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# MINEROLOGICAL STUDIES ON FIVE PLASTIC FIRE CLAYS
## DTA, TG and electron microscopy

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Mineralogical studies on five plastic fire clays of India have been carried out by DTA, TG and electron microscopy. Studies were done on both 'as received' and '<1 μ fraction' of clays. Results indicated that all the clays were predominantly kaolinite in nature and showed the main endothermic peak between 540° and 590°C and the exothermic peak between 920° and 985°C. A large exothermic peak at 810°C and a weight loss of 5.35% between 700° and 900°C in case of Barachatarma clay indicated the presence of graphitic carbon in the same. Both Neyveli and Badampahar clays contained illite and goethite. Electron micrographs of Mohuamilan and Neyveli clays showed hexagonal flakes of well-ordered kaolinite. Some tubular particles were seen in Chittorpur, Neyveli and Badampahar clays in addition to the kaolinite particles.

**Keywords**: mineralogy, plastic fire clays

## Introduction

The physico-chemical properties and application of any clay depend to a great extent on the nature of the constituent clay minerals as well as on the type and amount of accessory minerals present. To characterise a clay mineral completely, a clay mineral analysis is essential and usually it requires the use of two or more supplementary analytical techniques for establishing the nature of minerals present. The chemical analysis and X-ray diffraction analysis of the above five clays have been reported earlier [1]. The X-ray method was employed to obtain information on identification of clay and non-clay minerals, degree of disorder in

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the clay mineral lattice and to follow changes in mineralogical compositions induced by heat. But the information obtained by this method alone is not adequate especially in the case when some non-clay minerals are present in amount below the detection limit by X-ray. In the present communication, we have reported the DTA, TG and electron microscopic study of five plastic fire clays with a view to not only supplement the findings by X-ray method but also to give some new information on the mineralogical make-up of the clays.

## Experimental

To obtain the '<1 μ fraction' of the clays, a sedimentation process based on stokes' law was utilised with concentrated ammonia as a deflocculant [1].

Thermal analysis was carried out on the 'as received' samples after removal of organic matter as well as on the '<1 μ fraction' without removal. In order to remove the organic matter, all the 'as received' clays were treated with 10% hydrogen peroxide solution in a breaker on a hot plate maintained at low-temperature for 72 hours, washed with distilled water and dried in the oven. Before taking DTA, TG runs, the '<1 μ' samples were kept in a vacuum desiccator for at least four days over a saturated solution of $Mg(NO_3)_2 \cdot 4H_2O$ whereas in case of 'as received' clays, samples were previously dried in the oven at 110°. All the samples taken were passed through 200-mesh Tyler sieve.

The instrument used for DTA, TG measurements was Derivatograph (MOM, Hungary). Calcined alumina was used as the reference inert material. The weight of the samples taken for DTA, TG varied from 0.61 to 1.14 g depending on the density and packing of the samples. Measurements were made in the temperature range 25°–1000°C in air at a heating rate of 10 deg/min. The thermocouple used was Pt/Pt-Rh 10%. The sensitivity was 1/20 and 500 mg in case of DTA and TG respectively.

For electron microscopic study, the powdered clay samples were suspended in isopropyl alcohol and then set to ultrasonic vibration (frequency 20 kc per sec.). A drop of the suspension was placed over carbon coated grid and observed under Transmission Electron Microscope (Hitachi Model HU 11E) at 50 KV (high tension). Observations were made at different magnifications ranging from 40000 × to 68000 × depending on particle size of the specimen and suitability of the field under view.

In the following section the clays under study will be referred by their code in the bracket: Mohuamilan clay (M.C.), Chittorpur clay (C.C.), Barachatarma clay (B.C.), Neyveli clay (N.C.) and Badampahar clay (B.P.C.)

## Results and discussion

The differential thermal analysis curves of the clays, 'as received' and '<1 μ fraction', are given in Fig. 1(a and b). All the clays under study showed the main endothermic peak between 540° and 590°C and the exothermic peak between 920° and 985°C due to kaolinite. The endothermic peak corresponded to the decomposition of the mineral and elimination of hydroxyl group as water. The exothermic peak was associated with recrystallisation. Unlike the rest of the clays, B.C. (as received) showed a large exothermic peak at 810°C not corresponding to kaolinite. This clay showed relatively high loss on ignition (20.16%) and did not indicate any such impurity materials which could explain the high loss on ignition [1]. Carbon when present in the form of graphite gives a large exothermic peak at 820°[2]. Thus, the peak at 810°C was attributed to the presence of graphitic carbon in B.C. In the '<1 μ fraction' of the same clay, this peak occurred at 785°C and was very broad and small. Because of the removal of the coarser particles, the carbon content in the '<1 μ fraction' decreased, as reflected by the loss on ignition value (17.78%), and this resulted in a broad and small peak as compared to the 'as received' clay. N.C. ('as received' and '<1 μ fraction') showed oen very small en-

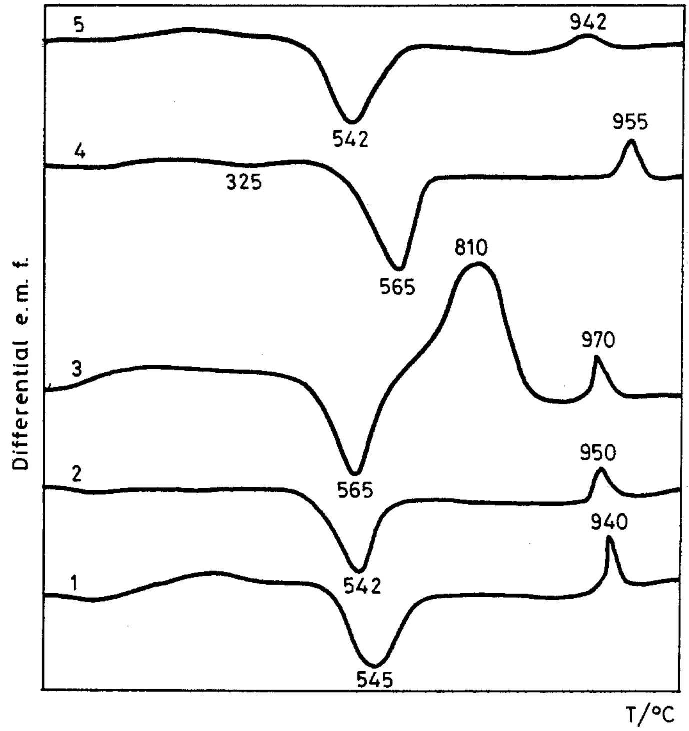

**Fig. 1a** DTA curves of clays (as received) (1) M.C., (2) C.C., (3) B.C., (4) N.C., (5) B.P.C.

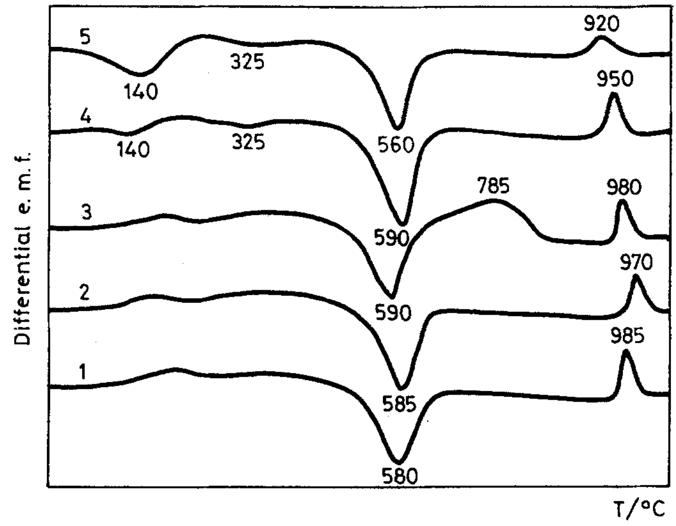

**Fig. 1b** DTA curves of clays (<1 μ fraction) (1) M.C., (2) C.C., (3) B.C., (4) N.C., (5) B.P.C.

dothermic peak at 325°C. In the '<1 μ fraction', B.P.C. also showed a very small endothermic peak at the same temperature but this peak did not occur in the 'as received' form. Many differential thermal curves for goethite have been published, and with one or two exceptions, all show a single large endothermic peak. Posrijak and Merwin [3] observed that the peak temperature varied with the particle size in 300°–400°C region, the higher peak temperature being associated with coarser samples. This was later confirmed in the comprehensive investigation of Kulp and Trites [4], a single peak at 385°–405°C being obtained for all coarsely crystalline samples. Thus the peaks at 325°C in N.C. and B.P.C. could be attributed to goethite. The reason for the occurrence of goethite peak only in the case of '<1 μ fraction' of B.P.C. and not in the 'as received' form of the same clay might be the increase in iron content from 4.20% in the latter to 5.66% in the former (1). In the DTA curves of '<1 μ fraction' of clays (Fig. 1b), only N.C. and B.P.C. showed low temperature endothermic peaks at 140°C. Grim [5–6] observed that the endothermic peak at low temperature may either be due to noncrystalline or imperfectly crystalline nature of kaolinite or sometimes due to the presence of illite or hydrous mica. Mclaughlin [7] showed that the nature of DTA curves of kaolinite and illite varied to a great extent according to the intimacy of mixing. The observation of Grim and Rowland [8] on the DTA curves of known mixture of kaolinite and illite suggest that the low temperature peak at 150°C obtained with a known mixture of kaolinite and illite becomes more and more sharp with increasing quantity of illite. The sharp exothermic reaction of kaolinite shown at a temperature of about 980°C is also affected by the presence of illite which catalyzes the reaction. Caillere and Henin [9] observed that the potassium and iron or illite lattice broaden and lower the peak temperature of the exothermic reaction. In case of N.C. and B.P.C. (Fig. 1b), the exothermic peaks occurred at relatively lower temperatures, 950° and 920°C respectively and the peak was broad in the latter case. N.C. and B.P.C. also showed comparatively higher moisture absorption values [10]. From the above facts, the endothermic peaks at

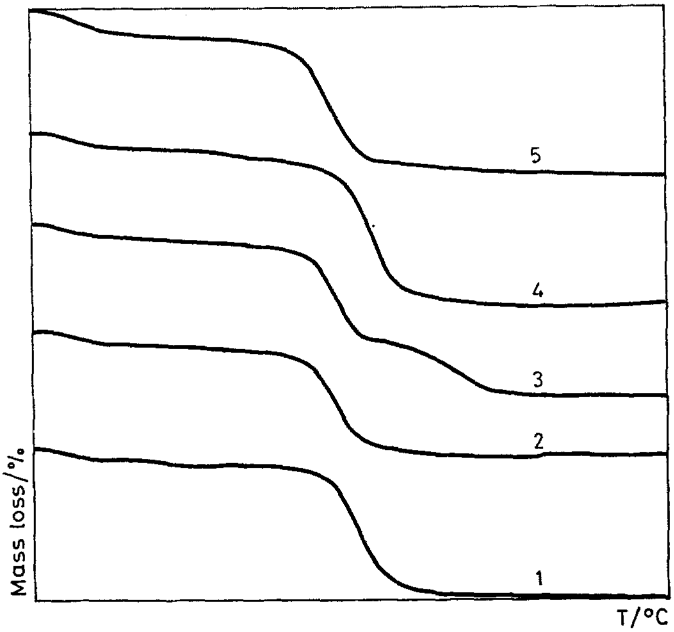

**Fig. 2a** TG curves of clays (as received) (1) M.C., (2) C.C., (3) B.C., (4) N.C., (5) B.P.C.

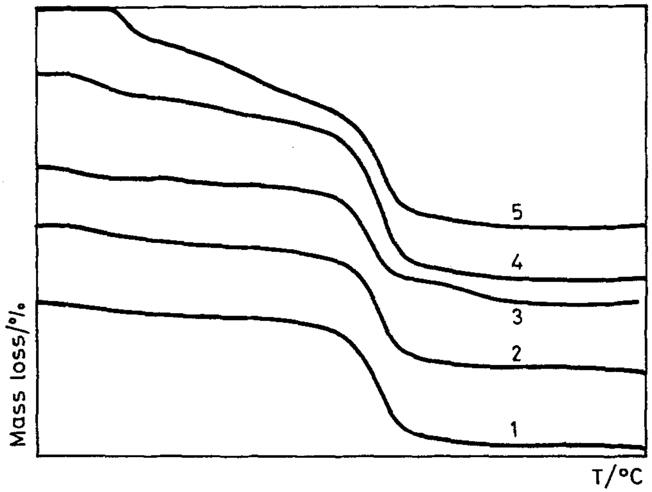

**Fig. 2b** TG curves of clays (<1 μ fraction) (1) M.C., (2) C.C., (3) B.C., (4) N.C., (5) B.P.C.

140°C could be attributed to the presence of illite with kaolinite in N.C. and B.P.C., the amount being comparatively high in the latter.

**Table 1** Thermogravimetric data of clays ( 'as received' and '<1 μ fraction')

| Sample | Weight loss %/ in the temperature range, °C | | | |
|---|---|---|---|---|
| | 25-200$^x$ | 300-400* | 500-700$^+$ | 700-900$^\#$ |
| M.C. (a.r.) | 0.57 | – | 7.68 | – |
| M.C. (<1 μ) | 0.60 | – | 10.84 | – |
| C.C. (a.r.) | 0.83 | – | 6.49 | – |
| C.C. (<1 μ) | 1.32 | – | 10.12 | – |
| B.C. (a.r.) | 1.41 | – | 10.56 | 5.35 |
| B.C. (<1 μ) | 0.82 | – | 12.13 | 2.62 |
| N.C. (a.r.) | 1.08 | 0.49 | 9.81 | – |
| N.C. (<1 μ) | 1.80 | 1.40 | 10.80 | – |
| B.P.C. (a.r.) | 1.52 | 0.39 | 8.00 | – |
| B.P.C. (<1 μ) | 2.21 | 2.21 | 7.76 | – |

$^x$ Loss of adsorbed water of clay

* Loss of structural water of goethite

$^+$ Loss of structural water of clay

$^\#$ Oxidation of graphite carbon

The TG curves of the clays, 'as received' and '<1 μ fraction' are shown in Fig. 2 (a and b) and the data are given in Table 1. In case of M.C. and C.C. (as received), the total weight loss up to 1000°C was found to be 10.61 and 9.17% respectively. In the '<1 μ fraction', the respective values increased to 13.85 and 13.91% because of the removal of appreciable amount of free silica and thereby increasing the clay content which contributed to the loss (1). B.C. in the 'as received' form showed a weight loss of 19.57% at 1000°C which was the highest of all and this was attributed to the presence of graphitic carbon as shown by the weight loss of 5.35% between 700° and 900°C. In the same temperature range, in the '<1 μ fraction', the weight loss was reduced to 2.62% because of the removal of coarser carbon particles and the total weight loss at 1000°C was 17.21%. The weight losses at 1000°C in case of N.C. and B.P.C. (as received) were 13.73 and 12.62% and the respective values increased to 16.50 and 15.93% due to the increase of clay and goethite content after the removal of free silica in the '<1 μ fraction'. These values were more than the theoretical value and the reason being mainly the presence of goethite as well as inclusion of free moisture.

The electron micrographs of the clays are given in Fig. 3. The electron micrograph of M.C. showed well-formed six-sided flakes of well crystallised kaolinite. The picture showed the difference in appearance of single crystals as opposed to oriented aggregates and most of the clay particles were in the ag-

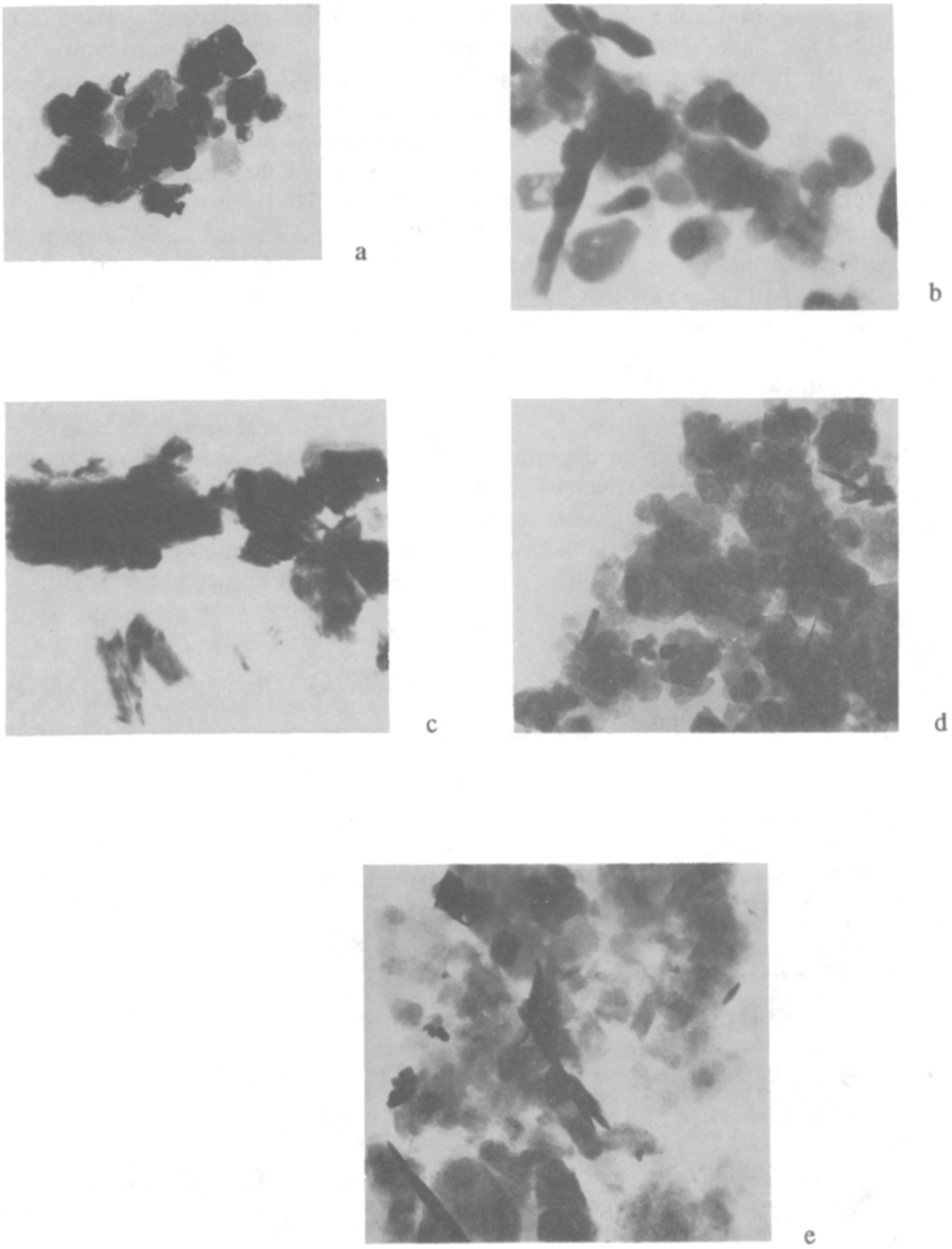

**Fig. 3** Electron micrographs of clays (<1 μ fraction) (1) M.C., (2) C.C., (3) B.C., (4) N.C., (5) B.P.C.

gregated form. Like M.C., the particles in C.C. also were mostly aggregates but kaolinite flakes were not very well-developed. Besides, tubular particle was seen in the figure, attributable to the presence of halloysite. Compared to M.C. and C.C., the electron micrograph of B.C. showed small particles with irregular border. The aggregates were flaky and did not show the perfection of crystal habit shown by china type of kaolinite. In N.C., some of the crystals showed well-formed hexagonal flakes and the overlapping of plates was distinct in this clay. Some short tubular particles were also present in N.C. which could be attributed to illite or halloysite. The electron micrograph of B.P.C. showed short and long tubular particles in addition to the discrete and aggregated particles of kaolinite.

## Conclusions

DTA,TG study is an important tool in the mineralogical study of clay particularly in the case when some non-clay mineral contents are too low to be detected by XRD. The present study revealed that the predominant mineral in all the clays was kaolinite with associated impurities like graphite, goethite, illite and halloysite and complimented the findings by XRD.

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**Zusammenfassung** — Mittels DTA, TG und Elektronenmikroskopie wurden mineralogische Untersuchungen an fünf plastischen Feuertonproben aus Indien durchgeführt. Die Untersuchungen wurden einerseits an den Tonproben durchgeführt, wie man sie erhielt, andererseits an einer '<1 μ-Fraktion'. Die Ergebnisse zeigten, daß alle Proben vorwiegend aus Kaolinit bestanden und intensive endotherme Peaks zwischen 540° und 590°C sowie exotherme Peaks zwischen 920° und 985°C aufwiesen. Ein intensiver exothermer Peak bei 810°C und ein Mas-

severlust von 5.35 % im Bereich von 700° bis 900°C bei dem Ton aus Barachatarma weisen auf die Gegenwart von Graphit in dieser Probe hin. Sowohl Ton aus Neyveli und auch aus Badampahar enthielten Illit und Geothit. Elektronenmikrographen von Ton aus Mohuamillan und Neyveli weisen hexagonale Flocken von geordnetem Kaolinit auf. Außer den Kaolinit-Partikeln konnten in den Tonproben aus Chittorpur, Neyveli und Badampahar auch noch einige tubusartige Partikel beobachtet werden.