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APPLICATION OF DSC–DTA TECHNIQUE FOR ESTIMATING VARIOUS CONSTITUENTS IN WHITE COAT PLASTERS

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ABSTRACT

The DSC–DTA combination technique has been used to estimate $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$, $CaCO_3$ and MgO, comprising three white coat plasters. Unhydrated magnesium oxide could be estimated by converting it to $Mg(OH)_2$ by autoclaving. An equation is derived from which unhydrated MgO can be determined by substituting the estimated values for $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$ and $CaCO_3$. Estimated values of CaO, MgO and $CaSO_4 \cdot 2H_2O$ obtained by the DSC–DTA technique correspond closely to those determined by chemical analysis.

INTRODUCTION

White coat plasters made from a mixture of dolomitic lime and plaster of paris may exhibit failure in service at periods ranging from 5 to 15 years. In such plasters a slight "bulging" or "popping" occurs as a prelude to final separation of the plaster from the base. In almost all cases the failure of the white coat plaster may be ascribed to the forces caused by the delayed hydration of magnesium oxide derived from the dolomitic lime[1–3].

One of the important methods of assessing the quality of a plaster mix is to identify and estimate its constituents before it is applied to the wall. In a failed plaster an estimation of the constituents, especially MgO and $Mg(OH)_2$, would also permit examination of the causes leading to the failure. The analysis of the constituents of an apparently good plaster (in service) may indicate its potential to failure under given conditions of exposure.

The presence of several components in a plaster such as free water, $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$, MgO, $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3 makes identification and estimation by chemical analysis time consuming. The techniques of DTA and DSC have been applied with some success to estimate semi-quantitatively the carbonates, hydroxides or sulfate hydrates when present in simple mixtures. In an earlier investigation[3] it was found that the constituents in the white coat plasters viz., $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$ and $CaCO_3$ yield distinct thermal inflections.

Hence, it was of interest to investigate the applicability of the DSC–DTA techniques to estimate the constituents of white coat plaster. Because the unhydrated MgO does not exhibit any inflection in the thermograms, an attempt was made to estimate it indirectly by converting it to $Mg(OH)_2$ by autoclaving.

EXPERIMENTAL

Materials

Three white coat plaster samples were collected from three buildings in Toronto. They are designated as plasters A, B and C. Plasters A and B had failed, plaster C appeared to be very sound. The samples were carefully separated from the base, dried and powdered to pass through 200-mesh sieve.

Analytical reagent quality chemicals $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$ and $CaCO_3$ were used for calibration purposes. The purity of these compounds was assessed and corrections were made in the calibration curves where necessary.

Techniques

A differential scanning calorimetric (DSC) cell supplied as a module to DuPont 990 thermal analysis system was used to obtain thermograms from room temperature to 550°C. The rate of heating was 20°C min^{-1} and ΔT = 5m cal sec^{-1} $inch^{-1}$. All the thermograms were obtained in air with a constant quantity of the sample.

Differential thermal analysis (DTA) curves were obtained with a DuPont 990 unit. Alpha-Al_2O_3 was used as a reference material. A constant amount of sample (30 mg) was heated at 20°C min^{-1} at a ΔT sensitivity of 1°C $inch^{-1}$. DTA thermograms were obtained in the range 550 to 850°C.

Magnesium and calcium present in plasters were quantitatively determined by Perkin–Elmer 403 atomic absorption spectrophotometer. Gypsum was quantitatively determined by the standard chemical method by precipitation as $BaSO_4$. The endothermal peak areas were determined with a planimeter.

Discs, $\frac{1}{2}$ in. in diameter were made with powdered plasters at a load of 3200 lb. and autoclaved for 1 hr at a steam pressure of 295 lb. sq. in^{-1}. The standard autoclave was used. Details of this procedure are described in another paper[1].

RESULTS AND DISCUSSION

Thermal curves were obtained by applying the DSC technique up to 550°C and the DTA technique, from 550 to 850°C. The DSC technique was more sensitive, gave a better base line and enabled a more accurate determination of the areas under the thermal inflections. The design features of the DSC, however, did not permit its utilisation for higher temperature studies. Hence the DTA technique was used to estimate $CaCO_3$ which showed an endothermal effect at about 800°C.

Each of the following chemicals viz, $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$ and $CaCO_3$ was mixed with α-Al_2O_3 in different proportions and subjected to DSC–DTA

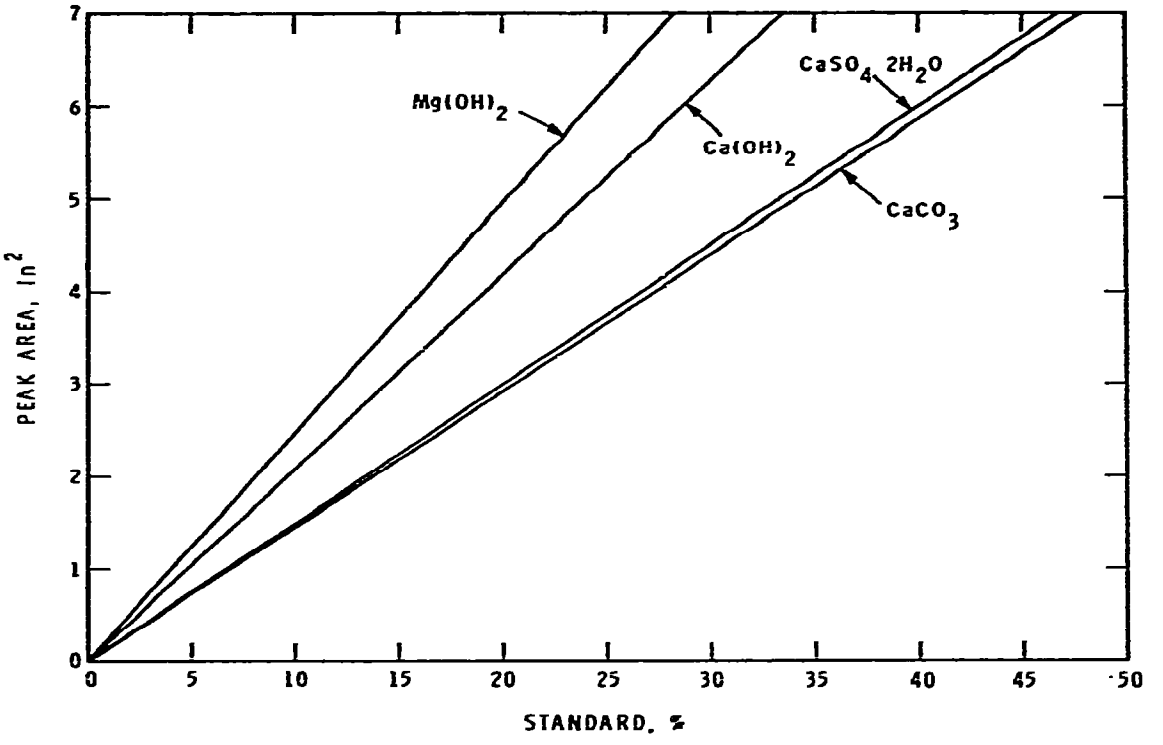

Fig. 1. Calibration curves obtained by DSC–DTA technique.

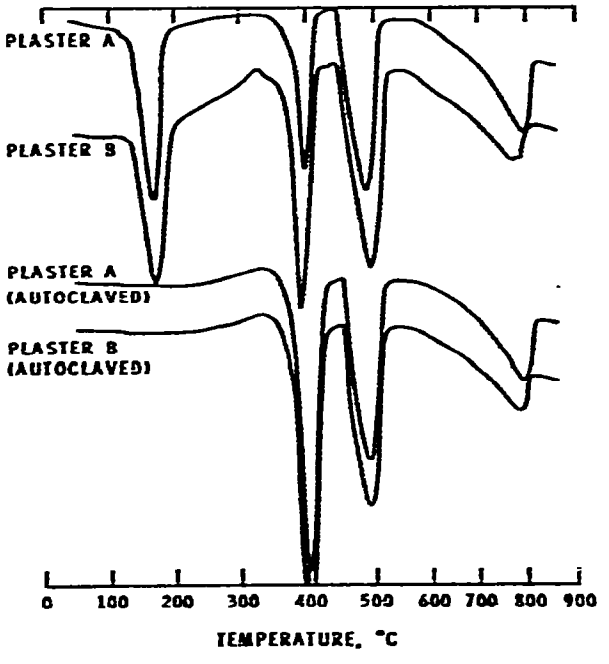

Fig. 2. DSC–DTA curves for plasters.

TABLE I

ANALYSIS OF CONSTITUENTS IN WHITE COAT PLASTER (A) BY DSC–DTA TECHNIQUE

Description	$CaSO_4 \cdot 2H_2O$	$CaSO_4$	$Mg(OH)_2$	MgO	$Ca(OH)_2$	CaO	$CaCO_3$	CaO	*Others*[a]
Unautoclaved									
(1) As received (%)	26.5	—	12.0	—	24.3	—	21.5	—	15.7
(2) Components expressed in terms of oxide and sulfate	—	21.0	—	8.3	—	18.4	—	12.1	15.7
(3) The above expressed as %	—	27.8	—	11.0	—	24.4	—	16.0	20.8
Autoclaved									
(4) Analysis (%)	0.0	—	28.5	—	25.0	—	18.2	—	28.3
(5) Components expressed in terms of oxide and sulfate	0.0	—	—	19.7	—	18.9	—	10.2	28.3
(6) The above expressed as %	0.0	—	—	25.6	—	24.5	—	13.2	36.7

[a] In unautoclaved plaster it represents unhydrated MgO, with some SiO_2, Al_2O_3 and Fe_2O_3. In autoclaved plaster it represents $CaSO_4$, SiO_2, Al_2O_3 and Fe_2O_3.

TABLE 2

ANALYSIS OF CONSTITUENTS IN WHITE COAT PLASTER (B) BY DSC-DTA TECHNIQUE

Description	$CaSO_4 \cdot 2H_2O$	$CaSO_4$	$Mg(OH)_2$	MgO	$Ca(OH)_2$	CaO	$CaCO_3$	CaO	*Others*
Unautoclaved									
(1) As received (%)	27.5	—	22.2	—	30.3	—	12.0	—	8.0
(2) Components expressed in terms of oxide and sulfate	—	21.7	—	15.3	—	22.9	—	6.7	8.0
(3) The above expressed as %	—	29.1	—	20.5	—	30.7	—	9.0	10.7
Autoclaved									
(4) Analysis (%)	0.0	—	28.3	—	32.5	—	11.5	—	27.7
(5) Components expressed in terms of oxide and sulfate	0.0	—	—	19.6	—	24.6	—	6.4	27.7
(6) The above expressed as %	—	—	—	25.0	—	31.4	—	8.2	35.4

examination. A calibration curve was obtained by plotting the percentage of the standard chemical against the corresponding endothermal area. A linear relationship was obtained for the plot of percentage of the chemical against the corresponding thermal peak area (Fig. 1).

The thermal curves obtained for plaster A and plaster B are shown in Fig. 2. Each sample exhibits four distinct endothermal peaks. The first, occurring at about 180°C, represents the dehydration of $CaSO_4 \cdot 2H_2O$ to $CaSO_4$. This is followed by another at about 390 to 400°C caused by the dehydration of $Mg(OH)_2$. A further peak at about 480 to 490°C is due to the dehydration of $Ca(OH)_2$ and the broad endotherm with a peak at 770 to 790°C is ascribed to the decomposition of $CaCO_3$.

By determining the endothermal area corresponding to each of the components of plaster and using the calibration curve, the amount of each of the constituents present in the plaster samples could be ascertained. In Tables 1 and 2 the first row refers to the amount of $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$ and $CaCO_3$ estimated by thermograms. The difference between 100 and the sum of the above is referred to as "others" and is composed of MgO, SiO_2, Al_2O_3 and Fe_2O_3. This corresponds to 15.7% in plaster A and 8.0% in plaster B. The first row indicates that more $Ca(OH)_2$ has carbonated in plaster A than in plaster B. Both plasters contain essentially the same amount of gypsum. There is more hydrated MgO in plaster B than in plaster A but it does not indicate how much of it is derived from the unhydrated MgO originally present.

Magnesium oxide present in the plaster samples cannot be estimated directly by the thermal method because MgO does not exhibit any thermal inflection in the temperature range studied. It can, however, be estimated indirectly, by autoclaving the plaster samples. By doing this all MgO in plasters A or B is converted to $Mg(OH)_2$. The endothermal peak area of the autoclaved material occurring at about 400°C accounts for all Mg present as $Mg(OH)_2$ in these samples (Fig. 2). In the autoclaved samples endothermal areas for $Mg(OH)_2$ are more intense than the corresponding areas for unautoclaved plasters. Autoclave treatment dehydrates $CaSO_4 \cdot 2H_2O$ to $CaSO_4$, as is evident by the absence of the endothermal peak corresponding to $CaSO_4 \cdot 2H_2O$ (Fig. 2). Consequently in row 4 (Tables 1 and 2) the last column under "others" represents $CaSO_4$, SiO_2, Al_2O_3 and Fe_2O_3.

The estimation of the amount of unhydrated MgO in the plaster samples is calculated as follows. Using the analysis of the starting sample (row 1, Table 1), the constituents are expressed in terms of the oxides, sulfate and "others" (row 3, Table 1). A similar calculation for the autoclaved plaster (row 6, Table 1) corresponds to 25.6% MgO, 37.7% CaO and 36.7% others (includes $CaSO_4$, Fe_2O_3, Al_2O_3 and SiO_2). The small amounts of Fe_2O_3, Al_2O_3 and SiO_2 and some carbonation of $Ca(OH)_2$ do not significantly influence the calculations. The amounts of different constituents in the autoclave material and those in the original sample (reported in rows 3 and 6) should be essentially the same. In other words, in the unautoclaved plaster A, total Mg expressed as MgO should be equal to 25.6%. Out of this 11% MgO is derived from $Mg(OH)_2$. The remaining amount of 14.6% (25.6 to 11.0%)

should exist as unhydrated MgO designated under "others". By computation, the amount of unhydrated MgO expressed in terms of the original plaster A is calculated to be 11.0%. Similar calculations for plaster B indicates that it contains 3.4% unhydrated MgO.

A general equation can be derived from which the amount of unhydrated MgO in a plaster sample may be calculated as follows.

In unautoclaved plaster (expressed in terms of oxides and sulfate) the MgO content corresponding to $Mg(OH)_2$ is

$$\frac{0.69W_{MH} \times 100}{100 - 0.21W_{C\bar{S}H_2} - 0.31W_{MH} - 0.24W_{CH} - 0.44_{C\bar{C}}} \quad (1)$$

W represents percentage weight of a component in the original sample. The subscripts represent the component estimated. The standard cement chemistry nomenclature is used. Thus $MH = Mg(OH)_2$; $C\bar{S}H_2 = CaSO_4 \cdot 2H_2O$; $CH = Ca(OH)_2$; $C\bar{C} = CaCO_3$.

In the autoclaved plaster (in terms of the oxides) the total Mg expressed as MgO is as follows

$$100 - \frac{0.69W'_{MH} \times 100}{0.31W'_{MH} - 0.24W'_{CH} - 0.44W'_{C\bar{C}}} \quad (2)$$

W' represents the percentage weight of a component in the autoclaved sample. The difference between eqns. (2) and (1) corresponds to the percentage of MgO remaining in the unhydrated form in the unautoclaved sample (expressed in terms of oxides and sulfate). By simple computation the amount of unhydrated MgO present in the plaster may be estimated by the following equation.

$$0.69\left[\frac{W'_{MH}(100 - 0.31W_{MH} - 0.21W_{C\bar{S}H_2} - 0.24W_{CH} - 0.44W_{C\bar{C}})}{(100 - 0.31W'_{MH} - 0.24W'_{CH} - 0.44W'_{C\bar{C}})} - W_{MH}\right]$$

TABLE 3

COMPARISON OF THE ESTIMATION OF COMPONENTS IN PLASTERS BY THERMAL AND CHEMICAL ANALYSIS METHODS

Sample	*Technique*	*$CaSO_4 \cdot 2H_2O$(%)*	*CaO(%)*	*$Mg(OH)_2$(%)*
Plaster A (unautoclaved)	Thermal	26.5	40.4	—
	Chemical	26.7	39.3	—
Plaster B (unautoclaved)	Thermal	27.5	39.7	—
	Chemical	26.5	40.7	—
Plaster A (autoclaved)	Thermal	—	—	28.5
	Chemical	—	—	27.5
Plaster B (autoclaved)	Thermal	—	—	28.3
	Chemical	—	—	27.5

TABLE 4

ESTIMATION OF THE COMPONENTS OF PLASTER BY DSC–DTA TECHNIQUE

Material	$CaSO_4 \cdot 2H_2O$	$Mg(OH)_2$	$Ca(OH)_2$	$CaCO_3$	*Unhydrated MgO*	SiO_2, Al_2O_3, Fe_2O_3	*Autoclave expansion (%)*
Plaster A (moderate failure)	26.5	12.0	24.3	21.5	11.0	4.7	13.1
Plaster B (extensive failure)	27.5	22.2	30.3	12.0	3.4	4.6	5.2
Plaster C (sound)	23.5	5.3	5.1	47.0	11.2	7.9	19.8

This equation requires estimation of $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$ and $CaCO_3$ in the unautoclaved sample and $Mg(OH)_2$, $Ca(OH)_2$ and $CaCO_3$ in the autoclaved sample. All these may be obtained by the proposed DSC–DTA technique.

A comparison of the estimation of the components by chemical analysis with that obtained by thermal techniques shows a good correlation (Table 3). In Table 4 the DSC–DTA analysis of the components of the three plasters is given along with the values for autoclave expansion. As would be expected plasters A and C containing larger amounts of MgO show larger expansions than plaster B. The relative amount of failure is related to the relative amounts of original MgO hydrated. Consequently, plaster C, which is apparently sound, contains a large amount of unhydrated MgO and hence will have a potential for expansion if exposed to humid conditions. The small amount of $Mg(OH)_2$, viz. 5.3, even if it is derived from MgO does not cause failure[3]. The large carbonation in plaster C, as evident from the $CaCO_3$ content, indicates that it might have acted as an inhibitor for the hydration of MgO particles.

The analysis can also be utilized to test if two plasters used in two different buildings were of the same composition when first applied. For example, plasters A and B (Table 3) have substantially the same composition indicating that they were probably obtained from the same supplier.

CONCLUSIONS

An estimation of the components in white coat plasters viz., $CaSO_4 \cdot 2H_2O$, $Mg(OH)_2$, $Ca(OH)_2$, $CaCO_3$ and MgO may be accomplished by applying DSC–DTA techniques. An equation is given that can be used to calculate directly the unhydrated MgO by estimating other components in the original, as well as in the autoclaved plaster. The results may be used to determine if two plasters used in two or more buildings are obtained from the same source. The potential expansive nature of the plaster may also be predicted. The analysis permits examination of the effect of environment on the reactions in plaster. The DSC–DTA technique, less tedious than chemical techniques, may be applicable as a routine quality control method in the manufacture of white coat plasters and related materials. The DSC–DTA combination for the estimation of constituents in plaster is not always necessary. The DTA method alone may be adequate for most routine analysis of plasters.

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