CERAMIC PROPERTIES OF CHIMALA KAOLIN CLAY

Leonard D. Akwilapo
Department of Chemistry ,University of Dar es Salaam
P.O. Box 35131, Dar es Salaam, Tanzania.

The physico-chemical properties of kaolinite clays occurring in abundance near Chimala were studied with a view of finding out their suitability in sanitary ware production. The viscoscity of the clay was found to be within the range acceptable in industrial application (≤ 500 cp for 70% solids) enhancing its prospects for the manufacture of slip cast shapes with satisfactory properties. The chemical composition of the clay reveals a high content of Fe_2O_3, 1.48%, which is expected to affect the translucency and colour of the finished ware. However, such quantity would not have detrimental effects in the production of sanitary ware. The content of other oxides falls within the range of commercial clays. The mullite phase, responsible for strengthening of the ware, is first detected after firing at 1200 °C for 8 hours. The results indicate a possible use of the clay as a ceramic raw material for stoneware and sanitary ware.

Keywords: *kaolin clay; rheology properties; mullitisation .*

INTRODUCTION

A wider variety of ceramic materials are abundant in Tanzania, however, many reserves are still not fully exploited for application in the ceramic industry. In this work, an assessment is being made on the suitability of Chimala kaolin clays in the fabrication of sanitary ware. This deposit is among the biggest in the country, second only to the Pugu kaolin deposit, on the tonnage content. It is estimated to contain about 10 million tonnes of kaolin believed to have been formed during the Pleistocene age, originating from the accelerated weathering under arid condition when the area was covered with water [Harris, 1968]. Preliminary investigation by Cilek [1979] did suggest the deposit to contain high content of kaolinite reasonably enough to support a very economical mining operation.

In this contribution an assessment is being made on the suitability of clays from this deposit in the manufacture of sanitary ware. The preparation of green bodies through slip casting is, undoubtedly; the primary method used for the production of sanitary ware ceramics. In this process, the formulation of a body composition with appropriate materials is an important stage [Norton, 1974; Phelps, 1982]. Hence, a careful investigation and selection of the potential raw material is needed [William, 1987]. It is also known that rheological properties of the resulting slip are factors of paramount importance in assessing the suitability of such raw materials.

Traditionally, Tanzanian clay works have been limited to pottery and brick making where the local manufacturers use try and error methods in their works as they do not have the vital knowledge of the chemical composition of different batch materials. With that setback producers are unable to obtain correct clay recipes for their products. In modern clay works, the properties of the clay need be known in order to prepare the correct recipe for the envisaged articles. This demand gives an impetus to the Tanzanian ceramists' attention towards the study of raw materials potentiality, especially in quality terms.

EXPERIMENTAL

The kaolin was collected by water washing method. The clay is dispersed in the water phase, and separated from the grove particles by decantation. The water in the slurry was evaporated and the white kaolin powder crushed down to a powder form. The powder was again mixed with water and wet sieved through a BS 410 mesh (53 μm) to obtain a finer clay of less than 53 μm. The yield was about 75% of the total material obtained after decantation. The finer clay product was then oven dried at 110 °C to dryness. The dried kaolinite was wet ground in ball mills of 4 kg capacity, with increasing periods of 6, 12, 18 and 24 hours. After each grinding the particle size distribution of kaolinite was determined with Andreasen Pipette and the viscoscity by Brookfield viscometer. Chemical analysis was carried only on the less than 53 μm fraction, which is considered to be of industrial interest. The determinations were performed by XRF using Phillips PW 1480 X-ray spectrometer. Standard procedures according to Link Analytical Co. [1997] were followed. In this method the clay samples are heated at 860 °C for 2 hours to remove molecular water and organic matter, and the residue, which is metakaolin, is ground and mixed with lithium tetraborate and melted to glass at 1100 °C. This was followed by the XRF determination, which was subsequently corrected to 100% against the loss on ignition.

The XRD determinations were performed using a Phillips PW 1050 goniometer and PW 1710 microprocessor based control and measuring system. Cu-Kα source at the wavelength of 1.5418 Å was used throughout. Combined thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was run on a Netzsch STA 409E simultaneous DTA/TG analyser at the heating rate of 10°C/min using Al_2O_3 as the reference material.

Green bodies were prepared by slip casting in plaster of paris moulds to obtain test bars of 17 cm x 1.5 cm x 0.5 cm. The bars were dried in air for 24 hours before drying in a laboratory oven at 110 ± 10 °C for 48 hours. After drying, the samples were taken through a firing schedule, which was performed at the rate of 300 °C per hour to a predetermined soak temperature followed by an 8 hours hold time. At standard heat treatment of these bodies, nearly all of the vitrifying action takes place at temperature above 1100 °C, thus the rate of heating and cooling below this temperature was not controlled. However, the cooling rate between 600 and 500 °C need to be low so as to limit the level of damage that can be caused by the β to α-quartz transition. The cooling rate at this interval was, therefore, set at 50 °C per hour.

The amounts of the crystalline phases after firing were determined by XRD using CaF_2 as the internal standard [Schieltz and Soliman, 1966; Galan et. *al.*, 1996]. Peaks chosen for the determination of mullite, cristobalite and quartz, and that of the internal standard (CaF_2), are indicated in Table 1. The selected peaks are distinct, highly resolvable and have high intensities to facilitate the detection of low concentrations of the analytes. The glass content in percentage can be calculated by difference.

RESULTS AND DISCUSSION

The grain size distribution of Chimala kaolin is given in Table 2. The distribution is compared to that of Standard China clay in which case it is seen that the test material is skewed on the large size grains rather than on the finer ones. However, as seen in Fig.1, the grain size distribution becomes finer with grinding and the optimal grinding is established after about 20 hours.

Table 1: Peaks used for the determination of the phases

Phase	**2θ angle (degrees)**	**d-spacing (Å)**	**I/I_o (%)**	**hkl values**
Mullite	32.22	2.694	40	220
Cristobalite	21.985	4.0397	100	101
Quartz	26.65	3.342	100	101
Fluorite (CaF_2)	28.267	3.1546	92	111

Table 2: Particle size distribution of Chimala kaolin clays in percentages.

COMPONENT	> 53 µm	> 10 µm	10 - 2 µm	< 2 µm
China clay standard	0	5	25	70
Chimala kaolin (as received)	6	40	42	12
Chimala kaolin (optimal grinding)	0	15	39	46

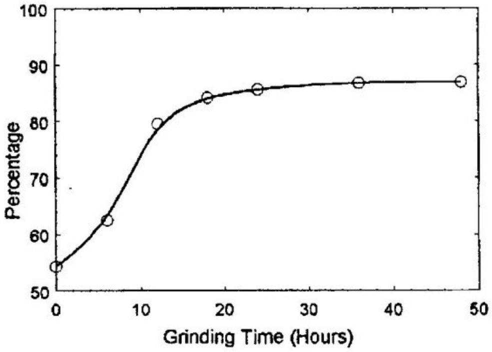

Figure 1: Percentages of kaolin particles with grain size less than 10 µm as a function of grinding time in hours.

For viscoscity measurements, different solid suspensions were prepared and the viscoscity at different speeds were recorded (Fig. 2). It has been proved that (a) the kaolinite suspension behaviour is pseudoplastic at low speed and from 15 rpm becomes newtonian; (b) minimum viscoscity was reached at 70% solid content. A further test on suspensions at 70% solid content was performed, to investigate the viscoscity change as a dispersant is added. The minimum viscoscity of about 459 cp is reached when 0.03 g of dolaflux/100 g solid is added (Fig. 3). This value fits well in the range of variations specified for industrial applications (≤ 500 cp for 70% solids).

A comparison between the chemical composition of Chimala clay with other commercial available china clays has been made. This comparison is displayed in Table 3. It is clearly shown that the

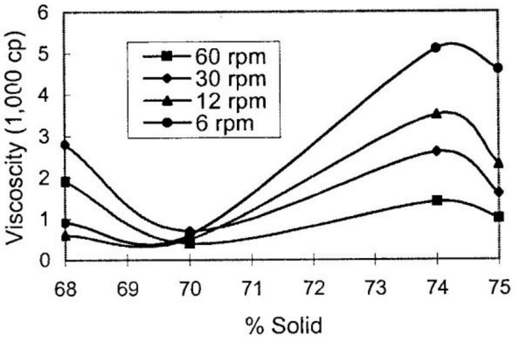

Figure 2: Viscoscity variation with different solid suspension.

chemical composition of Chimala kaolin clay is within the range of the commercial clays. The main setback is the content of iron oxide, which is as high as 1.48%, on the average, about two times that of New Jersey clay. It is expected that such a high level of iron oxide would affect the

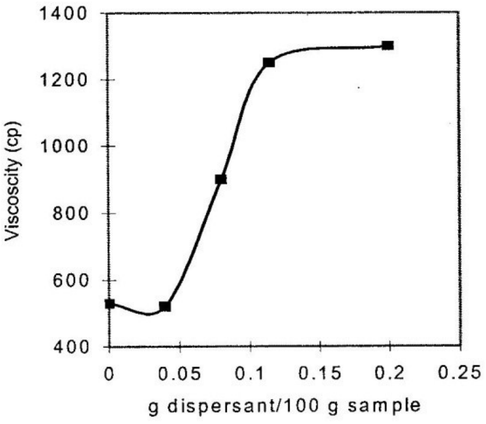

Figure 3 Viscoscity variation with the dispersant concentration (at 70% solid suspension).

translucency and colour of the finished ware. Total alkali content ($Na_2O + K_2O$) of the kaolin is on the lower side and as such it should not have much bearing on the properties of the clay. It can also be visualised that substantial amounts of the alkali metals lower the liquidus temperature and thus promoting vitrification reactions at a lower firing temperature, which is an advantage towards the minimisation of fuel consumption.

The XRD pattern of the clay (Fig. 4) indicates a low crystallinity, this measurement is determined by the Hinckley index which compares the intensity of the peaks within the 0, 211 domain region (2θ values ranging between 20 – 22). The Hinckley index could not be determined because the reflections to be used for this purpose at 20° – 23°. are forming a band that may also be affected by the reflection from plagioclase. The low crystallinity value does however suggest a higher level of plasticity. This is because irregular morphology and finer grain size of kaolinites have been usually associated with low crystallinity [Brindley et. al., 1986]. It is also noted that the finer component has a diminished quantity of quartz, as the quartz peak at 2θ = 26 is absent in the finer component's XRD pattern.

The results, given in Fig. 5 shows that the thermal behaviour of the clay is typical of that

Table 3: Chemical composition of Chimala kaolin clays in percentages in comparison to the kaolin clays of Pugu [Akwilapo and Wiik, 2003], Cornwall (England) and New Jersey (USA) [Weaver, 1988].

Oxide	C1	C2	C3	C4	C5	C6	Mean	Pugu	Cornwall	N. Jersey
SiO_2	47.32	46.20	47.65	47.08	44.32	47.50	47.34	46	44.15	41.76
Al_2O_3	37.20	37.10	37.30	36.60	39.42	36.92	36.86	36	38.99	37.86
Fe_2O_3	1.14	1.38	1.85	1.92	0.92	1.68	1.48	1.43	1.06	0.99
TiO_2	0.18	0.12	0.28	0.19	0.35	0.21	0.22	0.87	0.62	2.01
Na_2O	1.18	1.90	0.68	1.68	0.56	1.46	1.24	0.19	-	-
K_2O	0.96	1.20	0.62	1.08	0.98	1.16	1.00	0.31	-	-
LOI	11.90	11.85	11.54	11.28	12.16	10.98	11.62	10.5	12.96	13.28

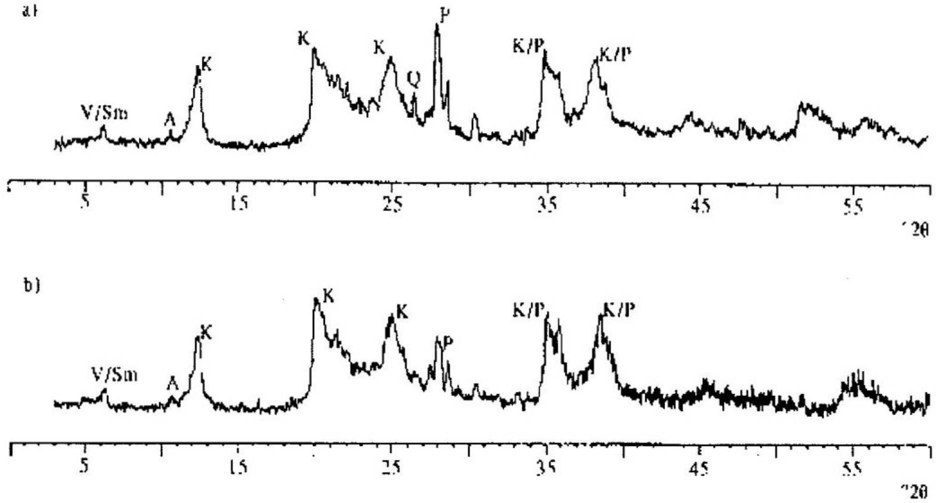

Figure 4:. Chimala kaolin XRD patterns (a) total sample (b) less than 53 μm component. (K: kaolinite, V: vermiculite, P: plagioclase, A: amphiboles, Q: quartz, Sm: smectites)

expected from kaolin (Brindley and Nakahira, 1959). Notably, the endothermic dehydroxylation peak indicating the formation of amorphous metakaolin between 530 and 750 °C, the peak is associated with weight loss of about 16% (from TG curve). Pure kaolin with stoichiometric formula, $Al_2O_3·2SiO_2·2H_2O$, would give a 13.98% weight loss on dehydration, the difference in this case is assumed to be due to the oxidation of organic matter and the release of non-molecular water. When kaolinite is heated, it transforms to mullite through two intermediate phases. The first phase, metakaolin is formed at around 600 °C and the second phase, a cubic spinel phase at 980 °C (Brindley and Nakahira, 1959). The two peaks are clearly distinct in the figure.

In this work the second DTA peak has been observed to occur between 984 and 998 °C, this is the exothermic peak associated with the decomposition of metakaolin to form the cubic spinel type structure, other products will include free silica and some minor amounts of mullite (Comer, 1961). It is actually known that the compound formed at 600 °C, amorphous metakaolin, decomposes to a spinel type structure between 925 and 1000 °C in a strong exothermic reaction (Brindley and Nakahira, 1959; Chakraborty and Ghosh, 1978). The spinel phase usually exists over a short temperature range before it is changed to mullite, at about 1100 °C.

Some authors believe that traces of primary mullite are formed and therefore can be detected during this transformation at about 1000 °C. The amounts are however too small to give a detectable peak in XRD analysis [Chakraborty and Ghosh, 1978]. The pioneering work of Brindley and Nakahira [1959] and the recent one by Galan et. al.(1996) have been able to detect cristobalite in kaolinite fired at 1050 °C. Brindley and Nakahira proposed the widely accepted reaction sequence for the events taking place when kaolinite is fired. The sequence has three stages,

$$2(Al_2O_3{\cdot}2SiO_2) \xrightarrow{980^{\circ}C} Si_3Al_4O_{12} + SiO_2$$

Metakaolin spinel amorphous (amorphous)

$$Si_3Al_4O_{12} \xrightarrow{1050-1100^{\circ}C} 2Al_2O_3{\cdot}2SiO_2 + SiO_2$$

Spinel transitional mullite cristobalite

$$2Al_2O_3{\cdot}2SiO_2 \xrightarrow{above\ 1100^{\circ}C} 2Al_2O_3{\cdot}\frac{4}{3}SiO_2 + \frac{2}{3}SiO_2$$

transitional mullite(3:2) cristobalite mullite (2:2)

Indicating that the 3:2 mullite and cristobalite are the stable phases of this system at high temperatures. It is shown in this study that cristobalite and mullite have significant rates of formation at temperatures above 1150 °C.

From the phase evolution properties shown in Fig. 4 and Fig. 5 the followings features can be concluded for the firing of Chimala kaolin clay:

- mullite and cristobalite contents steadily increase with temperature,
- the maximum content of cristobalite is reached earlier at 1250 °C for a longer hold time as compared to 1350 °C for a shorter hold time of 8 hours,
- the maximum content of cristobalite roughly coincides with the temperature at which the quartz content is diminished,
- longer firing time enhances the formation of mullite.

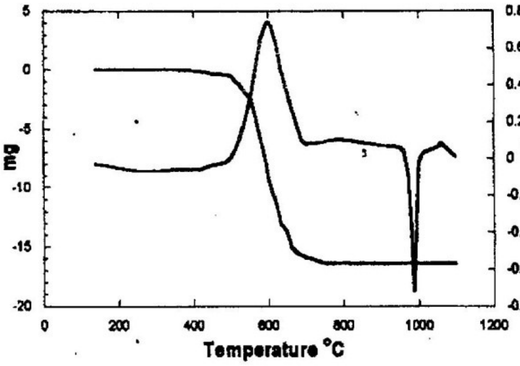

Figure. 5: TG and DTA curves of Chimala kaolin clay (heating rate 10oC /min).

According to the thermodynamic data of Schieltz and Soliman [1966] the ultimate stable thermal transformation of kaolinite which gives a maximum -ΔG, can be represented by the reaction:

$$Al_2O_3\cdot 2SiO_2 \longrightarrow \tfrac{1}{3}(3Al_2O_3\cdot 2SiO_2) + \tfrac{4}{3}SiO_2$$

The equation appeared to be valid since both mullite and cristobalite were observed in the diffraction studies. Based on this equation and the Al_2O_3-SiO_2 phase diagram (Fig. 8) the amount of amorphous silica liberated should be about 37 mass %. Referring to the same criteria it can be shown that the maximum quantity of mullite that can be formed during this transformation is 63 mass %. The experimental values are, however, lower than this maximum due to slow kinetics in the SiO_2-Al_2O_3 system.

It is expected that in a real ceramic mixture, which usually incorporates feldspar, the mullitisation process should be enhanced. Feldspars, known as fluxes in this system, lower the vitrification temperature of ceramic batches by giving a lower liquidus temperature [Kobayashi et. al., 1994].

In order to describe the microstructure of the fired products, SEM pictures were used. SEM observations were made on samples fired for 8 hours at the peak temperature. Samples were etched with hydrofluoric acid for one minute prior to scanning. The following were inferred: (a) at 1100 °C no mullite crystals were visible; (b) at 1200 °C some mullite needles were observed (Fig. 9); and (c) at 1400 °C mullite formation is enhanced and the interlocking mullite needles form a strengthening network (Fig. 10).

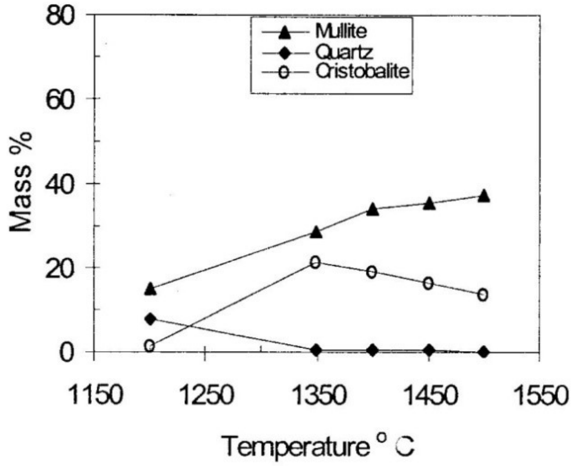

Figure. 6. Phase content of kaolin clay fired for 8 hours (heating rate 300 °C/hour).

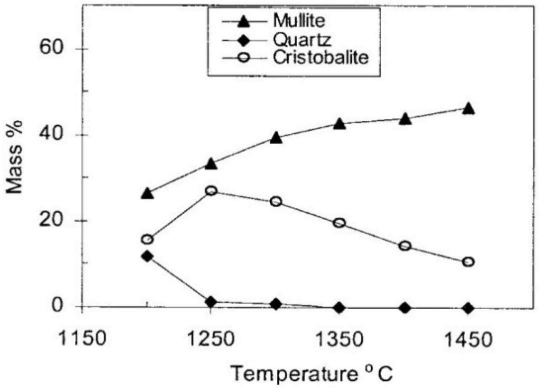

Figure. 7. Phase content of kaolin clay fired for 16 hours (heating rate 300 °C/hour).

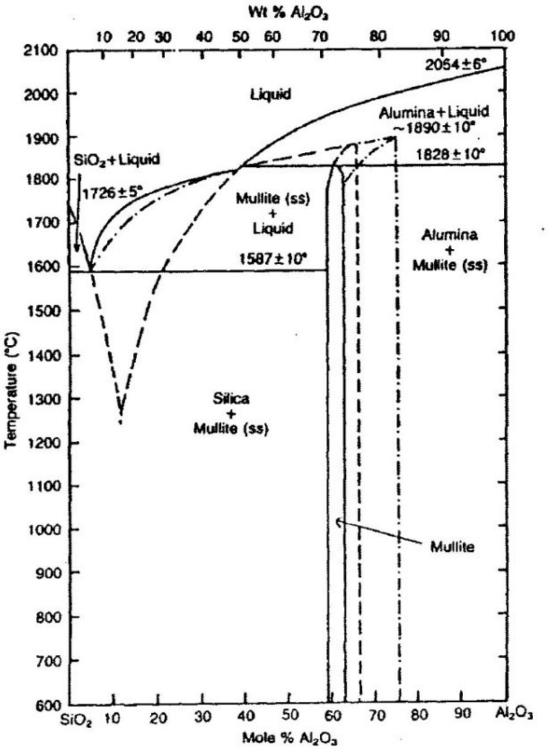

Figure. 8. The Al_2O_3 - SiO_2 phase diagram according to Aksay and Pask (1975).

Also observed from both images is the fact that mullite formation has no preferred orientation.

CONCLUSION

It has already been established that the content of kaolin in the Chimala deposit is sufficient for economical exploitation, although the content varies from one location to another on the deposit, but on the average kaolinite makes 48% of the material [Hills, 1962]. The report by Cilek [1979] reinforces this argument by indicating that the clay recovered under 100 µm is between 37 – 79% depending on the location of sampling. The prevalence of kaolinite clay was reported to range between 70 – 80%. Both reports suggest that the deposit is of a significant proportion for an economic mining operation.

In this contribution the ceramic qualities studied have ascertained the earlier predictions and thus concluding that the clay is suitable for the fabrication of ceramic materials. The chemical composition of the clay falls within the range of other commercial clays, namely, the Cornwall clays in England and the New Jersey clays in USA. The only setback being the content of Fe_2O_3 (1.48%) which appears to be on the high side, as compared to the recommended value of ~1% [Norton, 1974]. The high contents of iron oxides are associated to the pink coloration on the fired clay products [Mwakarukwa, 1988]. It is, however, envisaged that such limitation is minor for applications in wall and floor tiles, sanitary ware, pottery and refractories. The

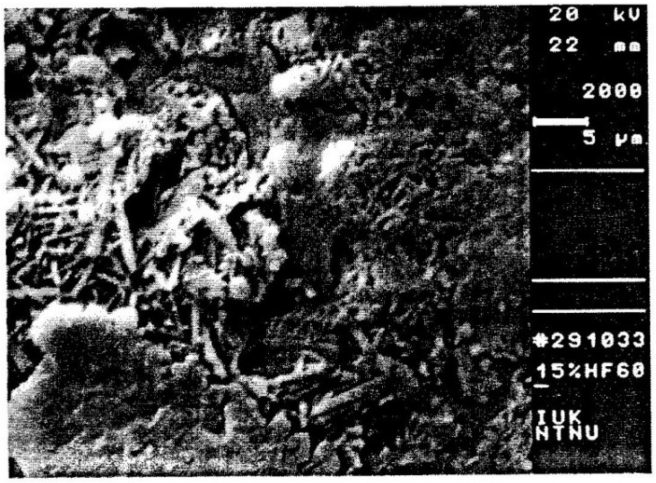

Figure. 9. Mullite needles on a fractured surface of a sample fired at 1200 °C for 8 hrs (sample was etched with 15% HF for 1 minute).

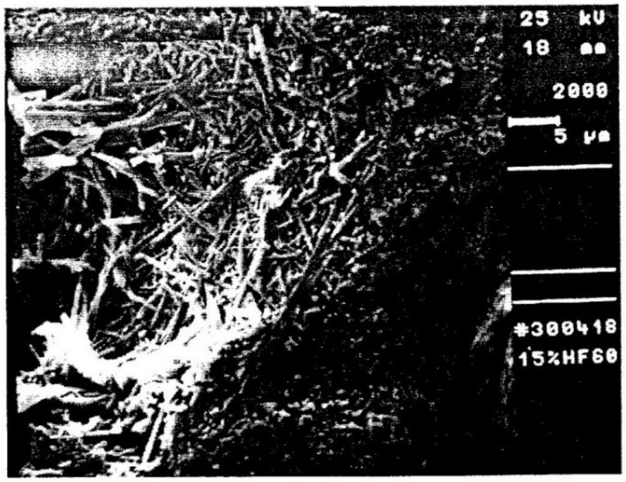

Figure. 10. Mullite needles on a fractured surface of a sample fired at 1400 °C for 8 hours (sample was etched with 15% HF for 1 minute

mullite phase which is responsible for the strengthening of ceramic ware is formed after firing at 1200 °C for 8 hours, the quantity of which increases tremendously for longer firing periods.

ACKNOWLEDGEMENTS

Professor Kjell Wiik of Norwegian University of science and Technology and his research group are recognised and thanked for the chemical analysis of kaolin and phase quantification of fired samples. NORAD is thanked for the generous financial assistance.

REFERENCES

1. Aksay, A. and Pask, J. A., *J. Am. Ceram. Soc.*, **58** (11-12) ,507-512, 1975.
2. Akwilapo, L. D. and Wiik, K. "Ceramic Properties of Pugu Kaolin Clays. Part I: Porosity And Modulus of Rupture" *Bull. Chem. Soc. Ethiop.* **2003**, 17(2), 147-154.
3. Brindley, G. W., Chih-chun, K., Harrison, J. L., Lipsicas, M. and Raythatha, R., *Clay Miner.,* **34,** 239-49, 1986.
4. Brindley, G. W. and Nakahira, M., *J. Am. Ceram. Soc.* **42**(7), 311-314, 1959.
5. Brindley, G. W. and Nakahira, M., *J. Am. Ceram. Soc.* **42**(7), 319-324, 1959.
6. Chakraborty, A. K. and Ghosh, D.K., *J. Am. Ceram. Soc.* **61**,170-173, 1978.
7. Cilek, V., "The Origin and Development of Primary and Secondary Kaolin Deposits in Tanzania", Czechoslovakia Academy of Sciences- Series of Mathematical and Natural Sciences, Vol. 89 ,Praha, 1979.
8. Comer, J. J., "New Electron-Optical Data on the Kaolinite-Mullite Transformation, *J. Am. Ceram. Soc.* **44**(11), 561-63, 1961.
9. Galan, E., Aparicio, P., Miras, A., Michailidis, K. and Tsira, A., *Appl. Clay Sci.,* **10**, 477-490, 1996.
10. Harris, J. F., "Kaolin Deposits of Tanzania" Int. Geol.Congr., 23rd, Czechoslovakia, Vol. 16 (Symp. 1. Proc.), Praha, 1968.
11. Hills, B. J. "The Beneficiation of Pugu Kaolinitic Sandstones for the Glass Sand" Unpub. Report Geol. Surv. Tanganyika. Report No. BJ/12, Dodoma, 1962.
12. Kobayashi, Y., Ohira, O., Satoh, T., and Kato, E., "Effect of Quartz on the Sintering and Bending Strength of the Porcelain Bodies in the Quartz Feldspar-Kaolin System" *J. Ceram. Soc. Jpn*, **102,** 100-105, 1994.
13. Link Analytical Co. *Chemical Analysis of Portland Cement, Raw mix and Related Raw Materials by EDXRF*, Application Note, Link Analytical, High Wycombe, Bucks; 1997.
14. Mwakarukwa, G. M., "Geologic and Economic Aspects of Clays in Tanzania" In Kimambo, R. H., Ed. "Development of the Non-metallic Minerals and the Silicate Industry in Tanzania", East African Publication Ltd, Dar es Salaam, 1988.
15. Norton, F. H., "Elements of Ceramics" 2nd Ed., Addison-Wesley, 1974.
16. Phelps, Q. W., "Slip Casting", Ceramic Monographs, *Interceram*, 31 (1-2), 1-9, 1982.
17. Schieltz, N. C. and Soliman, M. R.., *Clay and Clay Minerals,* **25,** 419-28, 1966.
18. Weaver, C. E., "Clays, Muds and Shales" Elsevier, Amsterdam, 1989.
19. William, M. J., "A Handbook of Determinative Methods in Clay Mineralogy", Chapman and Hall, 1987.