

Preliminary analysis of the thermal behaviour of an industrially used Ecuadorian clay

S.M. Faieta-Boada and I.J. McCole

*University of Bradford, Department of Industrial Technology, Bradford, West Yorkshire,
BD7 1DP, UK*

(Received December 1, 1992; accepted after revision February 1, 1993)

ABSTRACT

A clay mineral from Ecuador has been analysed mineralogically by X-ray, thermal and infrared analyses and shown to contain approximately 35% of a disordered kaolin phase. Following a dilatometric analysis the vitrification range is established as 1025–1350°C and an isothermal vitrification rate study is reported. The vitrification follows Arrhenius behaviour with $E_a = 147 \text{ kJ mol}^{-1}$ suggesting a viscous flow control process. Further analysis of the vitrification rate process leads to an equation enabling optimum firing conditions to be calculated:

$$V = \int_{h_0}^h e^{0.0085rh} + \frac{e^{13.23}}{e^{17.171/T}} h_s$$

where V is the total relative degree of vitrification, r is the heating rate, h is the heating time above 1298 K, T is the maximum firing temperature and h_s is the soaking period. Mechanical strengths of fired samples have maximum value for the optimum conditions.

A detailed athermal DTA analysis of the kaolin dehydroxylation and metakaolin to spinel/mullite transformation is presented and indicates that the shift in peak maximum temperature occurring with changing heating rate can be used to determine activation energies and provide insight into the transformation mechanisms.

INTRODUCTION

The ceramic whiteware and tile manufacturers around Cuenca, in Ecuador, use a local resource called simply C-1 as an additive clay to batches but little has been reported about this raw material. The intermittent work done with the resource using DTA and X-ray methods (Dorfner Laboratories, pers. commun., 1991; Basabe, 1992) shows a great variability from sample to sample from the same quarry, with resultant variability in manufacture. As part of a long-term project aimed at a thorough understanding of the thermal behaviour of Ecuadorian clays, this resource is being studied with respect to its mineral content, thermal analysis and the mechanical properties of fired products. Some of the initial findings are reported here.

One comparative feature of the clays chosen for this work is the activation energy of the dehydroxylation and metakaolin decomposition processes and to determine this the method of peak maximum temperature shift in a DTA scan as a function of heating rate has been selected. This athermal method for the estimation of thermal energy was first reported by Kissinger (1957) and Ozawa (1976) for n th order chemical reactions. Later modified Ozawa and modified Kissinger equations were derived on the basis of nucleation and growth equations for analysing crystallisation kinetics by thermal analysis (Matusita and Sakka, 1981; Hayward et al., 1987). The method has not been used widely for clay based samples but some activation energy data have been obtained by other methods (Brindley and Lemaitre, 1987; Redfern, 1987).

Using combined TG/DTA and dilatometry, the various stages of the chemical reactions undergone by the kaolin and the physical and chemical changes by the other minerals present, as well as the kaolin decomposition products, can be studied. The mineralogical content can be determined to some extent. However, the combined effects of the mineral content, chemical and physical interactions lead to the observed thermal behaviour and in particular, to the vitrification of the clay.

Vitrification is defined as the progressive reduction in the porosity of a body as a result of heat treatment and fusion, during which a glassy or non-crystalline material is formed. The vitrification range is the temperature interval between the temperature at which a body begins to fuse and the temperature at which the body begins to deform by melting. Thus vitrification is complete when maximum density or zero porosity is achieved without deformation. Bogahawatta and Poole (1991) measure vitrification rates of a series of Sri Lanka clays at a range of pre-deformation temperatures and make an interesting semi-empirical attempt to calculate heat treatment conditions using experimental observations of density and apparent porosity, among other properties, and an Arrhenius approach involving the temperature dependence of the vitrification rate. Hence the activation energy of vitrification may bear no relation to any specific kinetic chemical process. It is in fact a kinetic physical process and is related to capillarity and liquid phases present, liquid viscosities and their changes, etc. Hence the activation energy for dehydroxylation, which can of course increase porosity, and metakaolin decomposition may not show a correspondence to the vitrification activation energy which is the real direct processing parameter and whose values will be related to ease of firing and temperatures needed. Therefore it was decided to obtain values for the vitrification activation energy and to develop a thermal processing equation after the method of Bogahawatta and Poole (1991).

Thermal dehydroxylation and metakaolin decomposition activation energies have been found and are reported below; they show good agreement with earlier values for the dehydroxylation reaction (Brindley and Lemaitre, 1987; Redfern, 1987). High values for the activation energy of the metakaolin de-

composition have been found but no comparable data seem to be available in the literature. For this reason a sample of well-crystallised, high mineralogical content kaolin (>95%) from English China Clay Ltd. has been examined. The activation energy values are in good agreement and seem to show the effect of the disorder in the C-1 clay compared to the ECC sample. The data show also that the metakaolin transformation conforms to a bulk nucleation process with probably 2-D nuclei growing in 2-D. No similar firm indication for the dehydroxylation mechanism can be deduced from the data.

Vitrification of C-1 has been analysed after the method of Bogahawatta and Poole (1991) with activation energy values in the range they found for their clays, although no vitrification occurs in C-1 until some 175 K above their start of vitrification temperature of 1123 K. A heat treatment equation with time, heating rate and temperature parameters for C-1 has been established as shown below.

MATERIALS AND METHODS

The investigated materials were a sedimentary Ecuadorian clay named C-1 and a commercial sample of a well-crystallised kaolin, with a kaolinite content larger than 95%, from the English China Clay Ltd. The latter clay was used as reference material.

Clay C-1, as received and after being heated up to 700, 1050 and 1350°C, was analysed by X-ray diffraction using an Expectron XDC-700 Guinier-Hägg camera with $\text{CuK}\alpha$ radiation. The same samples were examined by infrared spectroscopy, using a Nicolet 205 FTIR Spectrometer, after being mixed with KBr and pressed into transparent discs.

For a compaction pressure against green strength investigation, the clay was ground mechanically for one and a half hours. Samples of the ground clay, containing about 8% moisture, were pressed in a hydraulic press into discs of 13.4 mm diameter and 3.5 mm thickness, using different compaction pressures in the range 141.4 to 424.2 MN m^{-2} . The maximum tensile strength of the discs were measured by diametral compression tests employing a universal machine with a crosshead speed of 0.1 mm min^{-1} . The particle size distribution of the ground clay was determined by laser diffraction using a Malvern Analyser.

Dilatometer traces of discs compacted under a pressure of 283 MN m^{-2} were made in a temperature range from room temperature to 1350°C, at a heating rate of 5°C min^{-1} , using a Netzsch 402 ES Dilatometer.

Combined TG/DTA traces of clay C-1 were obtained in the range ambient to 1350°C, at a heating rate of 5°C min^{-1} , using a Stanton Redcroft STA-780 Thermal Analyser. These analyses were performed in a dynamic N_2 atmosphere, with a flow rate of 40 $\text{cm}^3 \text{min}^{-1}$, employing $\alpha\text{-Al}_2\text{O}_3$ as reference material.

In order to determine the activation energy of the dehydroxylation and metakaolin decomposition processes, samples of C-1 and ECC kaolin were employed in DTA runs in the range ambient to 1350°C, using heating rates of 2, 5, 8, 10, 15, 20, 25, 30, 35 and 40°C min⁻¹. These runs gave a series of endothermic (dehydroxylation) and exothermic (metakaolin decomposition) peak maximum temperatures, that varied with the heating rate used.

For the dehydroxylation process, an Ozawa-type plot of ln(heating rate) against the reciprocal peak maximum temperature in K was drawn for both clays. The activation energy of dehydroxylation was calculated from the slope of the straight line, E_a/R , where R is the gas constant.

For the metakaolin transformation, two equations, modified Ozawa (Hayward et al., 1987) and modified Kissinger (Matusita and Sakka, 1981), were used to relate peak maximum temperature, T_p , and heating rate, α , and calculate the activation energy of the process. The modified Ozawa equation relates T_p and α as:

$$\ln \alpha = \frac{mE}{nRT_p} + C \quad (1)$$

where m and n are characteristic of various crystallisation mechanisms.

The modified Kissinger equation correlates both parameters as:

$$\ln\left(\frac{\alpha^n}{T_p^2}\right) = -\frac{mE}{RT_p} + C \quad (2)$$

For the analysis of the vitrification behaviour of clay C-1, discs pressed at 283 MN m⁻² and dried at 110°C for 24 hours were subjected to a range of heat treatments at a constant heating rate of 5°C min⁻¹ up to the desired soak temperature in the range 1025 to 1375°C, from which it was confirmed that no vitrification occurred below 1025°C. A closer examination was made in the range of 1225°C–1375°C for soaking periods of 1–4 hours. Bulk density from each fired disc was calculated from weight and physical dimension determinations, as well as by water displacement, following the ASTM method, C373-88. Apparent porosity and water absorption of the fired bodies were also measured in accordance with ASTM C373-88 specifications. Additionally, the maximum tensile strength of the disc was measured by using diametral compression tests.

RESULTS

XRD and IR analyses

An X-ray analysis of clay C-1 and all of the products from the firings has been made. The dried material contains kaolinite (30 wt%), quartz and cris-

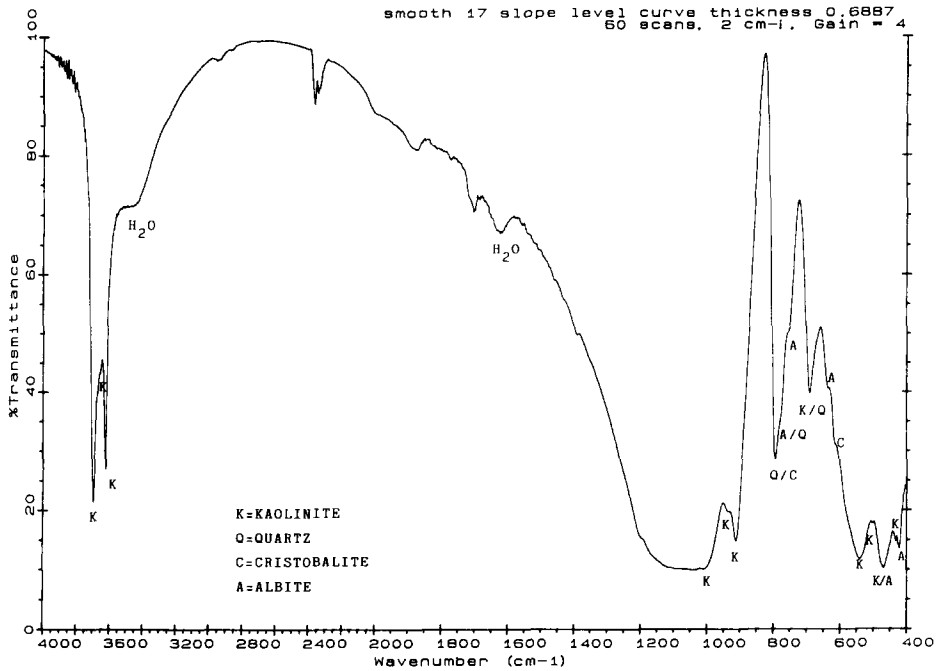


Fig. 1. IR spectrum of clay C-1 (dried at 110°C).

tobalite, albite and a small amount of an unidentified material by the presence of a few very weak X-ray diffraction lines unaccounted for. This analysis is in broad agreement with a commercial one made last year (Dorfner Laboratories, pers. commun., 1991). An infrared examination (Fig. 1) confirms the presence of kaolinite, suggesting strongly (single peak at 3657 cm^{-1} instead of the $3669\text{--}3652\text{ cm}^{-1}$ doublet) that the crystals are quite disordered. The large amount of quartz and cristobalite is emphasised by the strong peaks at 795 and 693 cm^{-1} .

Green strength and particle size determinations

A compaction pressure versus green strength investigation of C-1 as received, and ground to a particle size $< 100\text{ }\mu\text{m}$, is shown in Fig. 2. Although the maximum green strength, and therefore it may be assumed the best fired strength, would be obtained at a pressure of 354 MN m^{-2} , samples were intermittently capped. Therefore it was decided to use a lower compaction pressure of 283 MN m^{-2} for the samples made for dilatometry and vitrification analysis.

The particle size distribution for C-1 is very broad and quite uniform within the range from 3 to $88\text{ }\mu\text{m}$.

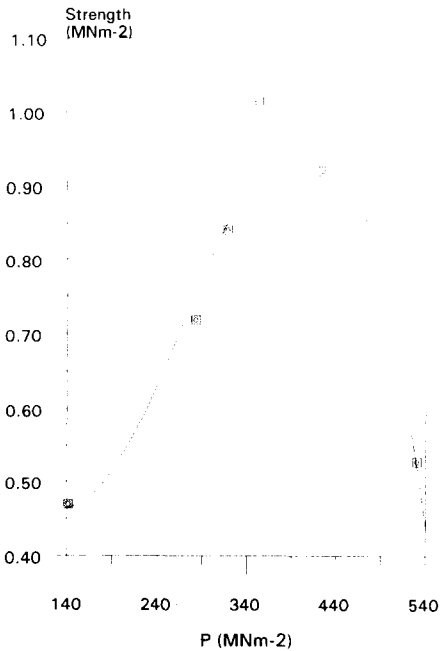


Fig. 2. Maximum tensile strength versus compaction pressure (C-1 as received).

Thermal analyses

Dilatometry

The dilatometer trace shown in Fig. 3 presents a shallow expansion beginning at 185°C up to 240°C confirming the presence of cristobalite for which this is the low to high transition. At 515°C a volume decrease is observed, mainly completed by 575°C, but showing a very small steady decrease up to 955°C; this corresponds to the dehydroxylation of kaolin. A reaction between 955 and 990°C is shown by an increase in the rate of volume decrease, corresponding to the metakaolin decomposition superimposed on the continuous slow loss of water. Rapid vitrification begins at 1050°C and continues up to 1350°C. This confirmed the visual observation of no apparent vitrification below 1025°C which was the temperature chosen as the base line for the vitrification analysis. Serious bloating and vapour evolution is observed beyond 1375°C when a highly porous, badly deformed disc results from the presence of excess liquid phase. None of the dilatometer changes for the C-1 sample were anything like as obvious as those found for the ECC test sample, with the exception of the cristobalite transformation, which is not present in the dilatometer trace of the latter sample.

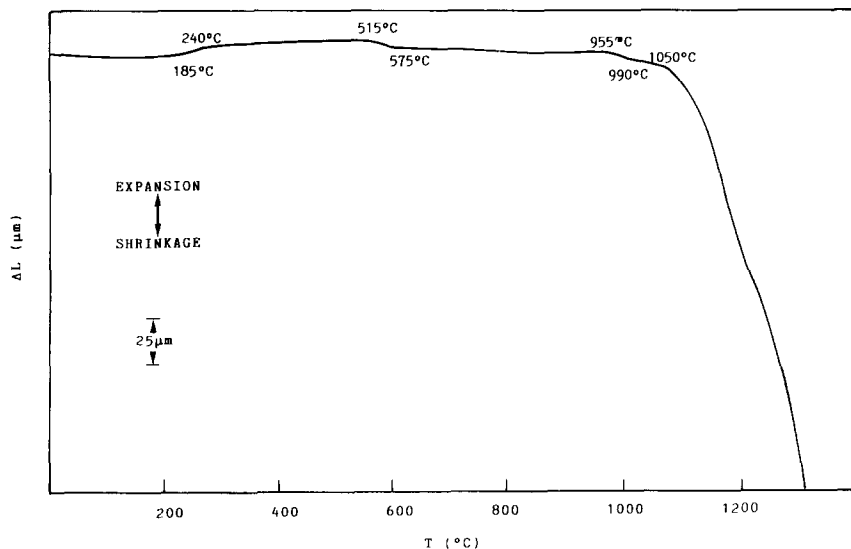


Fig. 3. Dilatometer curve of clay C-1.

DTA/TG

These techniques confirm the information present in the dilatometer trace and also allow some calculations of the mineralogical content to be made. From ambient to 110°C there is a 2.1% weight loss corresponding to the surface bound water, clearly shown in the DTA trace by an endothermic peak with maximum at 50°C. A small endotherm at 226°C with no corresponding weight change again confirms the large presence of cristobalite. Dehydroxylation was more sensitively detected to begin at 435°C with a peak maximum at 492°C and an overall 4.9% weight loss which corresponds to about 35 wt% kaolin. The thermal transformation accompanied by no weight change, beginning at 969°C with maximum exotherm at 995°C, is the metakaolin decomposition peak in good agreement with the dilatometry.

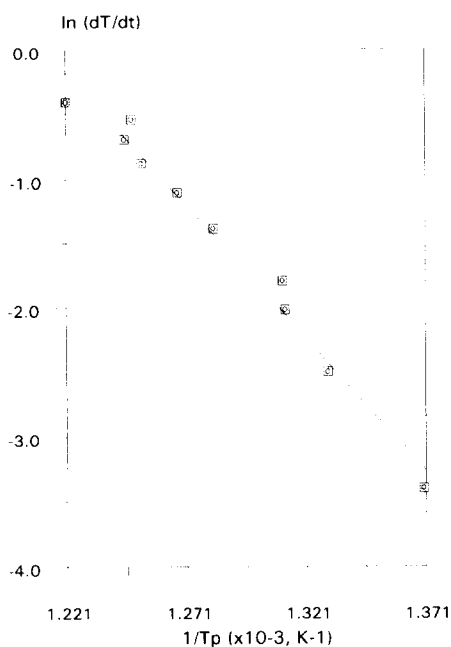
Determination of process activation energies

Table 1 clearly shows that as the heating rate is increased the DTA peak maxima, endothermic for the dehydroxylation and exothermic for the metakaolin transformation/decomposition, do move to higher temperatures. An Arrhenius representation of this data as $\ln(\text{heating rate})$ against reciprocal peak maximum temperature shows good linearity (Figs. 4 and 5). Using the slope of this plot and eqs. (1) and (2), the activation energies have been calculated to be 169.2 kJ mol⁻¹ for dehydroxylation and 954 kJ mol⁻¹ for the metakaolin decomposition. Similar values were found for the ECC sample with 202 kJ mol⁻¹ dehydroxylation and 1130 kJ mol⁻¹ for the metakaolin decomposition.

TABLE I

DTA peak maxima at different heating rates

Heating rate ($^{\circ}\text{C}$ min^{-1})	T_p dehydroxylation ($^{\circ}\text{C}$)	T_p metakaolin transformation ($^{\circ}\text{C}$)
2.0	457	975
5.0	479	987
8.0	489	992
10.0	490	996
15.0	507	1003
20.0	516	1009
25.0	526	1012
30.0	530	1009
35.0	528	1014
40.0	546	1014

Fig. 4. $\ln(\text{heating rate})$ versus reciprocal peak temperature for dehydroxylation of clay C-1.

Vitrification analysis

For each disc the density, apparent porosity and tensile strength were found. Some of this data are presented in Fig. 6, from which, and by visual examination of deformation, the optimum soaking period for each temperature was found. The plots of $\ln(\text{optimum soaking period})$ against the reciprocal tem-

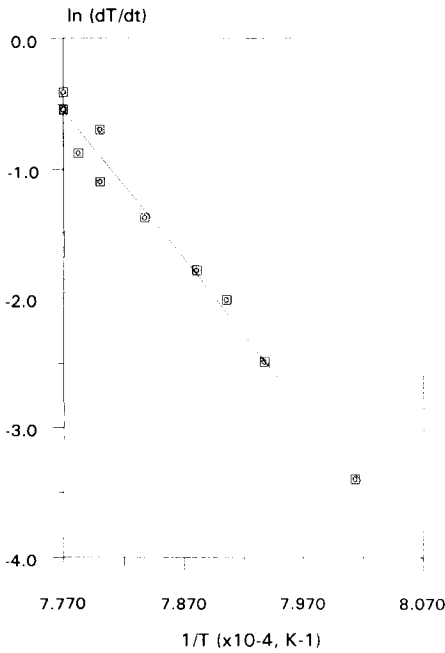


Fig. 5. ln (heating rate) versus reciprocal peak temperature for metakaolin transformation of clay C-1.

perature were made. Bulk density as calculated from weight and physical dimension determination gave a good linear fit as Fig. 7 shows. Bulk density and apparent porosity showed large scatter about a line of same slope as that in Fig. 7. The maximum tensile strengths present also a linear fit although only few data have so far been gathered.

The slopes of these lines were used in the estimation of optimum firing conditions for clay C-1, after Bogahawatta and Poole (1991). The equations of these lines are the logarithmic form of the Arrhenius equation and therefore their slope corresponds to the exponential factor E_a/R which for the clay C-1 was found to be 17,171 ($E_a=142.7 \text{ kJ mol}^{-1}$). This value was used in the following equation in order to determine the relative rates of vitrification at different temperatures of firing:

$$\ln k_T = \frac{E_a}{R} \left[\frac{1}{1298} - \frac{1}{T} \right] \tag{3}$$

where k_T is the rate of vitrification at T relative to that at 1025°C (1298 K), which was found to be the onset temperature of the vitrification process in clay C-1. A modified expression of eq. (3) is:

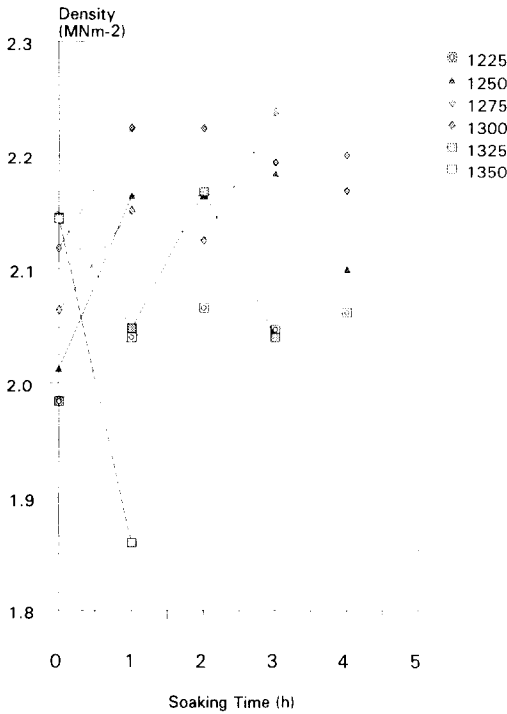


Fig. 6. Bulk density of fired discs versus soaking period (clay C-1).

$$k_T = \frac{e^{13.23}}{e^{17.171/T}} \tag{4}$$

and shows the temperature dependence of the rate of vitrification (k_T) for this clay. The values of k_T for firing temperatures between 1225 and 1350°C are shown in Table 2.

In order to obtain the relative degree of vitrification resulting from heating, the theoretical rate equation (4) should be integrated with respect to time. However, in the aim of simplifying the calculations, Bogahawatta and Poole (1991) use an empirical rate equation, which for clay C-1 can be expressed as:

$$k_T = e^{0.0085rh} \tag{5}$$

where r is the constant heating rate ($^{\circ}\text{C h}^{-1}$) and h is the heating time above 1025°C.

The relative degree of vitrification resulting from soaking was obtained by multiplying the rate of vitrification at the maximum temperature of firing (Table 2) by the soaking time.

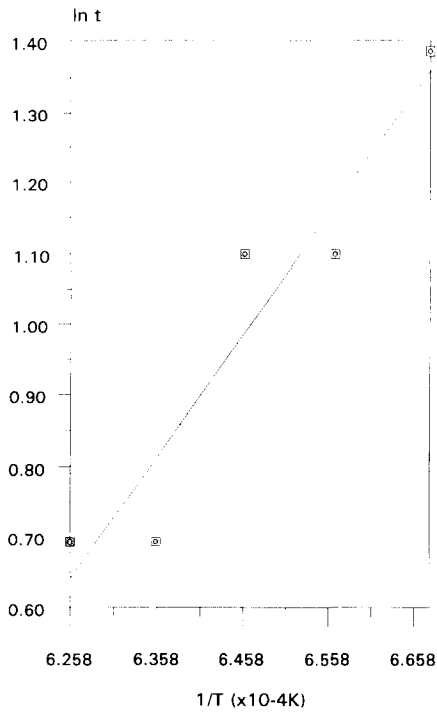


Fig. 7. ln (optimum soaking period) versus reciprocal firing temperature for clay C-1.

TABLE 2

Values of k_T for various firing temperatures (after eq. 4)

Firing temperature (°C)	k_T
1225	5.86
1250	7.07
1275	8.48
1300	10.11
1325	12.00
1350	14.16

The total relative degree of vitrification of the fired clay bodies was calculated by adding the two partial degrees of vitrification.

$$V = \int_{h_0}^h e^{0.0085rh} + \frac{e^{13.23}}{e^{17.171/T}} h_s \quad (6)$$

The obtained values are presented in Table 3 which shows that the highest

TABLE 3

Degree of vitrification of clay C-1 subjected to various heat treatments

Maximum firing temperature (°C)	Soaking period (h)	Relative degree of vitrification (heating) (arb. units)	Relative degree of vitrification (soaking) (arb. units)	Total relative degree of vitrification (arb. units)
1225	4	2.2	23.4	25.6
1250	3	2.7	21.2	23.9
1275	3	3.3	25.4	28.7
1300	2	4.1	20.2	24.3
1325	2	5.0	24.0	29.0

TABLE 4

Maximum tensile strength of clay C-1 after different firing schedules

Maximum firing temp. (°C)	Soaking period (h)	Maximum tensile strength (MN m ⁻²)
1225	4	8.699
1250	3	7.837
1275	3	12.925
1300	2	9.792
1325	2	21.532

degree of vitrification is achieved by the 1325°C heat treatment with 2 hours soaking period. The resulting bodies of this firing schedule possess superior physical properties, i.e. mechanical strength, as Table 4 shows.

DISCUSSION

It is emphasised here that these results will need more experiments in order to confirm the values quoted and in particular will need to be viewed alongside several other clay samples which are currently under investigation by these methods. However, from the regression analysis the values obtained for activation energy appear to be reliable with *R*-values in the range 0.983–0.991. Furthermore, where activation energies have been found for related materials by other workers they have good agreement to those reported here (Brindley and Lemaitre, 1987; Redfern, 1987). For example, Redfern calculates E_a for dehydroxylation of 222 kJ mol⁻¹ using an isothermal technique and the Avrami equation, which compares to the 202 kJ mol⁻¹ for the ECC sample. Finally it is encouraging to see that a well crystallised ECC sample of kaolin of high mineralogical purity gives close values for the decomposition reac-

tions; we have yet to subject this sample to a vitrification analysis by the method used here.

X-ray, infrared spectroscopy and thermal analysis methods are in broad agreement as to the content of C-1; some 30–35 wt% kaolin, quartz and cristobalite 30–35 wt% and albite–orthoclase feldspar 30–35 wt%. One very interesting feature of C-1 compared to the well crystallised ECC sample showed up strongly on the infrared examination, namely that C-1 has a quite disordered structure. This fact may account for the lower peak maximum temperatures for decomposition reactions found on the combined TG/DTA traces and also explain the lower E_a values found for both dehydroxylation and metakaolin decomposition; compare C-1 dehydroxylation $169.2 \text{ kJ mol}^{-1}$, ECC sample 202 kJ mol^{-1} and C-1 metakaolin decomposition 961 kJ mol^{-1} , ECC sample 1130 kJ mol^{-1} . It will be interesting in future studies to see if this is a real difference that can be used to assess disorder and to give weight to certain of the mechanisms for these transformations. Here it is worth noting that the peak maximum heating rate method gives values for activation energy that are in the middle of the range of values found by those using other methods (Brindley and Lemaitre, 1987), at least for dehydroxylation. As far as metakaolin decomposition is concerned there are little reported data with which to compare. This situation has probably arisen because of the uncertainties in the earlier approaches to crystallisation where orders of reaction have to be postulated but which have obscure physical meaning in a crystallisation process (Matusita and Sakka, 1981). Since the transformation, metakaolin to spinel phase, is one from amorphous to crystalline, then the newer approach of Matusita and Sakka (1981) is to be favoured where the crystallisation kinetics are analysed on the basis of nucleation and growth processes (Matusita and Sakka, 1981; Hayward et al., 1987). Using this approach the data found here do not give unambiguous results for the type of nucleation and growth mechanism encountered as shown in Table 5. First attempts using $n = 1$, $m = 1$ in eq. (2) give correlation coefficients less than 0.6 and so the concept of surface nucleation and growth for this transformation is not tenable, which may account for the non-dependence on particle size that is discernible in the activation energy values. The various bulk nucleation and growth mechanisms have to be assessed by considering the correlation coefficients for combinations of n from 2–4 and m from 1–3 and results do not clearly distinguish between any of the bulk nucleation possibilities. In fact, the method is not particularly sensitive and other types of observation must be used to form a conclusion (Hayward et al., 1987). In the case reported here some combinations give unrealistically high activation energies and so discount themselves, for example the 1-D growth of bulk nucleation with varying number of nuclei. Two and three dimensional growth from nucleation with varying numbers of nuclei are high but not so easily discounted. The models involving nucleation from a constant number of nuclei give very good R -values (Table 6) and can

TABLE 5

Values of correlation coefficient and activation energy for the metakaolin transformation (clay C-1), in linear regression equations for Kissinger-type plots

Crystallisation mechanism	m, n values	Correlation coefficient	Activation energy
<i>Surface nucleation</i>	$m = n = 1$	0.525	*
<i>Bulk nucleation</i>			
Constant number of nuclei:			
1-D growth	$m = n = 1$	0.525	*
2-D growth	$m = n = 2$	0.991	953.6
3-D growth	$m = n = 3$	0.991	957.1
Varying number of nuclei:			
1-D growth	$m = 1, n = 2$	0.991	1907.2
2-D growth	$m = 2, n = 3$	0.991	1435.6
3-D growth	$m = 3, n = 4$	0.978	1309.9

*Not calculated because of the low value of the correlation coefficient.

be related most easily to theoretical arguments regarding the mechanism of the process. For example, Brindley's model (Brindley and Nakahira, 1959; McColm, 1983, pp. 52–54) and Johnson et al.'s (1982) practical work imply a fixed population of nuclei on 2-D planes perpendicular to the c -axis of metakaolinite. Thus a bulk nucleation of a fixed number of nuclei with growth in two dimensions leads to an activation energy of $953.6 \text{ kJ mol}^{-1}$ as determined in this work.

The very large amount of experimental effort needed to provide data for a vitrification equation have given encouraging confirmation of the usefulness of the method as explained by Bogahawatta and Poole (1991). The activation energy for the physical process of vitrification, with a value of 143 kJ mol^{-1} , is in the range of 74 to 151 kJ mol^{-1} found for the Sri Lanka clays by Bogahawatta and Poole (1991). This value is well below the activation energy for the metakaolin crystallisation but as the dilatometer traces clearly show vitrification only begins after the transformation of metakaolin has occurred. The exothermic nature of the metakaolin transformation is possibly the "catalyst" for the vitrification. Activation energies for viscous flow of oxide material, such as SiO_2 , albite and soda glass are found to lie in the range $80\text{--}600 \text{ kJ mol}^{-1}$ for any one material since the plot of $\ln \eta$ versus $1/T$ is not a straight line (McColm, 1983, p. 141) and modifications to the Arrhenius type equation have to be made. When this is done activation energy values for viscous flow of about 200 kJ mol^{-1} are common, thus the vitrification E_a found here suggests that the controlling mechanism is simply one of viscous flow.

Finally the vitrification rate equation, eq. (6), is felt to be a useful tool for the Cuenca manufacturers in that optimum firing cycles can be calculated, hence removing some of the process uncertainties that exist at the moment.

CONCLUSIONS

The Ecuadorian clay C-1 contains 30–35 wt% kaolin, 30–35 wt% quartz, cristobalite and 30–35% albite, orthoclase feldspar, as determined by X-ray, thermogravimetric analysis and infrared spectroscopy methods.

Peak maximum temperature against heating rate can be used to find dehydroxylation and metakaolin decomposition activation energies. For dehydroxylation activation energy a value of 169 kJ mol⁻¹ has been found. For the metakaolin to spinel/mullite transition, by relating this to a recrystallisation process, activation energy is 954 kJ mol⁻¹ arguing from a bulk nucleated, 2-D growth model. These data alongside IR spectra show that the kaolin in this clay is crystallographically disordered.

An isothermal heating method shows that vitrification begins above 1025°C and has an activation energy of 143 kJ mol⁻¹, which by comparison suggests that viscous flow is the controlling mechanism.

A semi-empirical firing equation:

$$V = \int_{h_0}^h e^{0.0085rh} + \frac{e^{13.23}}{e^{17.171/T}} h_s$$

enables optimum firing conditions to be calculated.

The highest value of the maximum tensile strength of fired specimens, 21.5 MN m⁻², coincides with the optimum firing conditions determined from the vitrification analysis.

ACKNOWLEDGEMENTS

S.M. Faieta-Boada gratefully acknowledges the financial support of the British Council enabling her to undertake this research as part of the requirements for a Ph.D. degree.

The support of English China Clay Ltd. by way of kaolin samples is acknowledged.

REFERENCES

- Basabe, J., 1992. Caracterización múltiple de importantes materias primas cerámicas utilizadas por la industria nacional. PUCE, Quito.
- Bogahawatta, V.T.L. and Poole A.B., 1991. Estimation of optimum firing conditions for kaolinitic clay bodies. *Br. Ceram. Trans. J.*, 90: 52–56.
- Brindley, G.W. and Lemaitre, J., 1987. Thermal, oxidation and reduction reactions of clay minerals. In: A.C.D. Newman (Editor), *Chemistry of Clays and Clay Minerals*. Longman, Essex, pp. 319–370.

- Brindley, G.W. and Nakahira, M., 1959. The kaolinite-mullite reaction series: III, the high-temperature phases. *J. Am. Ceram. Soc.*, 47(7): 319-324.
- Hayward, P.J., Vance, E.R. and Doern, D.C., 1987. DTA/SEM study of crystallization in sphene glass-ceramics. *Am. Ceram. Soc. Bull.*, 66: 1620-1626.
- Johnson, S.M., Pask, J.A. and Moya, J.S., 1982. Influence of impurities on high-temperature reactions of kaolinite. *J. Am. Ceram. Soc.*, 65: 31-35.
- Kissinger, H.E., 1957. Reaction kinetics in differential thermal analysis. *Anal. Chem.*, 29: 1702-1706.
- Matusita K. and Sakka, S., 1981. Kinetic study on non-isothermal crystallization of glass by thermal analysis. *Bull. Inst. Chem. Res., Kyoto Univ.*, 59: 159-171.
- McColm, I.J., 1983. *Ceramic Science for Materials Technologists*. Leonard Hill, Glasgow. 357 pp.
- Ozawa, T., 1976. A modified method for kinetic analysis of thermoanalytical data. *J. Thermal Anal.*, 9: 369-373.
- Redfern S.A.T., 1987. The kinetics of dehydroxylation of kaolinite. *Clay Miner.*, 22: 447-456.