

The use of thermoanalytical techniques in the characterization of ancient mortars¹

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Abstract

Using different techniques (TG/DTA, XRD and chemical analysis), a comparative investigation on calcitic and dolomitic mortars, from two different Italian buildings of the 11th and 14th centuries, has been performed. By correlating the thermal effects and the steps in the TG curves, it has been possible to reach a semi-quantitative evaluation of the binders in both types of mortars, the results being in good agreement with the chemical data, and to explain the influence of the other components on the thermal behaviour of such complex systems.

INTRODUCTION

Many authors have studied the composition and ageing of ancient mortars by employing different techniques. The reported results are not always in agreement with each other, and several factors may be responsible for the differences observed [1,2].

We report here some data obtained from mortars derived from two different buildings, the cloister of an 11th century church near Reggio Emilia, Italy (RE samples) and a 14th century tower, situated near the Tirrenian sea (TD samples).

The binder in the RE samples was calcitic in origin, whereas for the TD samples, the binder was dolomitic, as shown by the presence of magnesium compounds.

The aim of this investigation was to show how simultaneous TG and DTA curves, corresponding to tests performed in different gaseous

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atmospheres, give information on the sample compositions, on their degree of crystallinity and on the influence of the other components on the events revealed in the thermal curves of the pure constituent compounds.

The results and conclusions are supported by chemical analyses and X-ray diffraction powder spectra.

EXPERIMENTAL

The thermal curves were obtained with a simultaneous TG–DTA Stanton 801 STA thermoanalyser, using Pt crucibles, at $8^{\circ}\text{C min}^{-1}$ heating rate, under 20 ml min^{-1} gas flow of air, nitrogen and carbon dioxide.

Analyses of Ca and Mg were performed by complexometric titration with EDTA. For the dolomitic mortars (the TD samples), the dissolution was obtained by heating the mortars at 900°C with mixtures of Na and K carbonates and treating with 2 M HCl. For the calcitic mortars (RE samples), the Ca dissolution was obtained by refluxing the samples in 6 M HCl; the results were comparable with those obtained by dissolving in carbonate melts.

X-ray diffraction patterns were obtained with a Phillips diffractometer.

RESULTS

Table 1 reports the Ca and Mg contents of the RE and TD samples determined by EDTA titration. In all the RE samples, XRD analysis indicated the presence of calcite (main component), quartz, gypsum, and feldspar in minor amounts. In two of these samples (RE C2 and C5), weddellite (calcium oxalate dihydrate) was also detected together with traces of muscovite and amphibole.

In the TD samples, we observed the presence of calcite (main component), hydromagnesite, quartz and halite (NaCl). The last phase obviously derives from marine aerosols, given the location of the tower

TABLE 1

Ca and Mg contents of the mortar samples

Sample	% Ca	% Mg	Sample	% Ca	% Mg
RE C2	21.2	–	TDN	19.1	8.1
RE C5	22.1	–	TDO	21.6	14.4
RE C7	23.1	–	TDE	23.2	10.0
RE C8	18.9	–	TDS	19.8	9.4

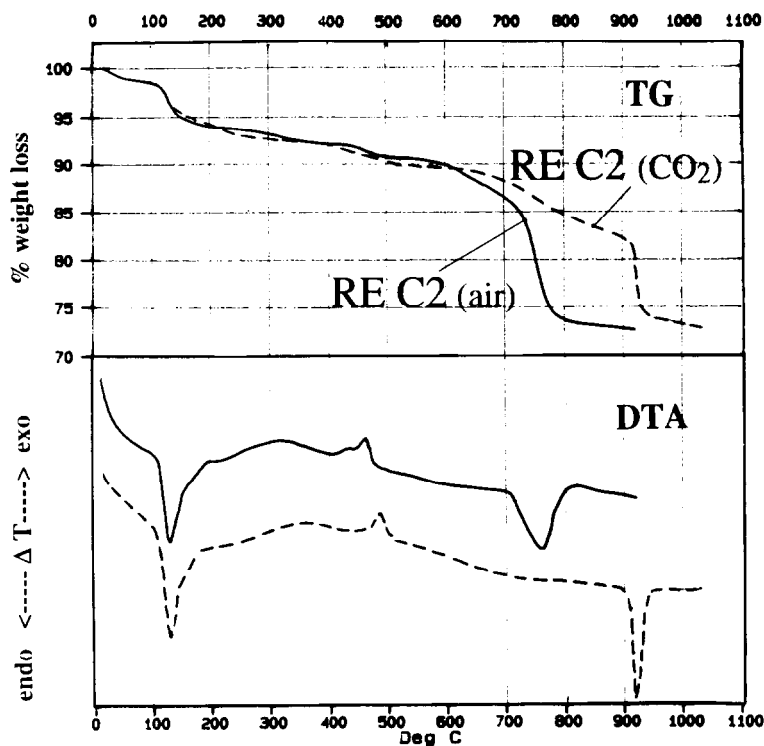


Fig. 1. Simultaneous TG/DTA curves of sample RE C2 in air and in carbon dioxide.

near the sea. Moreover, the amount of NaCl depends on the orientation of the wall of the building with respect to the sea.

Simultaneous DTA/TG curves of two typical RE samples, performed in air and in carbon dioxide atmosphere, are reported in Figs. 1 and 2. For both materials, the weight loss observed between room temperature and 200°C is ascribed to the elimination of the crystallization water of gypsum and calcium oxalate, the latter being derived by bacterial metabolism of the organic materials sometimes present in the mortars. The weight loss between 380 and 500°C corresponds to CO from the decomposition of Ca oxalate. Finally, the weight loss between 550 and 800°C is due to CO₂ derived from the decomposition of calcium carbonate.

Under CO₂ atmosphere, a shift towards higher temperatures can be observed for the weight losses involving CO₂, i.e. the oxalate decomposition (400–500°C) and the carbonate decomposition. The latter process occurs in two steps, between 550 and 700°C and between 700 and 850°C.

Figures 3 and 4 report the simultaneous TG/DTA curves, in air and CO₂ flows, of two TD samples derived from the east wall (TDE) and from the south wall (TDS), respectively. The weight change below 200°C is ascribed to the loss of crystallization water from hydromagnesite. Between 250 and

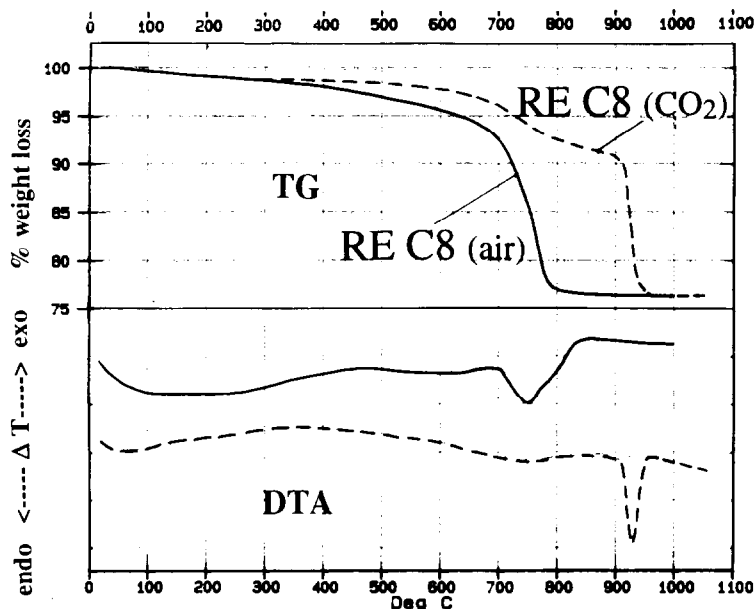


Fig. 2. Simultaneous TG/DTA curves of sample RE C8 in air and in carbon dioxide.

500°C, this compound decomposes into magnesium carbonate, with loss of constitutional water and part of its CO₂. Above 500°C the decomposition of MgCO₃ takes place, going to completion at about 550°C. Then decomposition of calcite occurs, which is complete at 800–820°C. With the help of simulating mixtures, we have been able to prove that the further weight loss in the range 820–950°C is due to NaCl loss, as shown from the example reported in Fig. 5.

These weight loss attributions are supported by the clear shifts towards higher temperatures of the Mg and Ca carbonate decomposition reactions in CO₂.

The presence of hydromagnesite (HY) is clear in the X-ray diffraction patterns of TD samples. However, the DTA curves show a thermal behaviour different from that of pure HY (Fig. 6). In fact, pure HY shows a sharp exothermic peak at 500°C due to the crystallization of a mixed Mg oxocarbonate phase [3]. The DTA curves of the TD samples do not show this exothermic peak, but show, instead, two endothermic peaks between 200 and 450°C, which are characteristic of the decomposition of the HY fraction, and correspond to evolution of constitutional water and part of the CO₂ (as proved by the shift to higher *T* of the last weight loss when the thermal analysis is performed in CO₂ atmosphere).

The absence of the exothermic peak at 500°C in the TD samples can be explained by considering the thermal analysis of mixtures of HY and calcite in different ratios (Fig. 6). As found by Yanat'eva et al. [4], the presence of

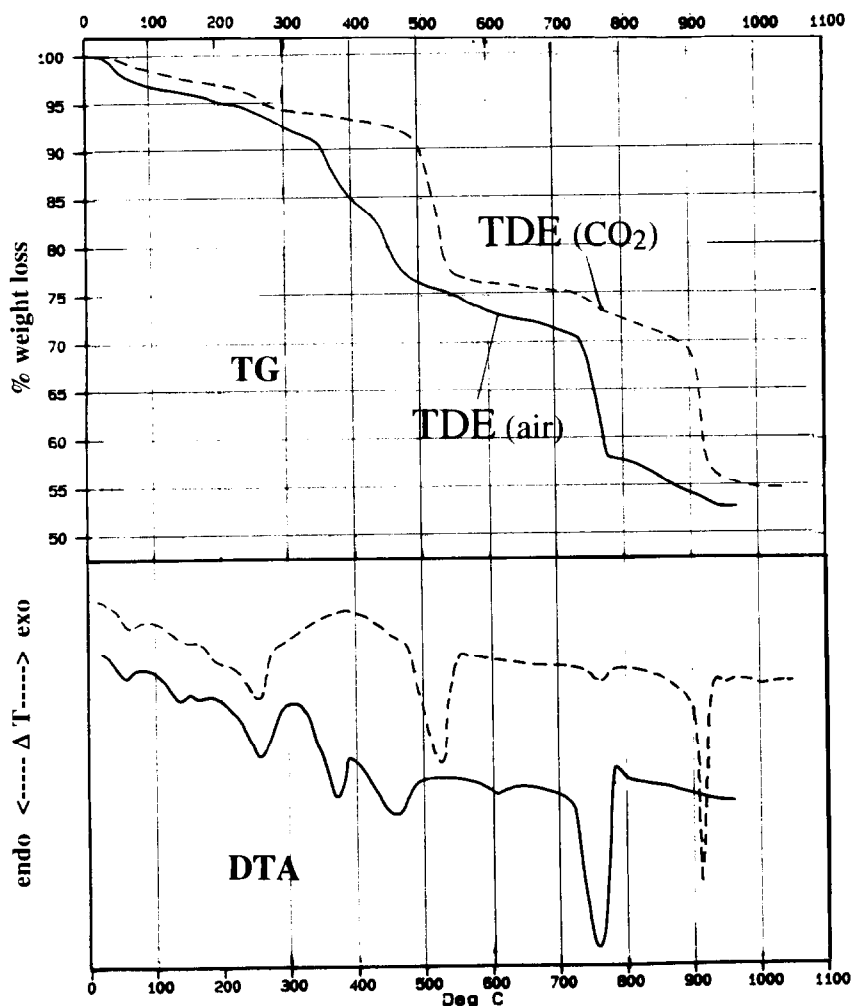


Fig. 3. Simultaneous TG/DTA curves of TDE sample in air and in carbon dioxide.

some impurities (such as chlorides or calcium compounds) hinders the crystallization of the Mg oxocarbonate phase during the HY decomposition, and the sharp exothermic peak at 500°C is due to this crystallization process. Moreover, in our TD samples HY is accompanied by Ca carbonate and the molar ratio Ca/Mg is sometimes greater than 2.

The weight losses of the TG curves under different gaseous atmospheres are characteristic of each component contained in the various samples, and make it possible to evaluate the amounts of Ca-based compounds (gypsum, Ca oxalate, Ca carbonate) and Mg-based compounds (HY) present and, hence, to calculate their respective Ca and Mg contents.

The amount of gypsum can be calculated from the weight loss of water between 100 and 200°C, by subtracting the crystallization water of the

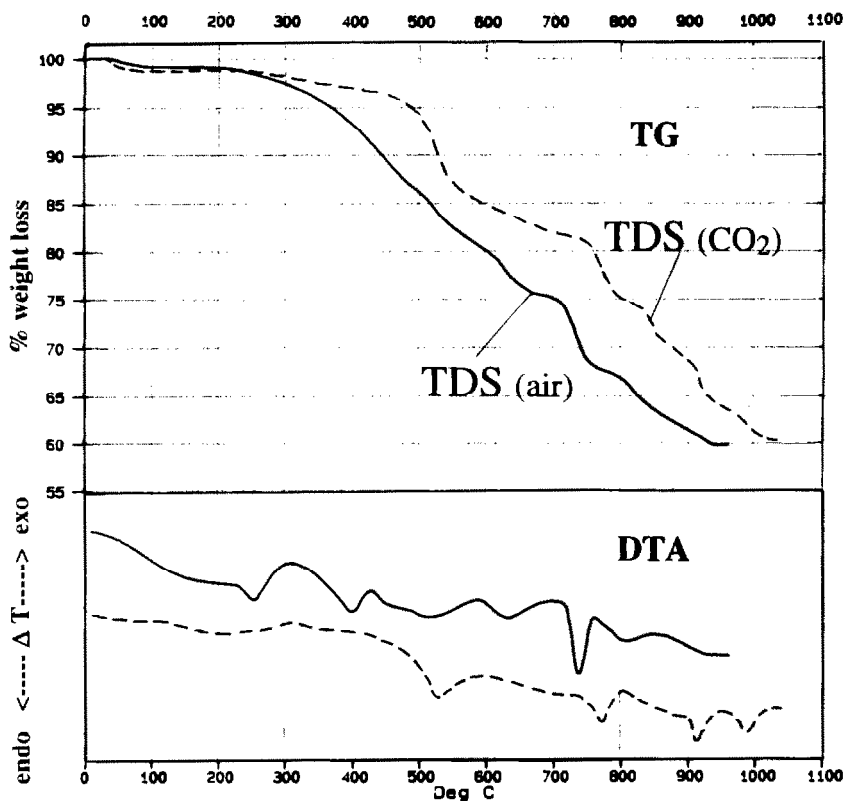


Fig. 4. Simultaneous TG/DTA curves of TDS sample in air and in carbon dioxide.

weddellite that can be present. The amount of Ca oxalate is calculated from the weight loss between 400 and 500°C corresponding to the CO elimination. The amount of HY is calculated from the weight loss between 250 and 500°C, and from the MgCO₃ decomposition in the range 500–550°C. The two weight losses in air between 550 and 830°C give the total amount of CaCO₃, probably present in different degrees of crystallization.

Table 2 reports the amounts of Ca and Mg in the samples under investigation as calculated from the TG curves. The results obtained from chemical analyses are also given for comparison. All the data are in quite good agreement, except for RE C5 and C7 (for Ca), and TDO (for Mg).

DISCUSSION AND CONCLUSIONS

The interpretation of the thermal decomposition of mortars is generally difficult because of the great variety of components used, which depend on country, source of binders, inerts, age, etc.

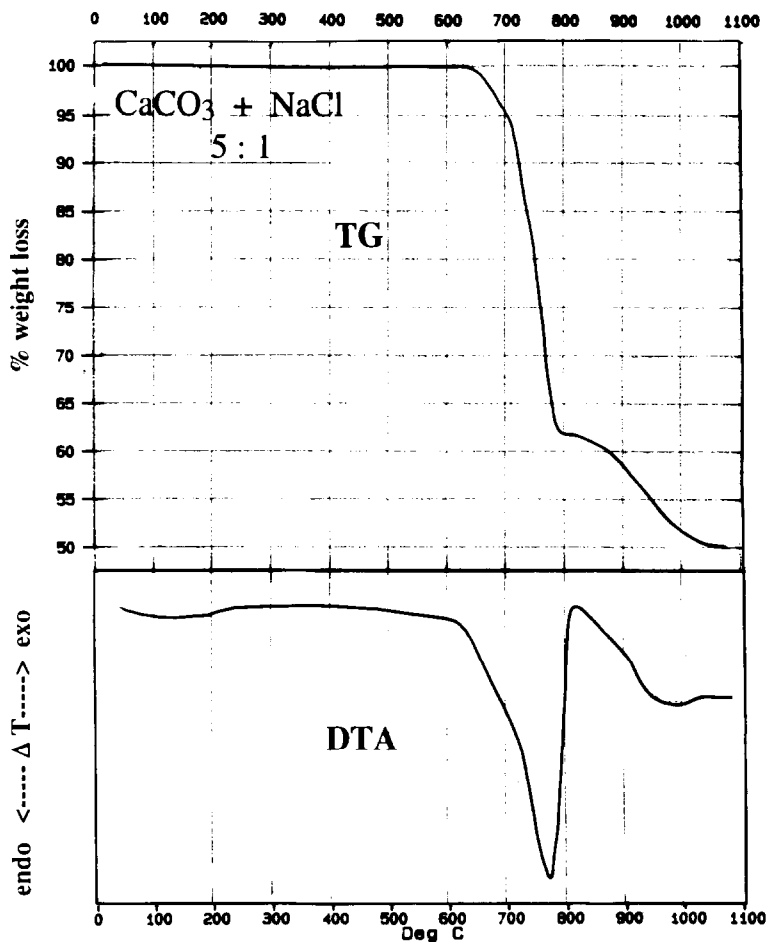


Fig. 5. Simultaneous TG/DTA curves of a 5:1 (w/w) mechanical mixture of calcite and NaCl.

The results of TG and DTA techniques applied to mortars (together with XRD and chemical analyses) make it possible to explain many of the thermal effects and to ascribe them to the different components. They also provide a fast semi-quantitative evaluation of the binders in both calcitic and dolomitic mortars.

The data of Table 2 shows good agreement (except for samples RE C5 and RE C7) between the Ca amounts detected by EDTA titration and derived from the weight losses in the TG curves, characteristic of the most common Ca-containing compounds. Calcite decomposition seems to occur in two or three successive steps above 550°C, as shown by the DTG curve: when operating in CO₂ atmosphere, it was observed that the weight loss between 550 and 800°C is shifted to higher temperatures, to a greater or lesser extent, which confirms that the overall weight loss in this range is due

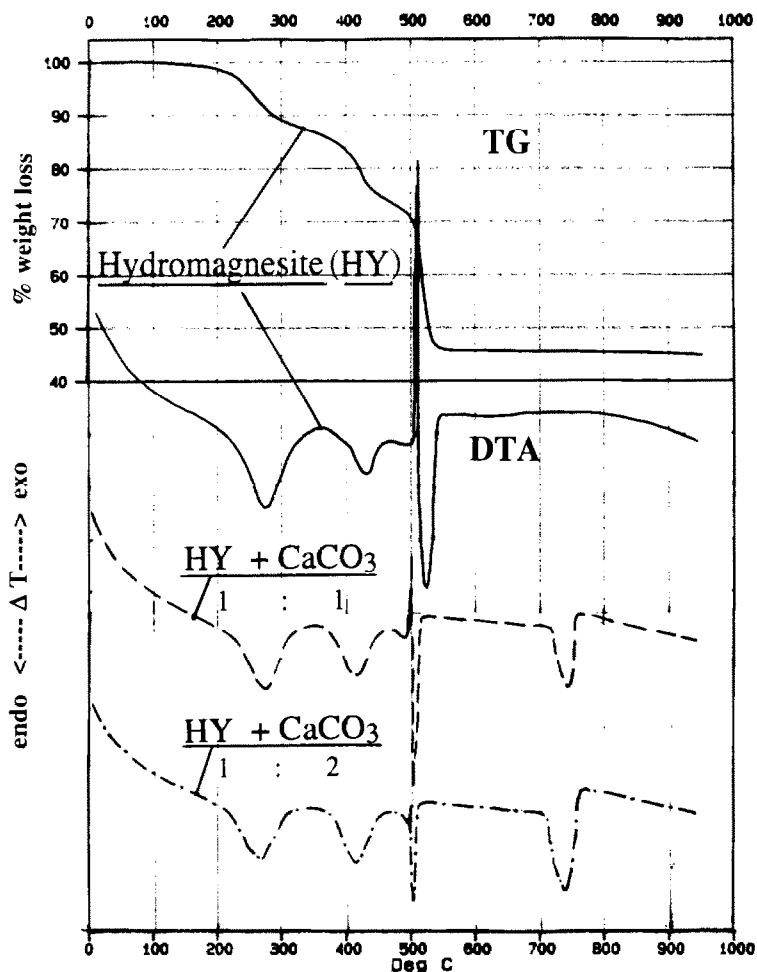


Fig. 6. Simultaneous TG/DTA curves of pure hydromagnesite (HY) and mechanical mixtures of HY and CaCO_3 in different molar ratios.

TABLE 2

Comparison of the Ca and Mg contents obtained by EDTA titration and derived from TG curves

Sample	% Ca		Sample	% Ca		% Mg	
	Tit.	TG		Tit.	TG	Tit.	TG
RE C2	21.2	21.1	TDN	19.1	19.1	8.1	7.8
RE C5	22.1	19.5	TDO	21.6	21.6	14.4	12.4
RE C7	23.2	22.4	TDE	18.5	17.9	10.0	10.0
RE C8	18.9	19.1	TDS	19.8	19.6	9.4	9.5

to the decomposition of various fractions of CaCO_3 , the only difference probably being in their degree of crystallinity.

The discrepancies observed for RE C5 and C7 are a real feature (as proved by three repeat tests), and can be explained by a reaction between Ca(OH)_2 and the siliceous components of the inert, which inhibits the complete carbonatation of lime.

In the case of dolomitic mortars (TD samples), we can observe good agreement for the Ca contents found with the two methods. For the Mg content, estimated from the weight losses of H_2O and CO_2 between 300 and 550°C (taking into account the accepted formula of the commercial hydromagnesite, $4(\text{MgCO}_3) \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O}$ and its thermal decomposition steps), a satisfactory agreement can be observed between the results of the two methods, except in the case of the TDO sample.

These temperature ranges were deduced from experiments with mixtures of calcite and hydromagnesite in different ratios which confirmed the validity of the temperature ranges used for the evaluation of the two components. Furthermore, they explain why the TD samples do not show the exothermic peak at 550°C , due to the crystallization of $x\text{MgCO}_3 \cdot y\text{MgO}$ phase [3], well evident in the decomposition of the pure hydromagnesite. It has been observed that the presence of impurities, such as Ca^{2+} or Cl^- , decreases the intensity of this exothermic peak [4]. Therefore, in a dolomitic mortar the absence of hydromagnesite crystallization during decomposition is most probably due to the presence of Ca.

Finally, it must be mentioned that an unexpected weight loss occurs above 850°C . This effect is clear in the TDS and TDE samples, but negligible in the other two TD samples. By comparing the TG curves of the TD materials with those of $\text{NaCl} + \text{CaCO}_3$ mixtures, it has been confirmed that NaCl is lost slowly after melting. Furthermore, the level of NaCl present in the four TD samples corresponds with the level of exposure to marine winds of the four walls of the tower from which the samples were taken.

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