Journal of Thermal Analysis, Vol. 31 (1986) 15–20

DILATOMETRIC STUDIES OF PURMANDAL CLAY: PART I

H. R. Khajuria, S. K. Mehta and *Ashok K. Gupta*

MINERAL DIVISION, REGIONAL RESEARCH LABORATORY,
JAMMU, INDIA

(Received October 23, 1984; in revised form December 23, 1984)

Clay from the Purmandal area of J&K State was separated into its different size fractions by the method of sedimentation and with Sharple's super centrifuge process. Dilatometric studies were performed on each clay fraction; the results obtained from the dilatation curves are discussed in detail. The results revealed that the finer fraction of clay is bentonitic in nature, whereas the other fractions are felsphatic and micaceous in nature.

In mineralogical investigations the dilatometric procedures find great application with a view to detecting the various types of phase changes. The measurement of length changes during heating provides characteristic data which permit the simultaneous identification and determination of several minerals present in clay.

There has been continuing interest in the thermal expansion of refractories for nearly half a century [1–6]. This ranges from the need for reliable engineering data for application to the design of refractory structures to an academic interest in the fundamental effects of the mineralogical constituents on the thermal expansion coefficients of these important materials.

Moravek [7] studied the dilatometric method of thermal testing in research and industry in ceramics, and reported the expansion/contraction curves for kaolin, halloysite, illite, bentonite and montmorillonite. Very interesting results were obtained by Pampuchowa [8] from a study of the dilatometric properties of kaolinite clays as a function of their mineralogical compositions. Phase changes during vitrification in mica felspar minerals have been examined by Moravek [9]. Krishnan et al. [10] pointed out that even single-phase polycrystalline materials introduce considerable complexity in the basic processes which determine the overall thermal expansion. The dilatometric measurements of clays from the Purmandal and Leh areas of J&K State (India) have never been attempted. This investigation is a systematic experimental study of the thermal expansion of clay samples which have been separated into various size fractions especially prepared

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

for and measured during this study. Part I of this paper relates to Purmandal clay. Part II, on Leh clay, is under preparation.

Experimental

Clay from the Purmandal area, latitude 32° 42′, longitude 76° 6′, about 33 km from Jammu, was collected for the present investigation. The clay as such is dull-white in colour; it occurs as fairly hard and compact lumps, with large dark-grey particles embedded in the clayey matrix; it has a sandy texture. The chemical analysis of the sample is shown in Table 1. The sample was ground in water [11] in a ball mill for 40 hours, passed through a 45 μm sieve and then treated with dilute HCl and H_2O_2 to remove carbonates and organic matter [12]. The clay was separated into various size fractions by sedimentation and with Sharple's super centrifuge process [13]. The various size fractions obtained and the numbers assigned to each fraction are given in Table 2.

Table 1 Chemical analysis

SiO_2	66.92%
TiO_2	0.11%
Al_2O_3	14.10%
Fe_2O_3	1.59%
CaO	2.28%
MgO	1.98%
K_2O	3.89%
Na_2O	0.19%
L.O.I.	9.05%

Table 2

Sample number	Size of fraction
1	whole clay
2	+10 μm
3	10–5 μm
4	5–2 μm
5	2–0.5 μm
6	less than 0.5 μm

Differential thermal analysis and dilaometric measurements were carried out on a MOM derivatograph (Budapest, Hungary) at a linear heating rate of 10 deg/min. The dilatation studies were made by making slight alterations to the derivatograph, i.e. mounting the dilatation accessory in the equipment as recommended by the manufacturers. Hollow cylindrical samples with lengths varying from 2.0 to 3.0 cm, pressed at a dead load of 5000 kg, were used for dilatometric measurements.

Results and discussion

Figure 1 (a–f) presents the dilatomevric curves of samples 1–6, respectively. The dilatometric curve of sample 1 shows an initial contraction from 150°, which continues up to 350°; this may be due to the removal of interlayer water. After this, a range of volume stability is observed. In the temperature zone 550–608°, the curve exhibits a slight expansion because of the presence of quartz, which undergoes the $\alpha \rightleftharpoons \beta$ transition at 573°. In spite of the dehydroxylation observed at 690° in the DTA curve in Fig. 2a for this sample, the volume stability is maintained in the region

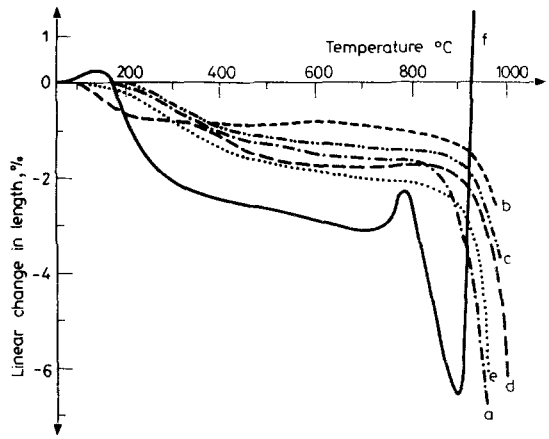

Fig. 1 Dilatometric curves of different fractions of Purmandal clay. a–f: samples 1–6, respectively

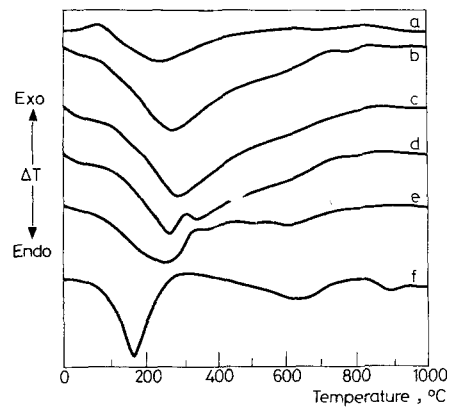

Fig. 2 Differential thermal analysis curves of different clay fractions from Purmandal area. a–f: samples 1–6, respectively

600–900° because the lattice collapse and recrystallization [14] of the clay mineral is insufficient to counterbalance the stabilizing influence of non-plastic components. At about 950°, alkalies from mica form an appreciable amount of liquid, which is manifested by a sharp and rapid contraction in Fig. 1a.

On the other hand, the dilatometric curves of samples 2 and 3 show a contraction from 200° up to 450°, which may be due to the loss of interlayer water. This is evident from the DTA curves in Fig. 2b and 2c. At about 550–600°, expansion occurs in these curves because of the quartz inversion at 573°. From 600° onward, samples 2 and 3 show volume stability up to 900° and 850°, respectively, because of the non-plastic impurities present, i.e. a high percentage of silica, which greatly reduces the firing shrinkage, apparently by acting as a non-reactive skeleton during heating. After 900°, the curves of these samples show contraction, because the alkalies from mica start to form liquid, thereby filling the pores. However, the percentage linear shrinkage is slight as compared with sample 1, because of the high silica and low alkali contents of these samples, which inhibit liquid formation. The principal feature in the dilatometric curve of sample 4 is that it shows contraction at 100–210° and then at 300–400°, which may be due to the loss of interlayer water in two stages; this is in conformity with the doublet observed in the DTA endotherm of this sample in Fig. 2d. The curve for sample 5 exhibits contraction attributed to the removal of interlayer water in one stage only. Figure 2e presents the DTA curve of sample 5.

From 500° onward, the dilatometric curves of samples 4 and 5 exhibit volume stability because of the presence of mica. This stabilizes the body and prevents the shrinkage attributable to lattice collapse and recrystallization of the mineral. Vitrification is observed at about 900°, at which point liquid starts to form from the mica present. The salient feature of these two curves is the large linear contraction of 3.5% and 4.2%, respectively, between 900 and 950°. The dilatometric curve of sample 6 presents strikingly different features. The curve exhibits slight expansion up to 150°, and after this temperature there is a contraction, which is attributed to the loss of interlayer water. This demonstrates that the adsorbed water is not released until close to 200°, the temperature at which the first endothermic effect was noticed in the DTA curve (Fig. 2f). Unlike the previous samples, this sample shows a slight contraction up to 700°. Between 700 and 750° there occurs a rapid expansion, possibly correlated with the development of the anhydrous form [15]. This expansion is immediately followed by a large contraction up to 890°, after which a rapid expansion is observed. This expansion results from the expansion of gaseous dissociation products within the material, which is pyroplastic even at this low temperature. Forbes [16] attributed this expansion to the typical swelling behaviour of bentonites.

Conclusion

From the dilatometric studies it is apparent that Purmandal clay is siliceous in nature and contains quartz and felsphatic/micaceous impurities. The presence of a large amount of free silica is indirectly supported by the high silica/alumina molar ratio. A high percentage of alkalies indicates the presence of either felspar or mica or both in it.

The fractionation of the clay helps to separate the non-clayey, non-plastic impurities from the clay. Coarser fractions are richer in quartz as compared with the whole clay. This is supported by the larger volume expansion, due to quartz inversion between 550 and 600°, in their respective dilatometric curves. On the other hand, the fraction having a particle size below 0.5 μm is richer in clay and from the behaviour of the dilatometric curve it has been identified as being bentonitic in nature.

* * *

The authors are grateful to Dr. C. K. Atal, Director, regional Research Laboratory, Jammu, for his kind permission to publish this paper and for providing necessary facilities. Thanks are also due to H. C. Gupta for typing the manuscript.

References

1 H. S. Holdsworth and J. W. Cobb, J. Am. Ceram. Soc., 6(5) (1923) 645.
2 F. H. Norton, J. Am. Ceram. Soc., 8 (12) (1925) 789.
3 R. A. Heindl, J. Res. Natl. Bur. Stand., 7 (16) (1933) 715.
4 O. J. Whithemore, Jr. and N. N. Ault, J. Am. Ceram. Soc., 39 (12) (1956) 443.
5 E. Ruh and R. W. Wallace, Am. Ceram. Soc. Bull., 42 (12) (1963) 52.
6 K. J. Chen, T. F. Lee, H. Y. Chang and Y. C. Ko, Am. Ceram. Soc. Bull., 1 (8) (1982) 866.
7 J. Moravek, Sprechsaal, 99 (18) (1966) 9184.
8 S. Pampuchowa and Basinka, Polska Akad. Nauk. Ceramika, 7 (1966) 33.
9 J. Moravek, Sprechsaal, 100 (13) (1967) 528.
10 R. S. Krishnan, R. Srinavasan and S. Devanarayanan, Thermal Expansion of Crystals, Pergamon, New York (1979) 2.
11 R. C. Mackenzie, R. Meldu and V. C. Farmer, Ber. Deut. Keram. Ges. 23 (1956) 222.
12 R. C. Mackenzie, Clay Min. Bull., 3 (1956) 4.
13 R. Roy and D. Lahiri, Trans. Ind. Ceram. Soc., 22 (1963) 67.
14 Grimshaw, Rex, W., The Chem. and Phys. of Clays, Ernest Benn Limited, London, 1971, p. 802.
15 W. Steger, Ber. Deut. Keram. Ges., 23 (1942) 46, 157.
16 D. W. A. Forbes, Ceramic Age, 81 (1965) 38.

Zusammenfassung — Ton aus dem Purmandal-Distrikt des J&K-Staates (Indien) wurden durch Sedimentation und mit Hilfe des Sharple-Superzentrifugenprozesses in Fraktionen mit unterschiedlicher Teilchengröße zerlegt. Die dilatometrische Untersuchung jeder Tonfraktion wird

beschrieben. Die aus den dilatometrischen Kurven erhaltenen Ergebnisse werden detailliert diskutiert. Die feinere Fraktion ist bentonitischer Natur, während alle anderen Franktionen vorwiegend Feldspat und Glimmer enthalten.

Резюме — Глина месторождения Пурманадал (Индия) была разделена на различные по размеру фракции методами седиментации и сверхскоростного центрифугирования. Проведены дилатометрические исследования каждой из этих фракций. Детально обсуждены результаты, полученные на основе дилатометрических кривых. Результаты показали, что фракция глины более тонкого помола является бентонитовой по природе, тогда как остальные фракции — полевой шпат и слюда.