Building Materials Studies :

Differential Thermal Analysis of Building Material

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Introduction

Differential Thermal Analysis-DTA-has been increasingly used for the past three decades as a helpful research and control tool. The technique has been extensively applied to the study of clay minerals in which the chemical compounds and crystal structure of several minerals are so similar that neither chemical analysis, nor x-ray diffration study readily differentiate them. The DTA technique has also found application in other branches of mineralogy. Its importance is increasing because of developments and refinement in equipment and because of the potential value of the data, with the growth of crystal chemistry and thermodynamics of the non-metallics.

The method of differential thermal analysis is of great importance in the structural studies of building materials. It is useful as a method of mineral analysis in its own right; but probably finds its most important application as a means of rapid mineralogical reconnaissance. There is a growing tendency to control the characteristics of raw minerals on the basis of clay mineral composition rather than by chemical analytical data.

Thermal Analysis consists in measuring, by a suitable experimental set-up, the temperatures at which thermal changes take place, their intensity and general characteristics. The thermal changes may be caused by dehydration, transition from amorphous to crystalline form, destruction of crystalline lattice, transition from one crystalline modification to another, oxidation or decomposition, etc. The temperature at which the thermal change takes place, its intensity and general nature are characteristic of the particular substance under study and hence DTA provides criteria for its identification.

In 1887, Le Chatelier[1] set up for the first time, a simple apparatus to record thermal reactions taking place in a material. In earlier studies the method consisted in placing the material in a small platinum crucible with a single thermocouple junction embedded at the centre of the sample. The whole mass was kept in a furnace and the temperature raised at a uniform rate. The thermocouple was attached to a sensitive galvanometer which either read directly or recorded photographically. Thermal reactions in the material resulted in a variation of the galvanometer record as compared to that obtained when the furnace contained no sample. In some of the early work[7] the method consisted essentially in taking a time-temperature record of a thermocouple embedded in the specimen and comparing it with the record given by a second thermocouple placed in a reference substance alongside it.

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The credit of inventing the differential thermal technique goes to a metallurgist, Robert Austen[8] who effected improvement by using a differential couple in place of the single couple. Burgess[9] effected improvements in the method of DTA. As applied to the study of clays, the method was found to be extremely valuable.[10] The papers of Orcel and coworkers[11,12] published during the years 1933-35, brought out clearly the importance of the technique for clay minerals.

Description of the Method

The sample to be studied is placed in one of the holes of the specimen holder made of platinum, silica, nickel, stainless steel or inconel. In the second hole of the holder is placed a material, usually α Al$_2$O$_3$, which does not undergo any transformation even up to a temperature of 1000°C. Two sets of thermocouples are placed and connected as in Fig. 1. The leg Pt-Rh of each couple is connected together and the two platinum wires are set free. This constitutes the differential thermocouple. Into the third hole of the specimen holder, containing inert materials, another thermocouple tip is embedded which measures the temperature of the specimen block. The thermocouples

Fig. 1

that are widely used are either Pt-Rh. or chromel-alumel, the latter being preferred as it gives higher e.m.f. Kracek[13] used Au-Pd vs Pt-Rh thermocouple as it is more sensitive at higher temperatures. Johnstone and Mequillan[14] have described W-Mo thermocouples which can be used upto a temperature of about 2000°C.

The block is placed in a furnace which is heated at a uniform rate. The temperature of the furnace is raised uniformly by an auto-transformer or by a motor-driven transformer. Different types of automatic controllers have been described in detail by workers in this field.

The differential couple records zero e.m.f. as long as the substance under investigation does not undergo any change. Whenever a thermal change occurs, there is either absorption or evolution of heat as a result of which the temperature of the substance becomes lower or higher than that of the inert material. A differential e.m.f. is thus set up, the direction of which depends on whether the reaction is endothermic or exothermic. The differential e.m.f. can be measured either by a potentiometer or galvanometer or automatically with an electronic device or photographically.

In the thermograms, usually the differential temperature ($\triangle$T) and the temperature of the furnace (T) are recorded or plotted such that the endothermal peaks are shown downwards and the exothermal peaks upwards with respect to the base line $\triangle$T = O.

Types of Thermograms

The various types of thermograms usually encountered can be discussed with the aid of *Fig* 2. In the figure the furnace temperature
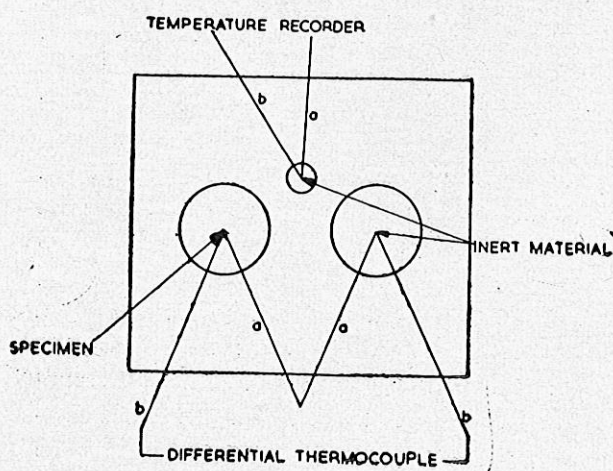
(T) is plotted against ($\triangle$T), the difference in temperature between the two substances. Where two exactly similar, thermally inert materials A and B are placed symmetrically in a furnace and temperature raised slowly, the temperature of A after a particular interval of time is the same as that of B (*ref. Curve 1, Fig. 2*). But if B is replaced by another substance C which has different thermal characteristics but is otherwise similar to A, a difference of temperature will arise between A and C when the temperature of the furnace is raised uniformly. Generally, this difference is small and will attain an almost steady value if the rate of heating is uniform as can be seen from *Curve 2*. If the substance is replaced by another substance D which undergoes either a physical or a chemical transformation at a particular temperature, then at the temperature of transformation of substance D, there is either a sudden absorption or evolution of heat depending on whether the transformation is endothermic or exothermic and this will temporarily retard or accelerate the rate at which the temperature of substance D increases. A difference in the temperature between A and D results during the thermal transformation. Further uniform increase in the temperature results in a small constant difference in temperature between the two samples (*Curve 3,*) provided no other
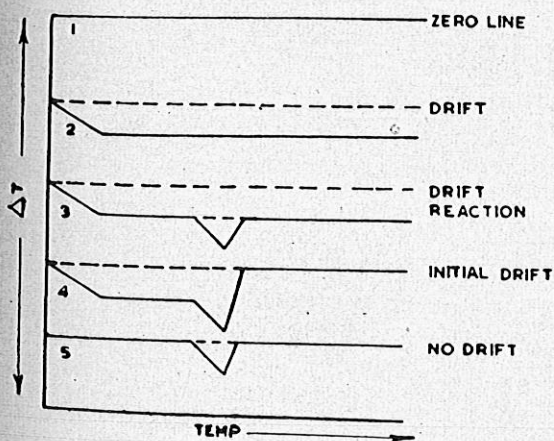
transformation takes place. No difference in temperature will occur if the thermal characteristics of A and the transformed substance are same (*Curve 4*). If the thermal characteristics of the inert material, and reactive material before and after transformation are almost same, a *curve of the type 5* may result, with negligible difference of temperature.

Theoretical Considerations

Speil and co-workers[15] derived an equation showing that the area enclosed under a thermal peak is proportional to the heat of formation. It can be briefly summarized with the aid of Fig. 3 in which the thermograph of the $CaCo_3$ decomposition is shown. The curve shows a reaction beginning at 'a' and continuing towards 'c'.

$$\text{Area abc} \propto \int_a^c T \, dT = \frac{M (\triangle H)}{gk} \quad ....(i)$$

where, M = mass of the reaction specimen

$\triangle$H = specific heat of the reaction

g = geometric shape constant and and

k = thermal conductivity of the reacting specimen.

Equation (i) neglects the temperature gradient as well as differential factors which are insignificant.

Transposing terms,

$$\text{Area abc} \propto gk \int_a^c T \, dT = M \triangle H = Q ...(ii)$$

where, Q = heat of reaction.

Thermographic base line in Fig. 3 is not linear, as is found to be the case with the decomposition of calcium carbonate. This is accompanied by a sharp change in thermal conductivity and specific heat capacity of the decomposed product of $CaCo_3$.

ZERO LINE

DRIFT

DRIFT REACTION

INITIAL DRIFT

NO DRIFT

TEMP

Fig. 2

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Wittels[16] has derived a precise relationship between the thermographic response and two functions, the heating rate and the mass of the specimen.
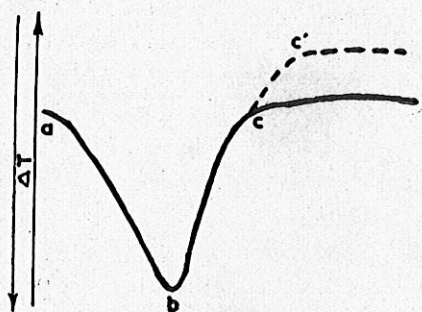
minerals. Figs 4 and 5 show the thermal behaviours of well crystallised common clay minerals and a few accessory minerals commonly found in clays.
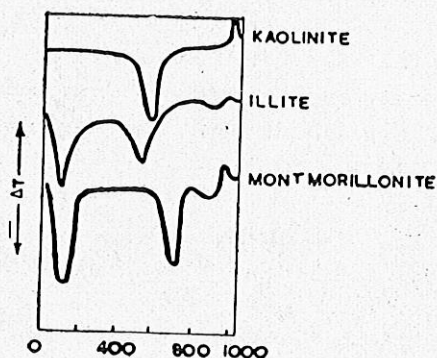

Fig. 3

Fig. 4

DTA OF BUILDING MATERIALS

Clays

In the field of soil mechanics and the technology of fired-clay products thermal analysis provides information about the mineralogical composition of mixtures of clays which classical methods of analysis, fail to reveal.

Clays are of special importance to the building industry because of their use in the manufacture of bricks, tiles and cement. Clays always contain accessory minerals such as quartz, calcite, feldspars, micas and iron exides, in varying proportions which influence their properties.

In principle, the method of using DTA for elucidating the mineralogical composition of a clay is simple. A thermogram of the clay is obtained and its mineral composition is deduced qualitatively or sometimes semi-quantitatively by comparison with themograms of pure clay minerals and accessory

The endothermic reaction of kaolinite at 550-600°C accompanies dehydration of the mineral and the exothermic reaction is associated with the formation of $\alpha Al203$[17]. Illites show endothermic peaks at 100-200°C, 500-650°C and about 900°C and an exothermic peak immediately following the third endothermic peak. The first endothermic peak is due to the loss of interlayer water, and the endothermic peaks at 500-650°C and 900°C are due to the accompaniment of loss of water from the lattice and the final destruction of the illiet structure respectively. The exothermic peak following the third endothermic peak is probably associated with the formation of spinel. The intensity of peaks in the case of illites is much lower than those of kaolinite They differ from kaolinities in showing an addtional endothermic peak at 100-200°C and 900°C. The montmorillonites show an initial endothermic effect at 100-250°C apparently representing the loss of water held between the basal planes of the lattice structure (swelling water). The second endothermic peak between 600 and 700°C corresponds to the loss of lattice water. The

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third endothermic peak at about 900°C corresponds to the final breakdown of the montmorillonite lattice. The exothermic peak following the endothermic peak is due to the formation of spinel. Like illites, montmorillonites exhibit three endothermic and one exothermic but they differ from illites by showing a more intense second endothermic peak taking place at about 100°C higher and by a more intense final endothermic and exothermic reaction.

DTA is useful in investigating and identify mixtures of two or more clays in a sample and also of the accessory minerals mixed with clay. The presence of organic materials and minerals like clarins, vitrain, marcasite, pyrite, etc. which are often associated with clays are indicated in thermograms as exothermic reactions due to oxidation.
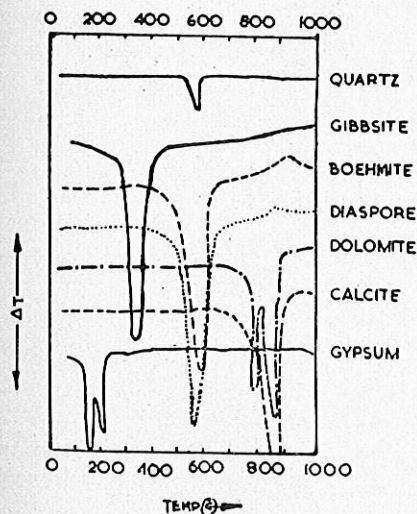

Fig. 5

From a DTA of prepared mixtures of various clays and accessory mineral it is possible to estimate quantitatively the amount of the various clays and accessory minerals in a sample.

Some of the general conclusions[18] that can be drawn from the thermograms of various clays are summarized below :

(a) An endothermic reaction below about 200°C usually indicates the presence of montmorillonite or illite. A clay material containing these components is apt to have high plasticity and high shrinkage and will probably be non-refractory and will burn red. In general the larger this reaction, the higher the plasticity and shrinkage.

(b) Endothermic reactions between about 300 and 500°C usually indicate a hydroxide of alumina or ferric iron oxide. If the component is a hydroxide of alumina the clay will be refractory and will have low shrinkage.

(c) A broad exothermic reaction between about 200 and 600°C is the result of organic material. Clays yielding such thermal reactions will frequently be very plastic and will require careful burning to insure complete oxidation of the carbon.

(d) A sharp exothermic reaction between 400 and 500°C indicates pyrite or marcasite.

(e) A sharp intense endothermic raction at about 600°C and a sharp exothermic reaction at about 975°C indicate the presence of kaolinite. A clay with this component is apt to be refractory and light firing and will have low plasticity and relatively long vitrification range.

(f) A clay with a slight endothermic reaction at about 500 or 700°C followed by another endothermic reaction at about 900C° and then a final slight exothermic reaction is composed of illite or montmorillonite. A clay containing either of the two is not refractory or light firing and is apt to have a

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short vitrification range. If the component is montorillonite it will also have high plasticity and shrinkage.

(g) A small endothermic break at 575°C indicates the presence of considerable free silica as quartz which will reduce the plasticity and shrinkage of the clay.

(h) A sharp intense endothermic reaction at about 850°C indicates the presence of calcium carbonate and therefore a clay requiring careful preparation and firing technique.

It must however, be emphasized that very careful study and experience are required to interpret the thermal curves. In studying certain clays, some inflections cannot be satisfactorily explained unless additional analytical data are obtained with x-ray and chemical analysis.

The predicting of firing behaviour of clay minerals was made by Everhart and Beck[19]. The presence of common impurities such as carbon, pyrite and lime was indicated by reactions that either absorbed or evolved heat. Such impurities determined the type of treatment necessary to obtain a fired product of desirable quality.

Hills[20] concluded from DTA studies of rehydrated and refired keolinites that the gain in strength of such keolinites depends upon the crystallinity, being small for poorly crystalline minerals.

DTA has been applied to examine fire-clay products for evidence of underfiring.

The underfiring is a manufacturing faul which results in subnormal strength, greater susceptibility to frost attack and often, a higher soluble salt content in the fired product ; in extreme cases it may leave the product susceptible to attack by water alone. An example of the application of DTA in such studies is provided by Honeyborne[21]. In Fig. 6 thermograms of brick-making clay from a certain locality is given. A refers to the clay of the locality, B,C and D showing thermograms of the same clay after firing to 600,800 and 1000°C respectively. The increase in firing temperature brings about a progressive modification of the thermograms until at 1000°C, only the peak caused by the reversible $\alpha \rightleftharpoons \beta$ quartz inversion remains. Hence the thermal curves of samples of bricks made from this type of clay can be used to provide information about the probable temperature at which the bricks were fired. An example of this application is given by *curve* E which refers to a sample of facing brick in which extensive decay had occurred, in some places to a depth of over an inch. Comparison of thermograms suggests that the bricks in question were made from locality from which A was taken, and further, that they were fired to a temperature between 600 and 800°C. It is said that the architect wished, for aesthetic reasons, to use pink bricks and the unusually low temperature might have been used deliberately to produce the desired effect. Large amounts of calcium sulphate were found in the brick in question, and the presence of this mineral accounts for the large endothermic peak at 160°C in the curve E. While this substance may have been present in the original clay, it could also have been formed by reaction between sulphur gases in the atmosphere and calcium carbonate in the brick. Its crystallisation in pores of the bricks is likely to have contributed much to the disintegration of poorly-bonded brick particles.

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Roofing slate :

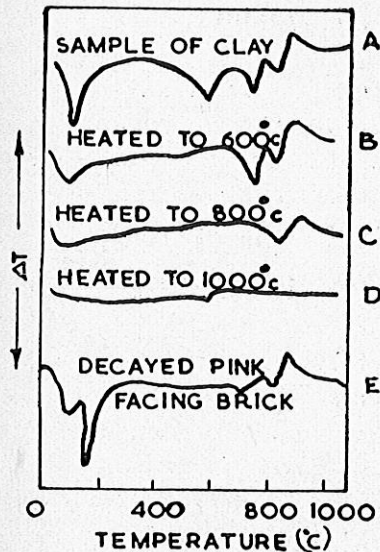Slate, although related to clay has not been studied by the DTA method to the

Fig. 6

same extent, but DTA is beginning to prove useful as an aid to the identification of slate of unknown origin.

Fig. 7 shows thermograms obtained with samples of roofing slate of three different qualities[21]. *Curve A* represents a slate of excellent durability. The peaks at 610°C and 850°C probably represent some type of chlorite ; quartz is represented by the small inflection at 575°C. This peak is due to $\alpha \rightleftharpoons \beta$ quartz modification and is clearer in the calcined material (B). *Curve C* is obtained with a slate that was found in practice to delaminate slowly on roofs even in districts where atmospheric pollution was slight. This poor durability is believed to be caused by a slow oxidation of pyrite in the slate and by the subsequent reaction between the oxidation product and calcite to form calcium sulphate. The presence of pyrite and calcite is indicated by the peaks

at 450°C and 770°C respectively. The fourth *curve D* of slate of very poor weathering quality, is dominated by a very large calcite peak. The exothermic peaks at 930°C and 420°C suggest the presence of a chlorite and a very small amount of pyrite respectively.
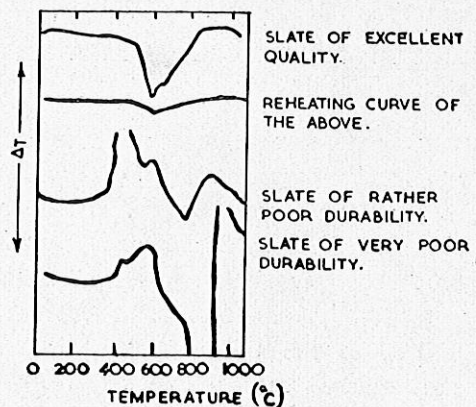

Fig. 7

Cements :

Work on hydrated and unhydrated cements has been done by means of DTA. Kalousek[22] has published valuable data on the reactions of cement hydration at elevated temperatures. The strengths of cement pastes have been discussed on the light of the results obtained by DTA.

DTA has proved valuable in the study of phase-equlibria as related to clinker composition. For many years it was thought that dicalcium silicate, one of the components of Portland cement clinker, existed in three forms α, β, γ the existence of the fourth form α has been demonstrated by DTA[23]. Thermograms have provided accurate inversion temperatures of these forms and have played an important part in establishing how they are related to one another.

Attempts have also been made to correlate DTA results of alumina cements with their mechanical properties[24].

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Building limes and plasters :

DTA has been used to study the thermal dissociation of dolomite and the effect on the reaction of the addition of small a mount of fluxes to the dolomite. Recently the technique has been made use of in the study of the hydration of dolomitic limes and in the estimation of lime composition[25].

A study of the reaction taking place in the ageing of gypsum-gauged dolomitic lime plasters has been made by Murray and coworkers[26]. Wells and his collaborators[27] used DTA to investigate plaster failures characterised by the formation of blisters and bulges in the finished coat after the lapse of several years. The failures were shown to be caused by the delayed hydration of incompletely hydrated dolomitic limes used in the plaster mix.

Hydrated dolomitic limes with mixtures of magnesite, calcite, strontium oxide, etc. have been studied by thermal analysis method to find out the reactivity of calcium oxide in lime used in chemical industry.

Other Uses :

Important data can be obtained speedily using DTA and this makes it useful in unexpected fields. Suppose a small quantity of a powered sample of a natural building stone is submitted for examination and is found to be contaminated with magnesium sulphate. The sample is obviously lime stone but it cannot be determined conclusively by microscopical examination whether it is a lime stone (dolomitic) or calcium lime stone contaminated with magnesium sulphate from an external source. By a thermogram which can be obtained in a much shorter time than chemical analysis (which might have established the point), it is easy to ascertain whether the limestone is dolomitic or not.

Acknowledgement

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