter, dehydroxylation of the clay mineral and decomposition of carbonates. However, the fact that no carbonates endotherm appear in the DTA profiles (Figure 2) suggest a low carbonates content. Thus, the contribution to the LOI from carbonates is expected to be low.

Regarding the free Al₂O₃ content, the value of 4.6% (Table 3) is not markedly different from values of the order of 3.7-6.2 reported for some other Trinidad clays¹. Similarly, at < 0.01%, the soluble sulphate and phosphate content is either lower than or comparable to values exhibited by some other Trinidad clays.

Finally, qualitative treatment of the clay with dilute HCL showed the presence of some carbonate minerals. As will be seen, calcite was subsequently detected by XRD.

3.2 Mineralogy

Figure 1 shows the XRD profile obtained from the bulk as-mined clay. This shows kaolinite to be the only clay mineral detected. In addition, quartz, mica, potash feldspar and calcite were also detected. That kaolinite is the only clay mineral present was confirmed by DTA (Figure 2).

Concerning the clay/non-clay mineral ratio, a value of 1.01 was obtained. However, this represents an overestimated approximation, since XRD revealed the presence of some fine quartz and mica in the separated 2 μm clay mineral fraction of the clay used in the determination, based on dehydroxylation weight loss. Nevertheless, the value of 1.01 is less than values within the range 2.09 - 3.63 reported for some other Trinidad clays¹.

3.3 Physical Properties

Figure 3 shows the fired shrinkage (drying shrinkage was 1.6%), apparent porosity, water absorption and bulk density of the clay as a function of temperature in the range 900°C - 1,300°C. As can be seen, all these parameters exhibit little change on firing at 900°C and

SAMPLE	ORGANIC MATTER	FREE Al ₂ O ₃	SULPHATE	PHOSPHATE
Valencia	0.15	4.61	0.01	< 0.01
Cocoloco	0.97	4.10	0.01	0.08
La Brea	0.58	4.50	0.04	0.04
Caparo	1.17	0.80	< 0.01	< 0.01
Flanigin Town	< 0.10	5.29	0.09	0.06
Mayo	2.44	0.81	0.18	0.06

Table 3: Organic Matter, Free Alumina Soluble Sulphate and Soluble Phosphate Content (wt.%) of The Clay. Included for Comparison is Corresponding Data for Clay Samples taken from Some Other Locations in Trinidad

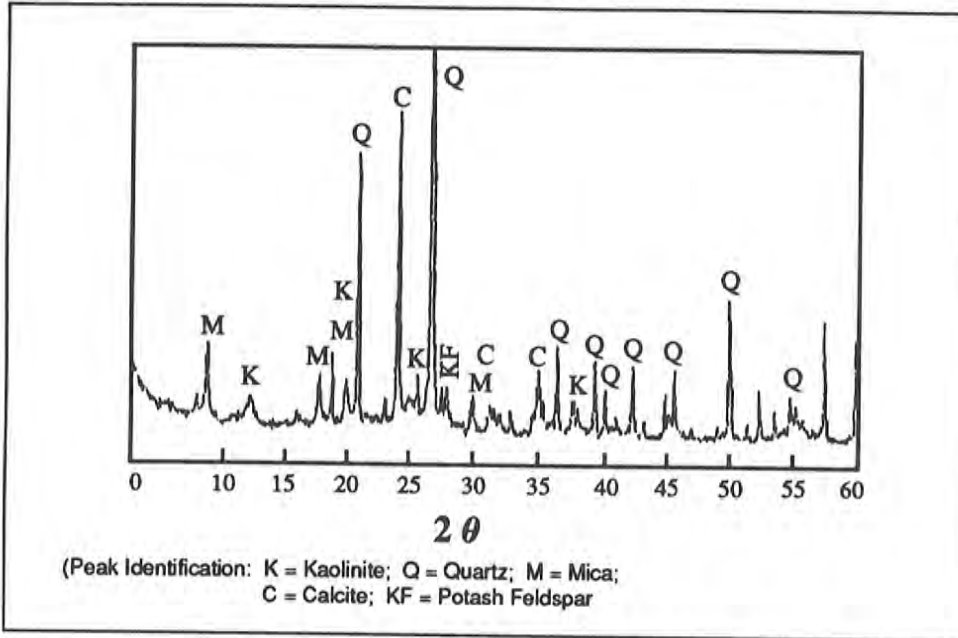


Figure 1: XRD Profile of The Clay

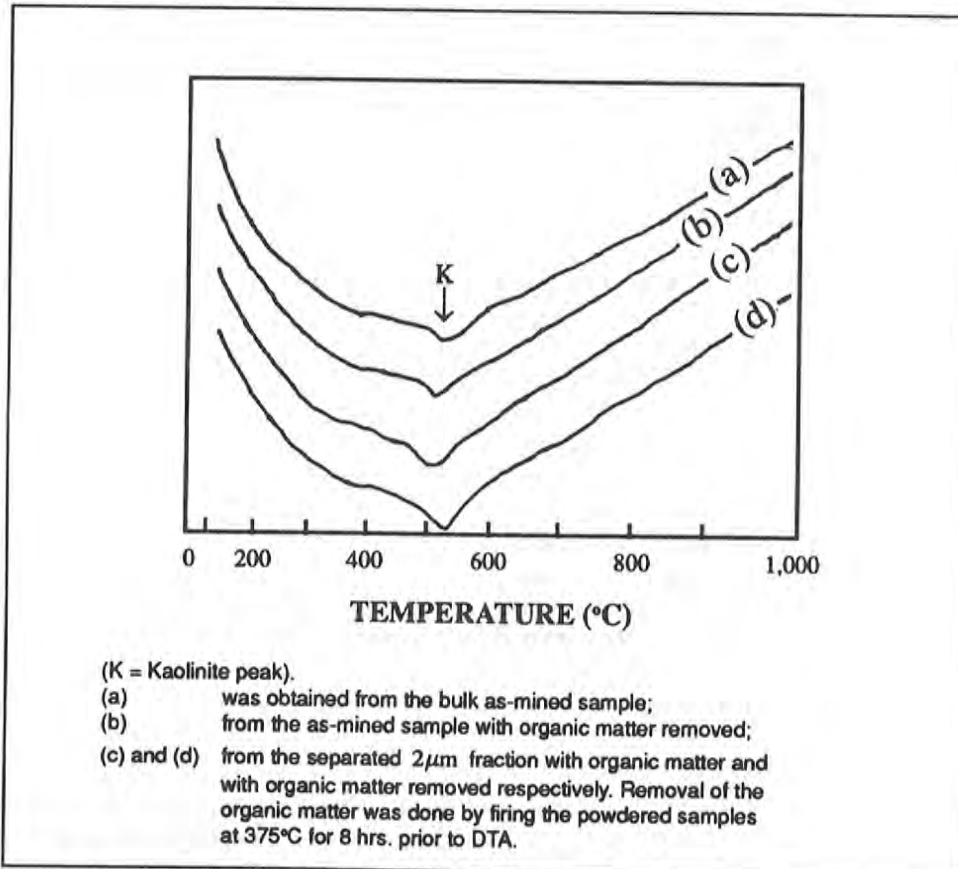


Figure 2: DTA Profile of The Clay

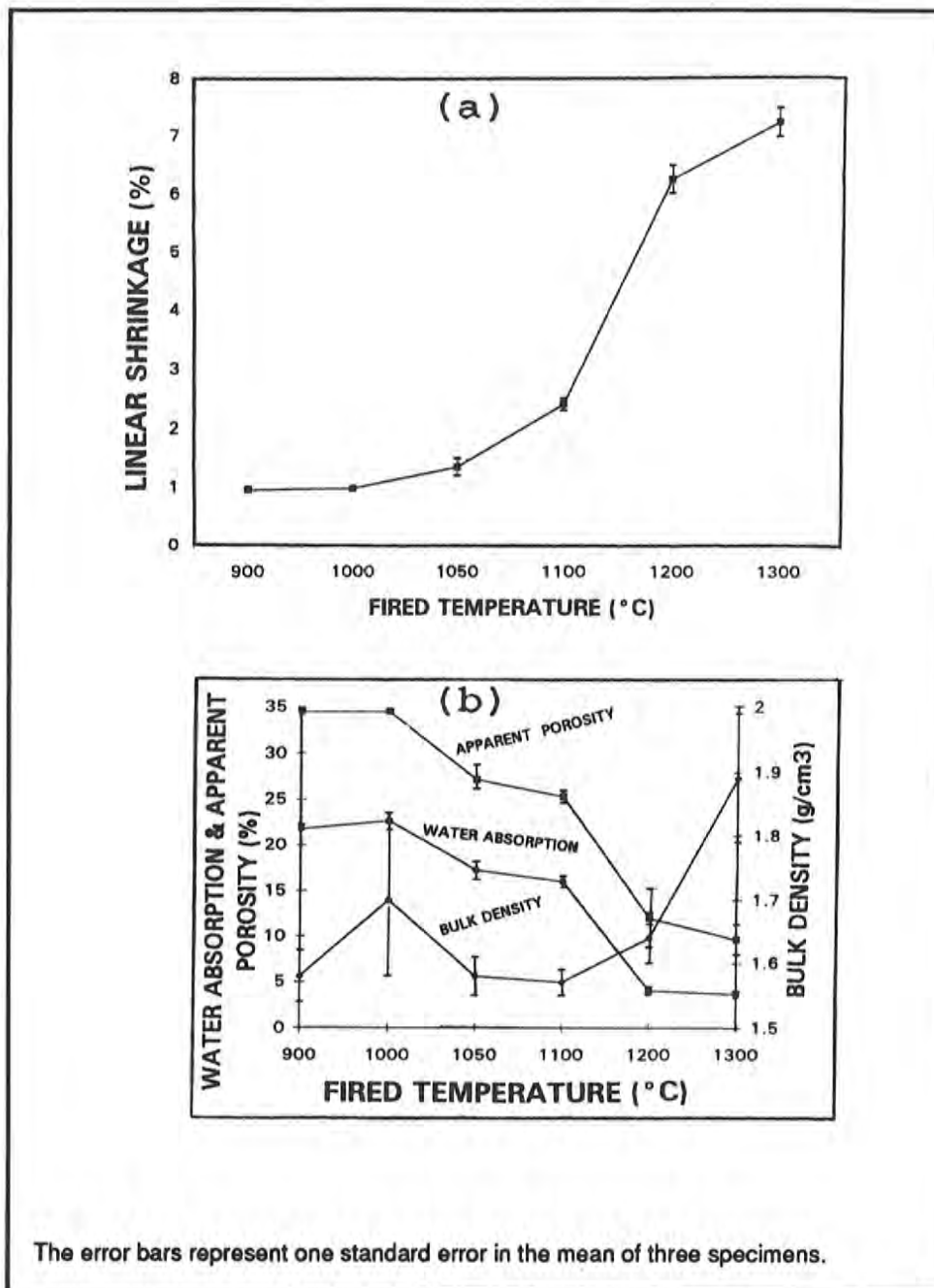


Figure 3: Variation of: (a) Linear shrinkage and (b) Apparent Porosity, Water Absorption and Bulk Density of The Clay as a Function of Firing Temperature

1,000°C. Thereafter, however, all the parameters either increase or decrease sharply with increasing firing temperature, indicating that significant vitrification of the clay commences only above 1,000°C. Nevertheless, the trend in variation of the linear shrinkage and bulk density (increasing) is consistent with that of the

porosity and water absorption which decrease with increasing firing temperature. However, while the linear shrinkage is as low as 2.2% on firing up to 1,100°C, the porosity and water absorption are relatively high at and below this temperature.

Finally, due to low viscosity of the vitrified clay

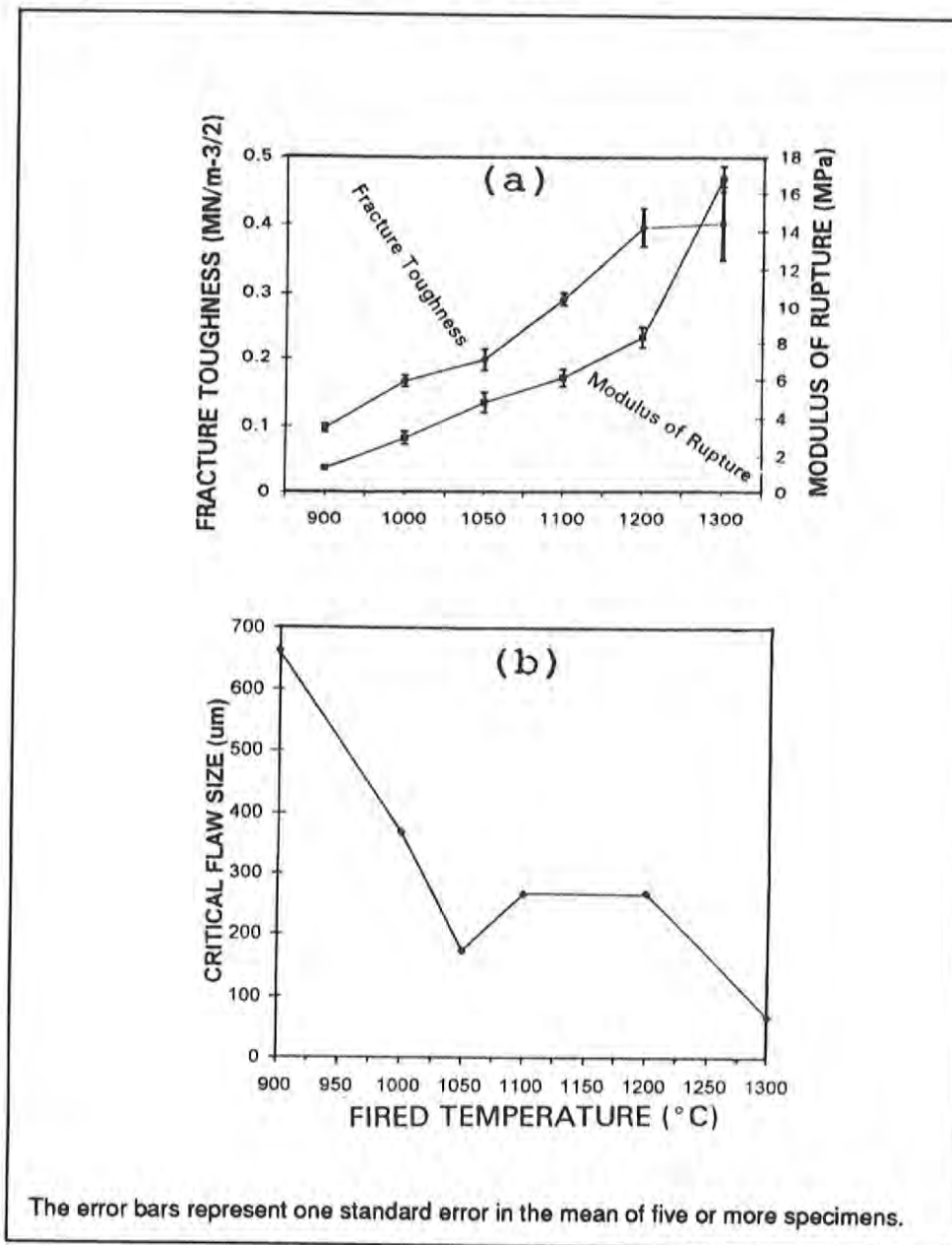


Figure 4: Variation of: (a) MOR and K_{IC} and (b) Critical Flaw Size for Fracture as a Function of Firing Temperature

at 1,400°C, test bars fired at this temperature warped and bloated and exhibited excessively high porosity (in terms of pore size and quantity) as a result of bubbles. Consequently, no measurements were taken for samples fired at this temperature.

3.4 Mechanical Properties

Figure 4(a) shows the variation of the MOR and K_{IC} of the clay as a function of firing temperature (mean

green strength was 0.26 MPa). As expected, both parameters increase with increasing firing temperature. However, on firing up to 1,100°C, the MOR and K_{IC} are only of the order of 7 MPa and 0.3 MNm^{-3/2} respectively; values which are low compared to values of the order of 16 MPa and 0.5 MNm^{-3/2} reported for some other Trinidad clays fired in the same temperature range². In fact, the MOR and K_{IC} values of these other

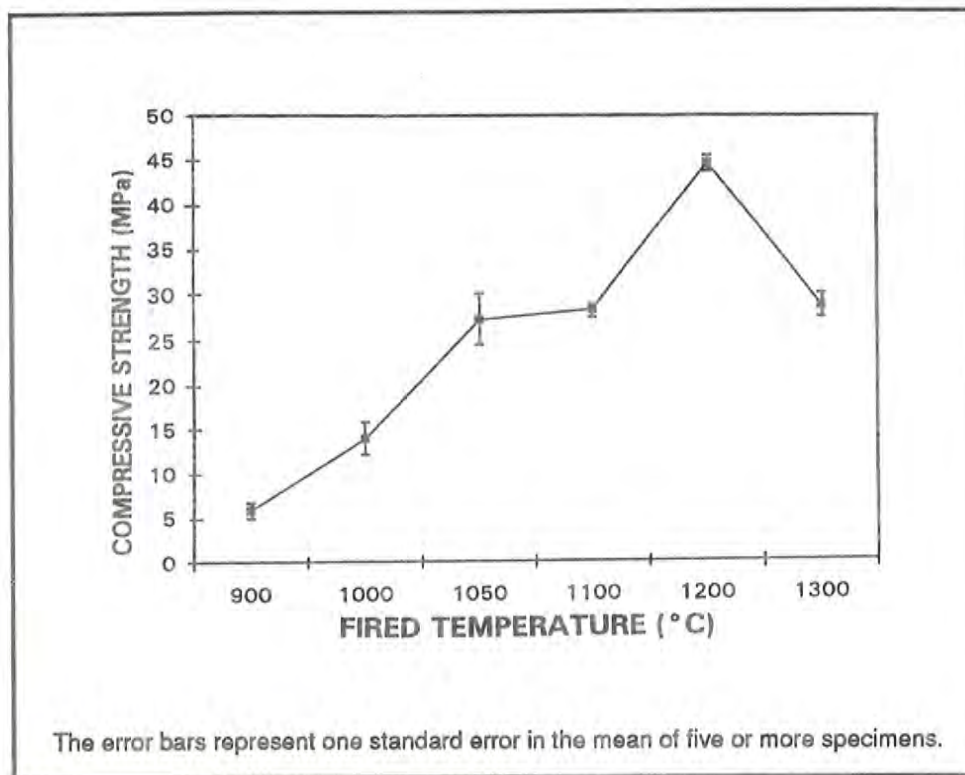


Figure 5: The compressive Strength of The Clay as a Function of Firing Temperature

Trinidad clays are achievable in the Valencia clay only on firing to as high as 1,300°C.

Given the relatively high porosity of the clay at and below 1,100°C, the low strength in this temperature regime is not surprising. Further, also mitigating against high strength and toughness in this temperature regime where the degree of vitrification is low is the relatively large critical flaw size (Figure 4 (b)). However, as the firing temperature is increased and vitrification becomes more advanced, the critical flaw size and porosity decrease and the strength and toughness increase significantly (Figure 4 (a)). The critical flaw size, C , was calculated from the established relationship $K_{IC} \propto \sigma_f C^{1/2}$ where K_{IC} and σ_f are measured fracture toughness and fracture stress (strength) in flexure respectively⁹.

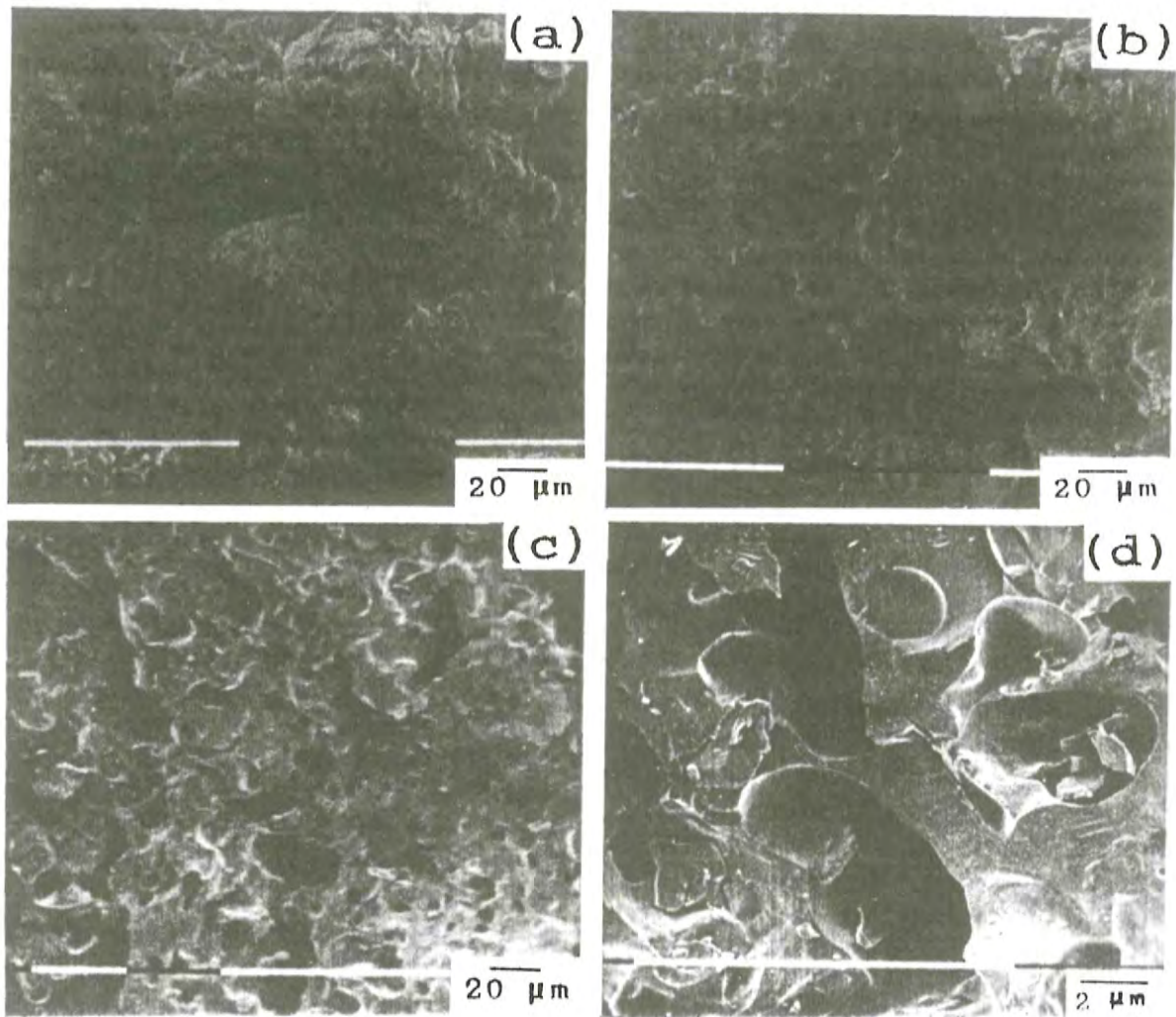
In Figure 5, compressive strength is plotted as a function of firing temperature for the clay. Between 900°C and 1,050°C, the compressive strength increases from about 5 MPa to about 27 MPa, thereafter

exhibiting only slight increase up to 1,200°C. However, between 1,200°C and 1,300°C where vitrification is well advanced, the compressive strength again increases sharply. It is not immediately clear why the compressive strength should tend to level off between 1,050°C and 1,200°C. Nevertheless, it is interesting to note that this occurs in the same temperature regime where the critical flaw size in the specimens show least variation with increasing temperature (Figure 4 (b)).

Finally, Figure 6 shows selected SEM micrographs of the fractured surfaces of specimens fired at 900°C, 1,100°C and 1,300°C. From the increased homogeneity of the microstructure and the increased density of the vitrified matrix, the increase in the degree of vitrification with increasing temperature is evident.

4.0 CONCLUSIONS

1. Kaolinitic in character, the clay contains quartz as the major non-clay mineral. However, mica, calcite and potash feldspar are also present.



(d) is a high magnification image of the microstructure shown in (c).
(M = Matrix; Q = Undissolved Quartz).

Figure 6: Selected SEM Micrographs of The Fracture Surface of The Testbars fired at:
(a) 900°C, (b) 1,100°C and (c) - (d) 1,300°C

2. A low iron content (0.3%) accounts for the white fired colour.
3. On firing, significant vitrification of the clay commences only above 1,000°C. Further, in the temperature range 900°C - 1,100°C (where many ceramic bodies are normally fired), the clay combines useful strength and toughness with relatively high porosity and low shrinkage. Additional enhancement of strength and toughness and further reduction of porosity occurs up to 1,300°C. However, at 1,400°C, the viscosity of the vitrified phase becomes so low (or the fluidity becomes so high) that warping and bloating occurs.
4. The natural and fired characteristics of the clay suggest possible potential suitability for applications such as wall tiles, domestic wares, compositional component for certain refractories and as a shrinkage reducing agent in high shrinkage clays.

5.0 ACKNOWLEDGMENTS

Professor R. Saunders of the Physics Department, UWI, St. Augustine is acknowledged for providing laboratory space. The Electron Microscopy Unit (UWI, Mona) and the Department of Soil Science (UWI, St. Augustine) kindly provided electron microscopy and x-ray facilities respectively. Mr Walton Reid (UWI, Mona) is particularly thanked in relation to the electron microscopy. Dr. L.H. Grierson (Chemistry Department, UWI, St. Augustine) advised on the chemical analysis. Finally, Ms. Hosein acknowledges financial support under a UWI scholarship.

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