

THE EFFECTS OF INTER-BLENDING WITH CALCINED Al_2O_3 ON THE CERAMIC AND REFRACTORY CHARACTERISTICS OF SOME TRINIDAD CLAYS

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ABSTRACT

Currently, there is interest in developing high-grade ceramic and refractory products from raw materials indigenous to the Caribbean region. To this end, the fired physical and mechanical properties of a high plasticity and a low plasticity Trinidad clay (respectively from Cocoloco Estate within the Talparo deposit and the Valencia deposits) blended to cover the range of composition 0 - 100% of one in the other have been studied after firing at 1100°C. Similarly, blends covering the range 0 - 40% calcined alumina in the low-plasticity Valencia clay have been investigated after firing at 1100°C. In the Valencia/Cocoloco system, up to 30% of the highly plastic Cocoloco clay may be added to the low-shrinkage Valencia clay without increasing the shrinkage of the Valencia clay by more than 1% while enhancing its strength and toughness. For additions of up to 10% Al_2O_3 , the strength and toughness of the Valencia clay are improved by up to 30% and 14% respectively. If however, in both compositional systems, the fired characteristics developed over the range of compositions are controlled by the degree of modification of the clay/non-clay ratio effected by blending.

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 centred around traditional pottery and coarse-finished structural products such as building

blocks, floor tiles and roofing tiles. Similarly, of the millions of tonnes of refractory grade calcined bauxite produced in Guyana and calcined alumina produced in Jamaica and Guyana, little is absorbed by regional ceramic and refractory industries.

In part, the under-exploitation of the clays of the region results from a lack of in-depth knowledge of their ceramic and refractory potential and application scope. However, recent investigation of samples from several deposits in Trinidad has established certain encouraging characteristics of some pertinent to possible gainful commercial exploitation^{1,2}. Of these samples from the Valencia deposit in the north-east of the island and from Cocoloco Estate (within the Talparo deposit in the Northern Basin) exhibited particularly attractive features in terms of chemistry, mineralogy and fired characteristics. For example, the low plasticity, low iron content Valencia clay burns near-white and exhibits relatively low shrinkage and high porosity in the firing temperature range 900-1100°C. On the other hand, the relatively low temperature-vitrifying, high-plasticity reddish-brown burning Cocoloco Estate clay exhibits significantly higher shrinkage, relatively low porosity and superior strength and toughness in the same temperature range.

Given these contrasting characteristics, it is expected that for certain applications, the unfavourable features of the fired properties of either can be improved by batching with suitable amounts of the other. However, in order not to adversely degrade the favourable properties, optimum relative proportions must be established. Consequently, the fired

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| CLAY | PLASTICITY* | SiO ₂ | Al ₂ O ₃ | SiO ₂ | SiO ₂ | FIRE COLOUR |
|----------|-------------|------------------|--------------------------------|------------------|------------------|---------------|
| Valencia | Low | 71.8 | 16.9 | 1.5 | 4.1 | Near-white |
| Cocoloco | High | 66.3 | 14.1 | 4.1 | 4.1 | Reddish-brown |

* Estimated qualitatively, between fingers.

Table 1: Some Basic Features and the Major Oxides Content of the Two Clays Involved in the Study

characteristics of blends covering the range 0 - 100% of each in the other have been investigated. Similarly, with the Valencia clay exhibiting certain desirable refractory properties (e.g., low shrinkage, high porosity, low iron content and near-white burnt colour) blends of this clay with up to 40% commercial grade calcined alumina have also been investigated. This paper presents the results pertaining to physical and mechanical properties and microstructure obtained from samples fired at 1100°C in both compositional systems, termed the Valencia/Cocoloco and Valencia/Al₂O₃ systems.

2.0 EXPERIMENTAL

2.1 Materials

Based on qualitative x-ray diffractometry (XRD) and differential thermal analysis (DTA), previously reported work¹ showed that the two clays, subject of this study, are kaolinitic with some quartz, mica, potash feldspar and calcite incorporated in the deposits. However, while the kaolinite content of the Cocoloco Estate clay was observed to be significantly higher than that of the Valencia clay, the mica and quartz content of the Valencia clay was markedly higher than in the Cocoloco Estate clay. Full details of the chemistry, mineralogy and fired characteristics of both clays may be found in References 1 and 2. However, **Table 1** gives a summary of their basic features and major oxides content.

After drying, the as-mined clays were gently crushed and the fractions passing through a 500 μm mesh used in the experiments. Particle size distributions (obtained by wet sieve analysis) in these fractions are shown in **Figure 1**. For the Valencia/Cocoloco compositional system, the two clays in the powdered form were thoroughly mixed in the desired

proportions to achieve homogenous dispersion. Eighteen percent water was then added to each blend to form a plastic dough which was hand-worked to optimum consistency. In a similar manner, the Valencia clay was mixed with different proportions of calcined Al₂O₃ and for each composition, a plastic mass formed with 20% water. Particle size distribution of the Al₂O₃ (also obtained by wet sieve analysis) is given in **Figure 1**.

For the various blends in both compositional systems, test bars were fabricated from the plastic dough in a metal mould, under a forming pressure of 2MPa applied in a hydraulic press. On removal from the mould, the test bars were air-dried at room temperature (typically 30°C and average relative humidity 80%) and their drying shrinkage measured using vernier calipers. Firing was subsequently done

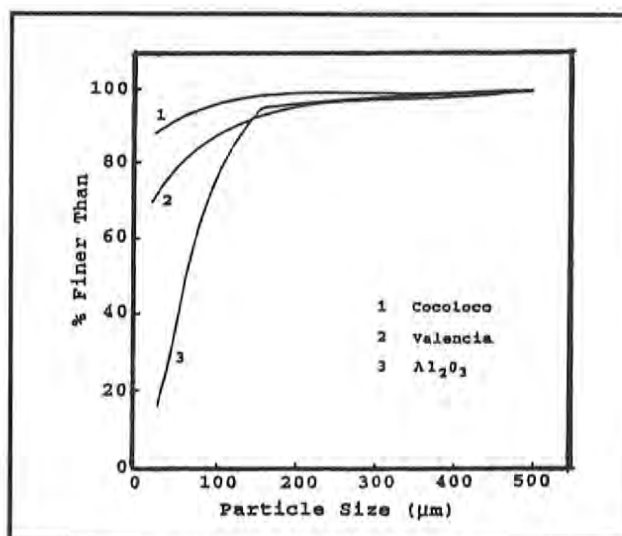


Figure 1: Particle Size Distribution in the Valencia and Cocoloco Clays and the Alumina with which the Valencia Clay was blended

at 1100°C, at a heating rate of 5°C/minute and for a soaking time of four hours in an electric furnace.

2.2 Physical Characteristics

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

2.3 Mechanical Properties

For the various blends in the two compositional systems modulus of rupture (MOR) was determined in three-point bend using a specimen span of 2.5cm (specimen width and depth depended on percentage shrinkage). Similarly, fracture toughness, based on the K_{IC} concept³, was determined in three-point bend using single-edge notched bars of notch depth 'a' such that $0.45 < a/w < 0.55$, where w is the specimen depth. In all cases, MOR and K_{IC} were averaged over values obtained from five or more specimens.

3.0 RESULTS AND DISCUSSION

3.1 The Valencia/Cocoloco System

Figure 2 shows linear shrinkage, apparent porosity, water absorption and bulk density as a function of composition in the Valencia/Cocoloco system. As expected, increasing amounts of the Valencia clay decreases the linear shrinkage and increases the porosity of the high plasticity Cocoloco Estate clay. Conversely, increasing amounts of the Cocoloco Estate clay increases the shrinkage and decreases the porosity and water absorption of the Valencia clay. However, for additions of up to 30% of the Cocoloco clay to the Valencia clay, the increase in total shrinkage (i.e., drying plus firing shrinkage) of the Valencia clay is only of the order of 1% with an associated decrease in porosity of about 2%. Regarding bulk density, the change appears to be marked only in the decrease seen for additions of 10 - 30% of the Valencia clay in the Cocoloco clay.

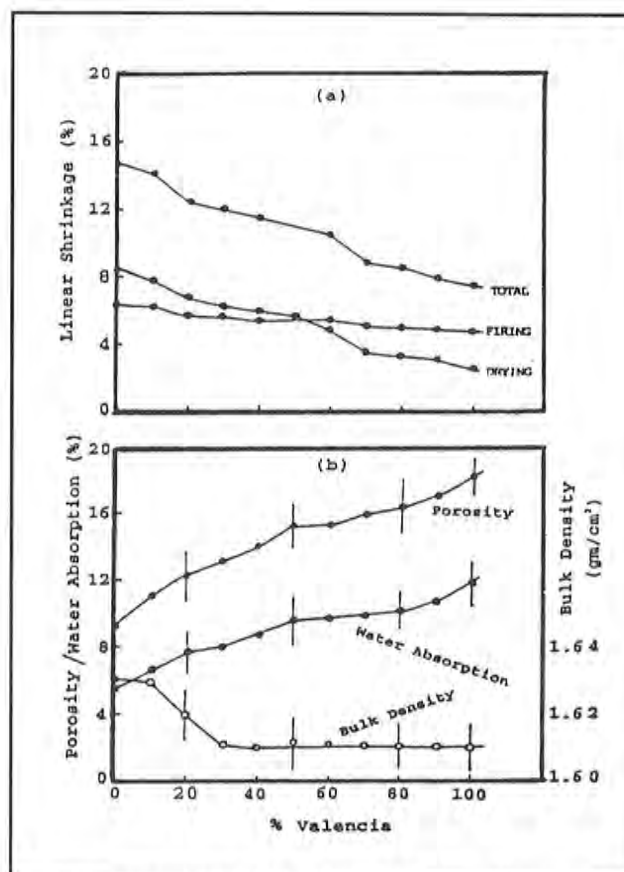


Figure 2: Variation in (a) Linear Shrinkage (drying, firing and total shrinkage) and (b) Apparent Porosity, Water Absorption and Bulk Density as functions of Composition in the Valencia/Cocoloco System

Figure 3(a) shows the variation of MOR and K_{IC} as a function of composition. As can be seen, increasing amounts of the Cocoloco Estate clay progressively increase the MOR of the Valencia clay. (Conversely, the MOR of the Cocoloco Estate clay is decreased by the Valencia clay). Further, the variation of the MOR is consistent with the variation in porosity (Figure 2(b)), in that significant increase in strength of the Valencia clay occurs at compositions (0 - 30% Cocoloco) where there is significant decrease in porosity. Similarly, almost linear decrease in strength of the Cocoloco clay occurs at compositions (0 - 30% Valencia) where the porosity increases approximately linearly (Figure 2(b)). Generally, the trend in variation of the K_{IC} with composition is similar to that of the MOR.

Using the measured MOR and K_{IC} values and the established relationship $K_{IC} \propto \sigma_f \sqrt{c}$, where is σ_f the fracture stress and c the critical flaw size controlling fracture, an estimate was made of c at the various compositions. **Figure 3(b)** shows the results. Consistent with the variation in strength and toughness, the critical flaw size increases at compositions where the strength and toughness of the Cocoloco Estate clay decreases (0 - 30% Valencia) and decreases at compositions where the strength and toughness of the Valencia clay increases (0 - 30% Cocoloco). As with the MOR and K_{IC} there is little change in the critical flaw size at the intermediate compositions.

Figure 4 shows optical micrographs of the typical fired microstructure of selected compositions in the Valencia/Cocoloco system. Consistent with the characteristics of the two clays in the raw state¹, a comparison of the micrographs seem to confirm that the predominant effect of adding increasing amounts of the Valencia clay to the Cocoloco Estate clay is increased quartz content in the Cocoloco Estate clay, resulting in the observed decrease in shrinkage but increased porosity and lowered strength and toughness. Similarly, addition of the Cocoloco clay to the Valencia clay effectively increases the clay mineral content of the Valencia clay, and thus the amount of vitrified phase formed leading to increased shrinkage but decreased porosity and increased strength and toughness. However, in addition to the blending modifying the clay/non-clay ratio of the two clays, increasing amount of the Cocoloco clay increases the iron content of the Valencia clay, resulting in the fired colour changing from near-white to a progressively deeper shade of reddish brown.

3.2 The Valencia/ Al_2O_3 System

Figure 5 shows linear shrinkage, apparent porosity, water absorption and bulk density as a function of composition in the Valencia/ Al_2O_3 system. As expected, the drying and firing shrinkage both decrease with increasing amounts of Al_2O_3 . However, the decrease is such that for compositions containing higher than 20% Al_2O_3 , the drying shrinkage is under 1%. Similarly, an addition of 20% Al_2O_3 results in the overall shrinkage (firing plus drying) being approximately halved compared to the value at 0%

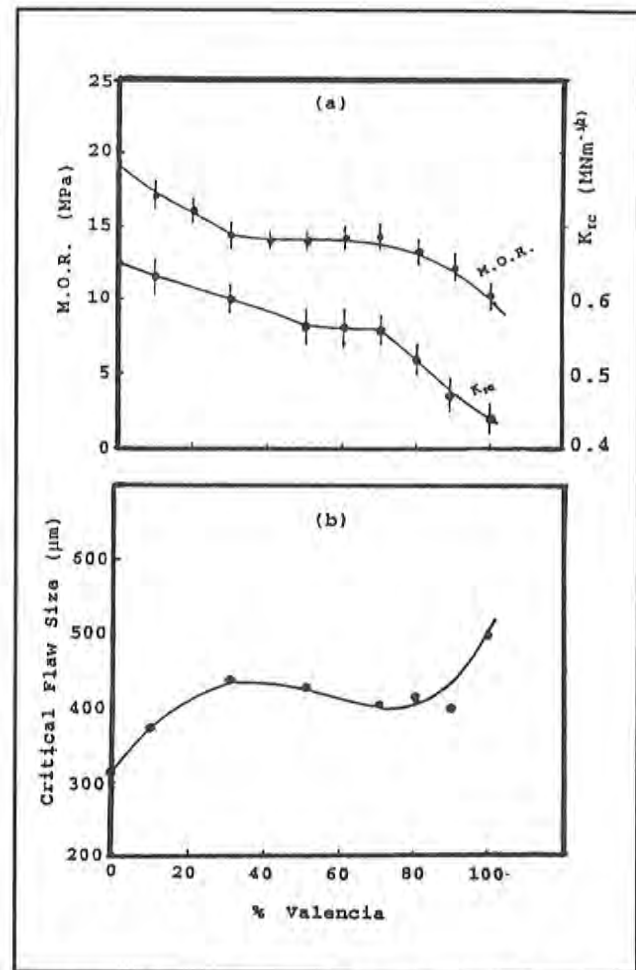


Figure 3: Variation in (a) MOR and K_{IC} and (b) Critical Flaw Size with Composition in the Valencia/Cocoloco System

Al_2O_3 . For 30% Al_2O_3 , the overall shrinkage is down to approximately 2% from 8% at 0% Al_2O_3 .

Regarding apparent porosity and water absorption, **Figure 5(b)** shows that both parameters decrease slightly with increasing amount of Al_2O_3 up to 10%. Thereafter, both parameters generally increase with increasing amounts of Al_2O_3 . Further, for compositions containing 10 - 40% Al_2O_3 , the overall increase in porosity and water absorption is quite substantial: approximately doubles for both parameters.

The initial decrease in porosity (at composition between 0 - 10% Al_2O_3) and consequently water absorption was unexpected. However, as will be seen later, microstructural investigation indicated that this,

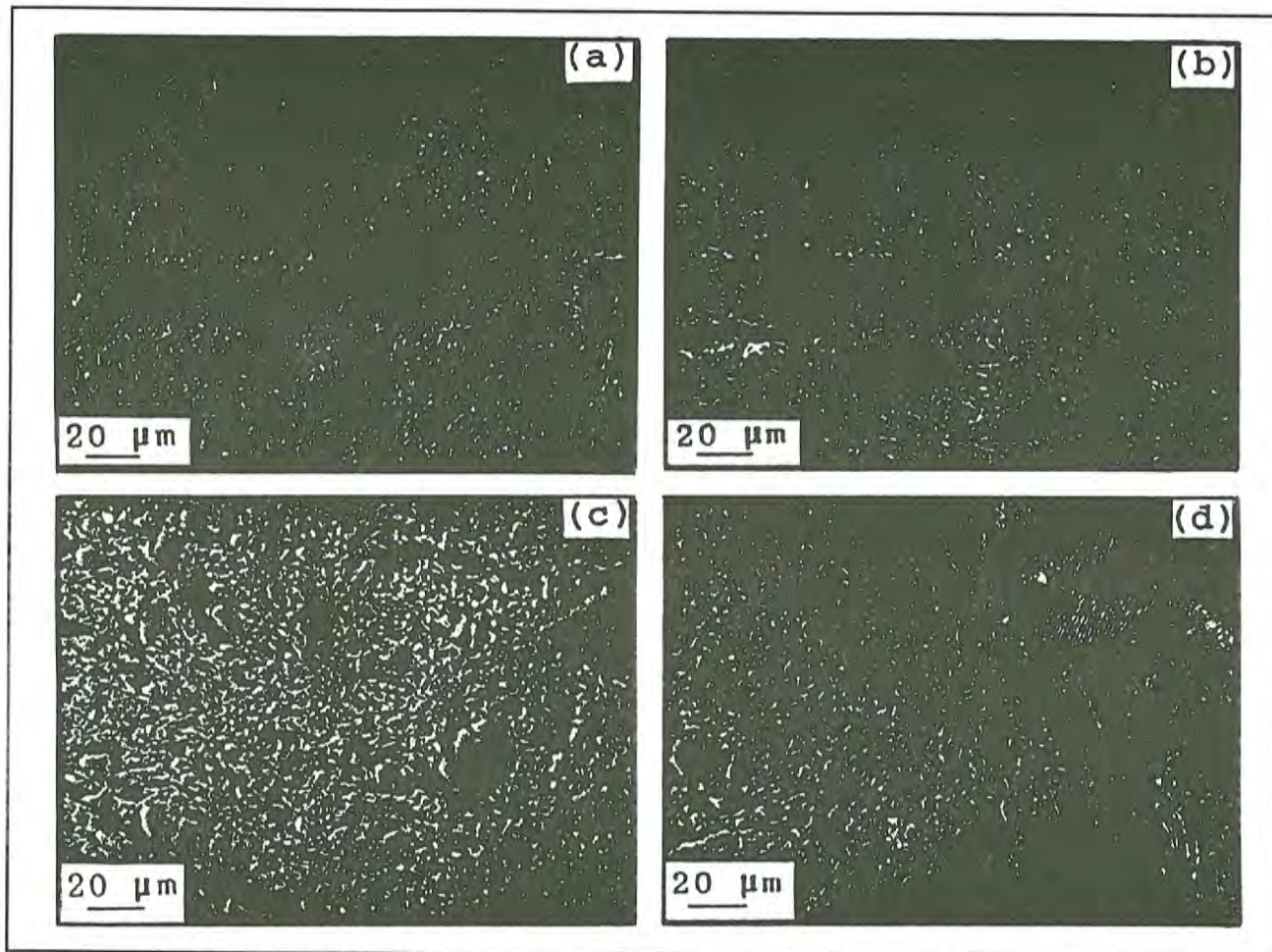


Figure 4: Optical Micrographs of the Fired Microstructure of Some Selected Compositions in the Valencia/Cocoloco System: (a) 20%, (b) 50%, (c) 70% and (d) 80% Valencia. In all cases, the light grey continuous phase is the vitrified matrix, the light grey angular particles quartz and the dark dispersed phase pores.

together with the subsequent increase in porosity for compositions containing more than 10% Al_2O_3 , is related to the relative amounts of vitrified phase and Al_2O_3 present and the dispersion of the Al_2O_3 particles in the vitrified phase. Consistent with the variation in porosity, bulk density generally decreases for compositions containing higher than 10 - 15% Al_2O_3 .

Figure 6(a) shows the variation in MOR and K_{IC} of the Valencia clay with increasing amounts of Al_2O_3 . Consistent with the decrease in porosity for compositions containing up to 10% Al_2O_3 , both the MOR and K_{IC} are enhanced. Further addition of Al_2O_3 up to 30% resulted in a gradual decrease in the MOR while the K_{IC} decreases initially then appears to level

off. However, it is noteworthy that although maximum strength and toughness occur at 10% Al_2O_3 , at all compositions up to 25% Al_2O_3 , the strength is higher than the value at 0% Al_2O_3 .

Figure 6(b) shows the variation in critical flaw size (determined as already described for the Valencia/Cocoloco system) as a function of composition. Consistent with the variation in strength and toughness, the flaw size initially decreases with increasing percentage Al_2O_3 , exhibiting a minimum value in the vicinity of compositions where the strength and toughness are highest, then increases as the strength and toughness fall off.

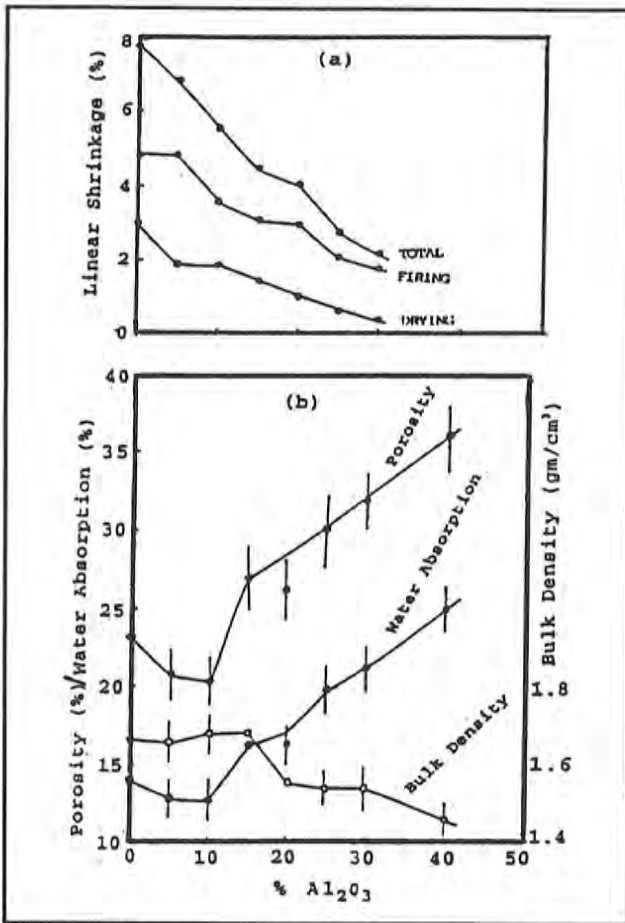


Figure 5: Variation in (a) Linear Shrinkage (Drying, Firing and Total Shrinkage) and (b) Apparent Porosity, Water Absorption and Bulk Density as a Function of Composition in the Valencia/Al₂O₃ System

As with the variation in porosity, and as will be seen later, the trend in the behaviour of the MOR, K_{IC} and critical flaw size results from the relative amounts of vitrified clay and Al₂O₃ present at each composition and the dispersion of the Al₂O₃ in the vitrified matrix.

Figures 7 and 8 show optical micrographs of the microstructure of some selected compositions of the fired samples. As can be seen, for compositions up to about 10% Al₂O₃ (Figures 7(a) and 7 (b)), there is sufficient vitrified phase to completely "coat" the Al₂O₃ particles. The microstructure is therefore one in which the isolated Al₂O₃ particles are randomly dispersed in a continuous vitrified bonding matrix. In this

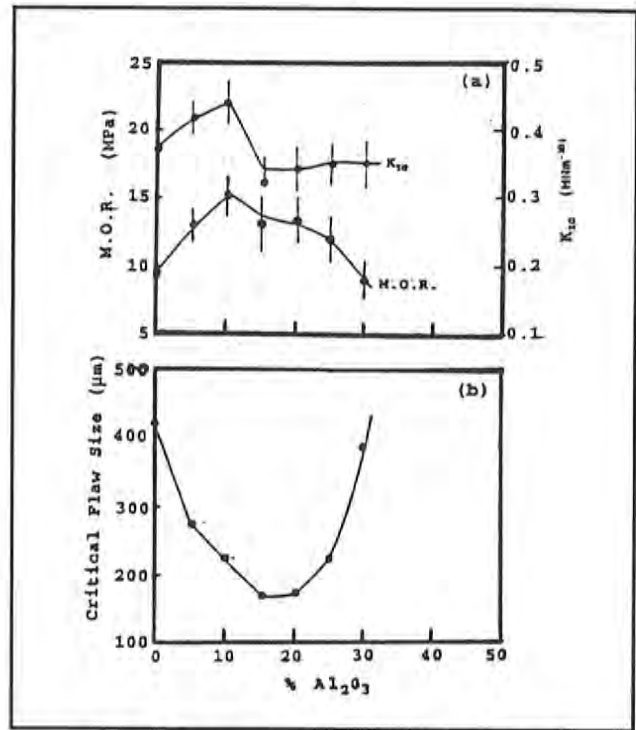


Figure 6: Variation in (a) MOR and K_{IC} and (b) Critical Flaw Size as a Function of Composition in the Valencia/Al₂O₃ System

compositional regime, some of the Al₂O₃ particles are also believed to act to fill pores hence the decrease in porosity observed. This decrease in porosity combined with the possible crack-blunting effect of isolated Al₂O₃ particles embedded in the continuous vitrified matrix is believed to effect the increase in MOR and K_{IC} observed for compositions containing 0 - 10% Al₂O₃.

As the amount of Al₂O₃ is increased above 10%, Figures 7(c) and 7(d) and Figure 8 show that there is insufficient vitrified phase to "coat" all the Al₂O₃ particles. In fact, the Al₂O₃ particles effectively act to disrupt the continuity of the vitrified bonding matrix. Further, since at the firing temperature studies (1100°C), the Al₂O₃ particles do not fuse to any significant degree, the result is reduced bonding and increased porosity with increasing amount of Al₂O₃. This therefore explains the increase in porosity and decrease in strength and toughness for compositions containing higher than about 10% Al₂O₃. The trend in

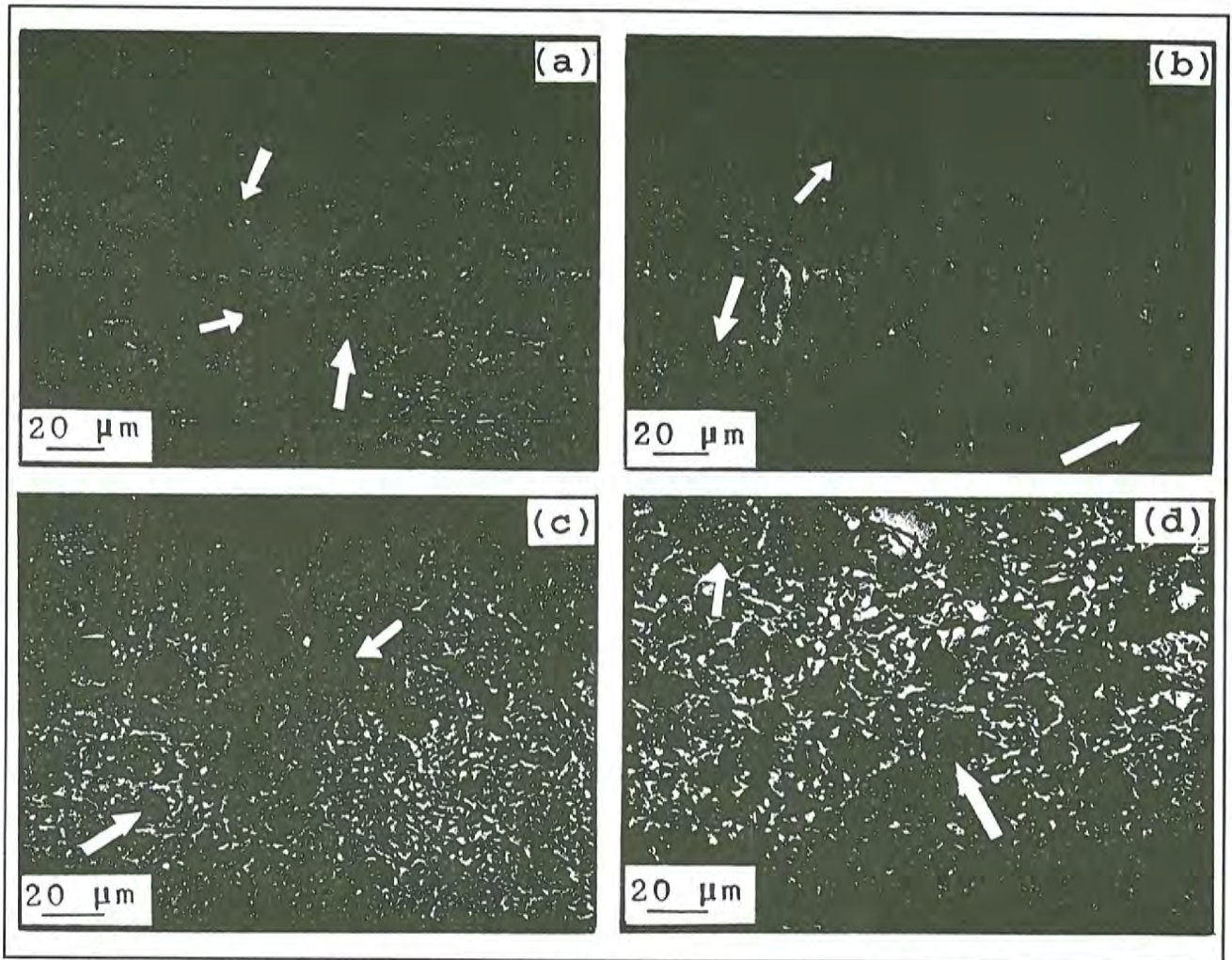


Figure 7: Optical Micrographs of the Fired Microstructure of Some Selected Compositions in the Valencia/ Al_2O_3 System: (a) 5%, (b) 10%, (c) 15% and (d) Al_2O_3 . In all cases, the light grey phase is the vitrified matrix (and the light angular cristasis quartz particles) while the darker spherical particles (some indicated by arrows) are Al_2O_3 particles.

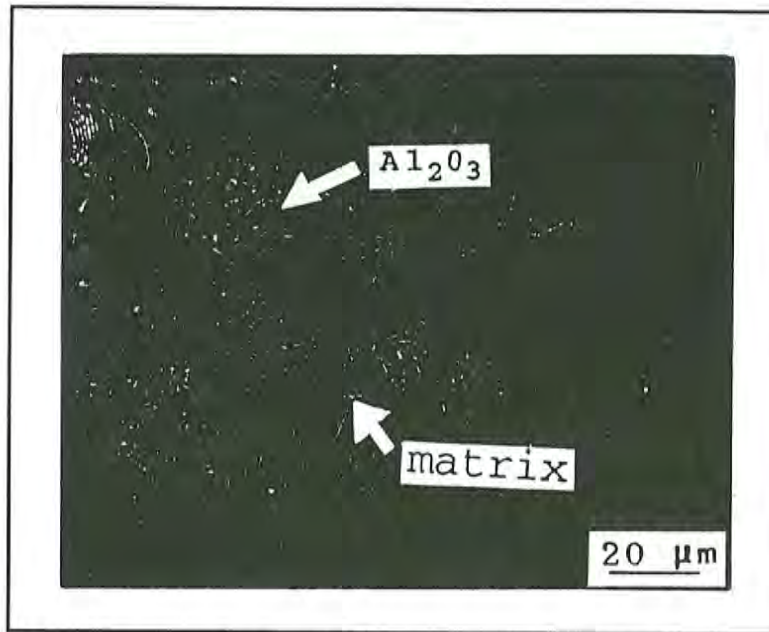


Figure 8: High Magnification Optical Micrographs of the Typical Fired Microstructure of the Samples containing 20% Al_2O_3 . Note how the Al_2O_3 particles (spherical) disrupt the continuity of the vitrified matrix phase (light grey).

the variation of the critical flaw size is also consistent with relative amounts of Al_2O_3 to vitrified phase and the dispersion of the Al_2O_3 particles.

4.0 CONCLUSIONS

4.1 The Valencia/Cocoloco System

1. Up to 30% of the high plasticity Cocoloco clay may be added to the low plasticity Valencia clay without increasing the shrinkage of the Valencia clay by more than 1% while decreasing its porosity by some 2% and enhancing its strength and toughness by 40% and 27% respectively.
2. Increasing amounts of the Valencia clay in the Cocoloco clay results in progressive decrease in strength, toughness and shrinkage of the Cocoloco clay but progressive increase in porosity and water absorption. However, while up to 30% of the Valencia clay in the Cocoloco

clay decreased the shrinkage of the Cocoloco clay by up to 3%, there is a loss in strength of up to 30% and an increase in porosity of up to 4%.

3. The resultant physical and mechanical properties developed over the range of compositions depend on the modification of the clay/non-clay mineral ratio effected by the blending.

4.2 The Valencia/ Al_2O_3 System

1. The linear shrinkage of the Valencia clay gradually decreases with increasing amount of Al_2O_3 up to 30%. However, for additions of up to 10% Al_2O_3 the porosity is decreased by up to 2% while the strength and toughness are enhanced by up to 30% and 14% respectively. Above 10% Al_2O_3 , the porosity gradually increases with increasing amounts of Al_2O_3 while the strength and toughness generally

decrease. Nevertheless, for additions of up to 25% Al_2O_3 , the strength is higher than for the raw clay without any added Al_2O_3 .

2. The variation in the various physical and mechanical properties is directly controlled by the relative amounts of vitrified bonding phase and Al_2O_3 present at each composition and thus by the clay/non-clay mineral ratio.

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