Thermochimica Acta, 76 (1984) 87–96
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INTERPRETATION OF EGA AND DTG ANALYSES OF CHRYSOTILE ASBESTOS

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(Received 28 November 1983)

ABSTRACT

Five grades of commercial asbestos of the chrysotile variety were studied by means of TG, DTG and EGA in order to identify the decomposition products.

It has been shown that the magnesite and calcite in asbestos decompose in the same temperature zone as chrysotile, brucite is often associated with intermediate carbonate species, and the shoulder preceding the major dehydroxylation peak on the DTG trace belongs mostly to the chrysotile dehydroxylation.

INTRODUCTION

Chrysotile asbestos [$Mg_3Si_2O_5(OH)_4$], is mainly associated very intimately with several other mineralogical species, whose detection and analysis necessitate the use of several analytical methods. The principal minerals encountered are brucite [$Mg(OH)_2$], magnesite [$MgCO_3$], dolomite [$MgCO_3 \cdot CaCO_3$], calcite [$CaCO_3$], talc [$Mg_3Si_4O_{10}(OH)_2$] and magnetite [Fe_3O_4]. With the exception of magnetite, these minerals can be identified by thermogravimetry (TG) and its related technique, derivative thermogravimetry (DTG), since their thermal degradation involves a mass loss and a characteristic temperature corresponding to a maximum rate of decomposition [1,2]. However, the qualitative and quantitative determination of each of these is difficult when they are associated with chrysotile asbestos, because several decomposition zones overlap. Thermal analysis provides no direct information about the decomposition of the asbestos, especially concerning the nature of the gases released. As a result, it would be of interest to combine the techniques of evolved gas analysis (EGA) with thermogravimetry in order to identify the decomposition products.

0040-6031/84/$03.00

TABLE 1

Chemical analysis of major components of chrysotile asbestos

Grade	% CO_2	% CaO	% MgO	% SiO_2	% FeO	% Fe_2O_3	% Al_2O_3
J.M. 7RF-02	0.50	0.23	39.1	37.7	1.73	4.44	0.95
Jaquays Arizona 3Z	5.65	5.65	37.1	36.8	0.01	0.75	0.40
Calidria RG-144	0.78	0.12	40.6	40.8	0.35	2.08	0.40
Carey 7M-90	1.93	0.01	41.8	35.1	0.54	5.08	0.25
Cassiar AS	0.76	0.01	40.2	40.1	0.10	2.22	0.75

It should be noted, however, that with the very small sample masses taken, together with possible sample inhomogeneities (invariably associated with a natural product like asbestos) generated in the sample selection, the reproducibility of the results of this study should be treated with some caution.

EXPERIMENTAL

Five grades of commercial asbestos of the chrysotile variety, part of a selection of materials chosen for the "Second Asbestos Thermogravimetry Round Robin" *, were studied in this present context, by means of TG, DTG and EGA, the latter being coupled with a mass spectrometry (MS) system. The following experimental conditions were observed for the thermal analysis procedure: a heating rate of 5°C min^{-1}; a dynamic dry nitrogen atmosphere of 25 cm^3 min^{-1}; and a sample mass of about 15 mg. The thermal traces were obtained on a Perkin-Elmer TGS-2 apparatus.

The gas analysis was made on 11–15 mg of sample of the same heating rate, and with the system pressure maintained at 10^{-6} to 10^{-7} Torr.

The measurement of the released gases is performed by a mass spectrometer (UIT C-100).

RESULTS AND DISCUSSION

Table 1 gives the chemical analysis of major components of the chrysotile asbestos samples under study.

Grade 7RF-02

Jeffrey Mine, Johns-Manville Canada Inc., Asbestos, Québec, Canada.

This grade of commercial asbestos is characterized by very short fibres having a relatively low surface area and containing a significant quantity of non-fibrous rock dust.

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* An on-going co-operative research program sponsored by the Quebec Asbestos Mining Association (QAMA), University of Sherbrooke, Sherbrooke, Québec, Canada.

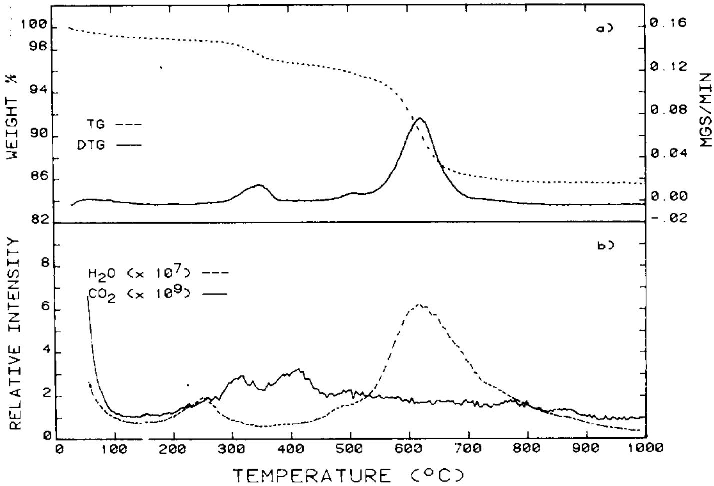

Fig. 1. (a) TG–DTG curves of grade J.M. 7RF-02 at 5°C min^{-1}. (b) EGA curves of grade J.M. 7RF-02 at 5°C min^{-1}.

The thermal traces obtained for this material are presented in Fig. 1. The derivative of the TG trace, as well as all subsequent DTG traces, are standardized to a mass of 15 mg. On Fig. 1, four principal mass loss zones are noted. The first is situated in the region 30–150°C and corresponds to the loss of physiosorbed substances, mostly water. Brucite decomposition appears in the second zone between 250 and 400°C. The region between 450 and 550°C is associated with the decarboxylation of magnesite, while the major mass loss following this results from the chrysotile dehydroxylation. These reactions can be summarized as follows

Zone 1 (dehydration)	$H_2O(l) \rightarrow H_2O(g)$
Zone 2 (brucite)	$Mg(OH)_2 \rightarrow MgO + H_2O(g)$
Zone 3 (magnesite)	$MgCO_3 \rightarrow MgO + CO_2(g)$
Zone 4 (chrysotile)	$2\ Mg_3Si_2O_5(OH)_4 \rightarrow 3\ Mg_2SiO_4 + SiO_2 + 4H_2O(g)$

The EGA traces showing the evolution of water and carbon dioxide are presented in Fig. 1b. These profiles of gas evolution permit the comparison of the principal decomposition zones with those outlined by the TG and DTG traces. Note, however, that the amplification factor is 100 times greater for CO_2 than for H_2O.

At temperatures below 100°C, the signals obtained result from the pumping out of the ambient atmosphere as well as physiosorbed species on the asbestos surface, and do not represent useful information. The water evolution curve shows the characteristic dehydroxylation of chrysotile asbestos in the region 500–720°C. This decomposition increases towards the higher temperatures on the EGA trace. A "shoulder" precedes the major peak of chrysotile. The brucite decomposition appears in the region 150–350°C. Finally, on the CO_2 evolution profile, faint traces of CO_2 are observed betwen 250 and 450°C.

Comparing the DTG and EGA (H_2O) traces, a displacement of the peak associated with the brucite is noted at 350°C for DTG and at 250°C for EGA. The reversible nature of this decomposition, and its high degree of dependence on the system's partial pressure of water, helps in producing the reaction and thus diminishes the peak's temperature [3]. Note that the water vapour pressure is much lower under vacuum (EGA) than it is in a flow of nitrogen at atmospheric pressure (TG/DTG). The peak at 500°C on the DTG trace was normally associated with the decomposition of magnesite [2,4] but the appearance of the shoulder preceding the major dehydroxylation peak on the water evolution trace exactly at the same temperature observed on the DTG trace, leads us to believe that this shoulder on the DTG trace is due mostly to the chrysotile dehydroxylation. The faint traces of CO_2 between 200 and 450°C on the CO_2 evolution profile (Fig. 1b) show the existence of a mixture of intermediate carbonates relatively less stable than the magnesite. This decomposition as shown on the DTG trace must be located toward the higher temperatures, probably masked by the shoulder preceding the dehydroxylation. The rest of the total of 0.5% of CO_2, determined by chemical analysis, is distributed over a wide temperature range and is derived from calcium carbonate.

Grade 3Z

Jaquays Asbestos Corporation, Globe, Arizona, U.S.A.

This grade consists of long, relatively low surface area fibres, indicating a low degree of defibrillation of the asbestos bundles. It is derived from an ore drawn from limestone host rock, and may therefore be expected to be richer in carbonate minerals than asbestos samples from a non-carbonate source, such as the Quebec chrysotile varieties (cf. Table 2).

Its thermal behaviour is a typical case demonstrating the magnesite ambiguity in the region 500–750°C. In Fig. 2a, a small mass loss is observed

TABLE 2

Determination of carbonate minerals in chrysotile asbestos by chemical analysis

Grade	% CO_2	% $CaCO_3$	% $MgCO_3$
J.M. 7RF-02	0.50	0.41	0.61
Jaquays Arizona 3Z	5.65	10.08	2.34
Calidria RG-144	0.78	0.21	1.31
Carey 7M-90	1.93	0.02	3.68
Cassiar AS	0.76	0.02	1.44

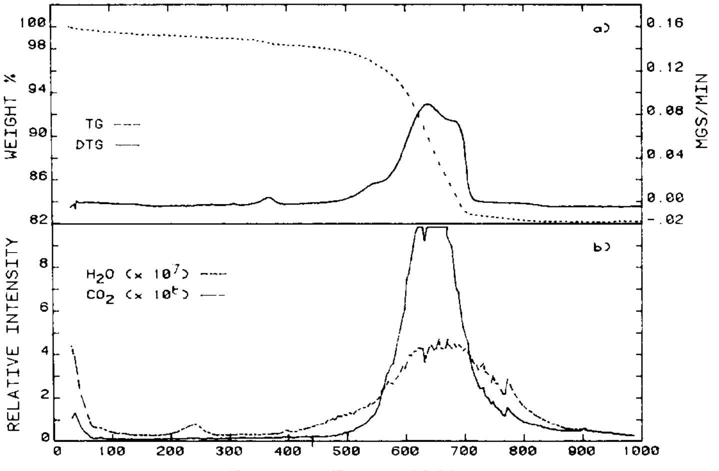

Fig. 2. (a) TG–DTG curves of grade Jaquays Arizona 3Z at 5°C min^{-1}. (b) EGA curves of grade Jaquays Arizona 3Z at 5°C min^{-1}.

between 300 and 400°C, followed by a shoulder, and a considerable mass loss in two steps (DTG trace) between 500 and 750°C. Knowing that the theoretical mass loss is 13.0% for pure chrysotile (from the stoichiometry), and that we have obtained a value of 16% in this region, we can easily conclude that some of the associated minerals in the asbestos are decomposing at the same time. But the identification and quantification of these minerals cannot be made from this analysis alone. Only the brucite decomposition (with a mass loss between 300 and 400°C) presents no problem. This affirmation is verified by the EGA profiles (Fig. 2b) which show the presence of $Mg(OH)_2$ without any trace of carbonate in the region 150–300°C. In the zone characteristic of the chrysotile dehydroxylation (500–800°C), a large quantity of CO_2 is seen on the EGA profile in Fig. 2b, again recalling that the MS amplification factor must be taken into account; in this case, it is ten times smaller than in Fig. 1b. The simultaneous decomposition of the carbonate and chrysotile shows to what extent care must be taken in the interpretation of the thermal analysis results. TG under a CO_2 atmosphere (not illustrated here) and the results of the chemical analyses of this material show the existence of a calcite-type of compound associated with the asbestos, but the chemical analysis also reveals the presence of magnesium carbonate in a non-negligible quantity (about 20% of total CO_2). This fact leads us to believe that not only does the calcite decompose in the same region as the chrysotile, but also the magnesite, as confirmed by DTG under nitrogen and EGA under vacuum. A study of thermal analysis with a nitrogen atmosphere, together with a certain partial pressure of water, at ambient temperature, demonstrates the agreement of the $MgCO_3$ decomposition (in dolomite) with the dissociation temperature of

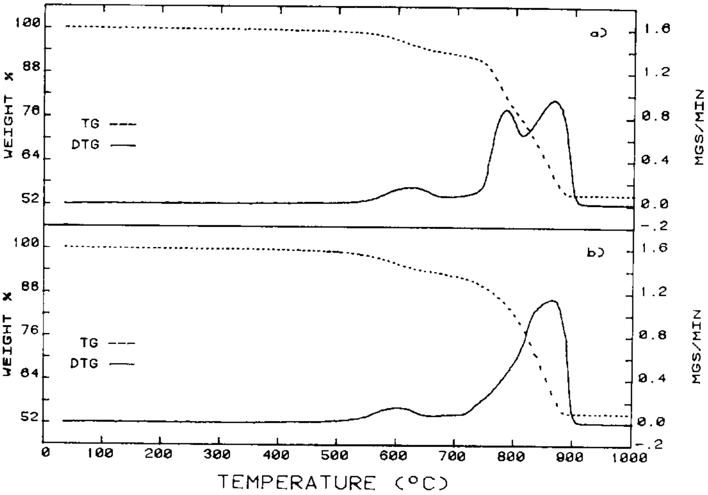

Fig. 3. (a) TG–DTG curves of dolomite at 20°C min^{-1} under 1 atm dry N_2. (b) TG–DTG curves of dolomite at 20°C min^{-1} under 1 atm N_2 partially saturated with water vapor.

$CaCO_3$, as presented in Fig. 3. This observation convinces us that the carbonate compound found in this sample of Arizona asbestos must be dolomite or dolomitic calcite. Finally, note that the EGA water evolution profile extends over a greater temperature range than that of the DTG trace.

Calidria RG-144

New Idria Mine, Union Carbide Corporation, California, U.S.A.

This asbestos grade is composed of extremely short, highly defibrillated (and hence, of extremely high surface area) chrysotile fibres, with very few contaminating rock particles. It is produced from its ore by an unusual wet milling procedure, which is unique in an industry which otherwise produces asbestos by conventional dry milling techniques.

Figure 4a (TG and DTG thermal traces) shows a very small mass loss in the brucite decomposition region (300–400°C). This mass loss is followed by a shoulder approaching a peak, (more pronounced than in the results described above) located before the chrysotile dehydroxylation peak. The EGA water profile (Fig. 4b) for Calidria RG-144 indicates that the shoulder appearing at around 530°C, seen in the previous Johns-Manville 7RF-02 sample, is caused by the dehydroxylation of the chrysotile, and not by the decarboxylation of the magnesite. Indeed, the shoulder corresponds well with that on the DTG trace and would result from the dehydroxylation either from the highest surface area fibres or the most exposed part of the brucite layer of the chrysotile fibrils. We are convinced, moreover, that this shoulder on the DTG trace does not belong mainly to the magnesite, because careful calculations yield a result of 2.5% $MgCO_3$, whereas the maximum value permitted by chemical analysis is only 1.5%. As for the EGA water profile in Fig. 4b in the range 750–950°C, it can be attributed to talc or to the last structural water molecules from the chrysotile. The EGA water maximum at 270°C reveals the presence of brucite. The EGA CO_2 profile between 200 and 500°C shows that the mineral responsible is apparently formed from an intermediate carbonate structure of indeterminate composition (x $MgCO_3 \cdot y$ $Mg(OH)_2$). However, this carbonate decomposes in the region 450–650°C in the DTG thermal trace, and so negates all attempts to quantitatively determine magnesite and chrysotile from an analysis of this trace. Finally, the absence of any major peak on the EGA profile proves that Calidria RG-144 possesses little, if any, magnesite.

Grade 7M-90

Carey Mine, Carey Canada Inc., East Broughton, Quebec, Canada. (Note: this is not a sample of asbestos from the QAMA Second Thermogravimetry Round Robin.)

This material is somewhat similar to the first asbestos sample described (Johns-Manville 7RF-02) at least in physical properties (it does have a higher surface area, though); however, the geological properties of its host rock and fibre paragenesis has resulted in it containing a higher than average content of brucite than in Quebec asbestos grades from other mines. Consequently, a significant mass loss in the brucite zone of the DTG thermal trace, as shown in Fig. 5a, is noted, followed by a small shoulder preceding the chrysotile dehydroxylation between 450 and 650°C. Figure 5b reveals that an important fraction of the CO_2 evolved is derived from magnesite (peak at

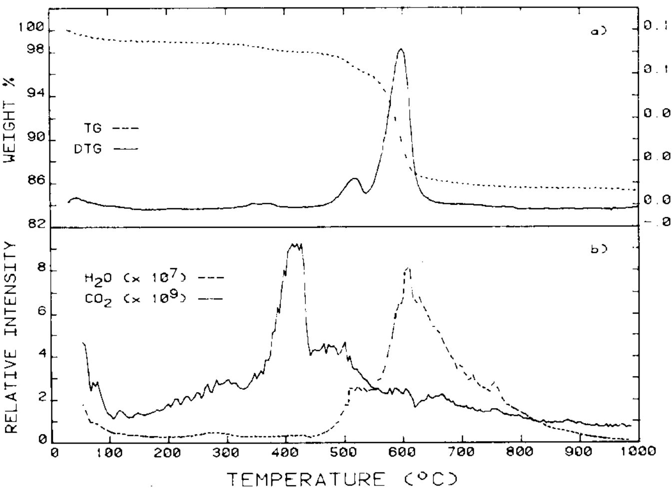

Fig. 4. (a) TG–DTG curves of grade Calidria RG-144 at 5°C min^{-1}. (b) EGA curves of grade Calidria RG-144 at 5°C min^{-1}.

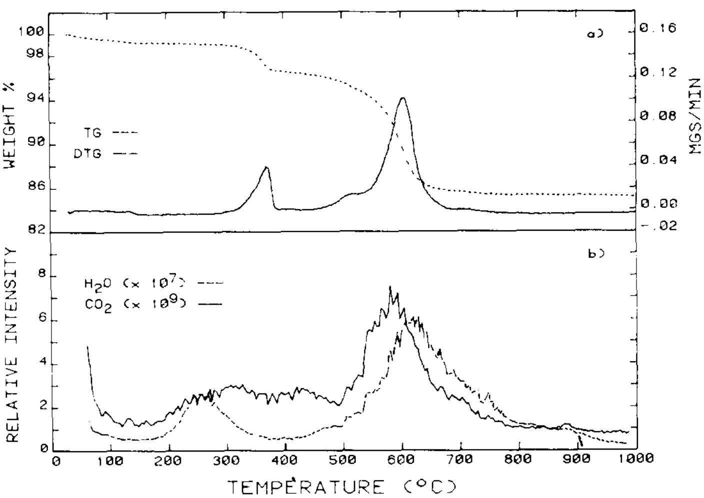

Fig. 5. (a) TG–DTG curves of grade Carey 7M-90 at 5°C min^{-1}. (b) EGA curves of grade Carey 7M-90 at 5°C min^{-1}.

600°C), which again implies that under nitrogen the decomposition of magnesite is masked by that of chrysotile. Moreover, all the CO_2, appearing in the region 500–800°C, must be derived from magnesite, because chemical analysis reveals no trace of calcium, and hence, none of calcite. As well as being wider than the DTG trace, the EGA water evolution curve shows that the dehydroxylation of chrysotile begins at a temperature as low as 400°C, but ends only at around 950°C. The simultaneous appearance of CO_2 and H_2O between 150 and 500°C gives an additional example of the presence of one or several types of intermediate carbonates. These results agree with the data of Bonneau [5] who described, by infrared studies, that chrysotile asbestos, originating as an ultrabasic mineral, is intimately associated with various types of more or less well defined carbonate species. For this reason, a spread-out CO_2 signal is observed in the EGA profile (Fig. 5b) between 150 and 500°C, without having any significant peak attributable to CO_2 emission in this range.

Grade AS

Cassiar Resources Ltd., Cassiar, British Columbia, Canada.

This is a very long grade of asbestos fibre, suitable for spinning and textile applications. It has an average surface area, and is exceptionally clean and free of impurities, both mechanical and mineralogical [6].

The TG and DTG thermal traces given in Fig. 6a show not only the absence of brucite, but a remarkable feature is also observed: the principal zone of chrysotile dehydroxylation is composed of two peaks, with one maximum at 650°C and the other at 720°C. Several thermal analyses done

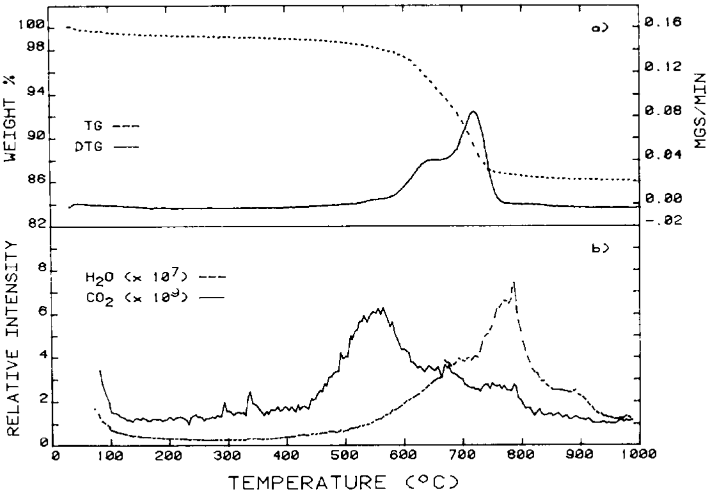

Fig. 6. (a) TG–DTG curves of grade Cassiar AS at 5°C min^{-1}. (b) EGA curves of grade Cassiar AS at 5°C min^{-1}.

beforehand, some on long asbestos fibres, and some on samples of short asbestos fibres, have demonstrated unequivocably that a relationship exists between the length of the fibres and the dehydroxylation temperature [7]. Indeed, the most exposed surfaces of the fibrils would be subject to a more rapid water loss than the compacted bundles of long fibres.

Meanwhile, the EGA profiles in Fig. 6b provide additional proof that the shape of the DTG peaks is highly characteristic of the chrysotile in this material, taking into account that the water evolution trace, which is wider, is displaced towards the higher temperatures. The CO_2 evolution trace shows that the magnesite decomposes simultaneously with the chrysotile. However, the chemical analysis of Cassiar AS reveals no trace of calcite in this material. Finally, there is no significant trace of intermediate carbonate minerals in this sample.

CONCLUSION

We have seen that the detection of evolved gases is an interesting and valuable technique to aid in the identification of the nature of the mass losses associated with the TG and DTG thermal traces. EGA permits us to confirm the hypothesis that the shoulder on the peak around 500°C on the DTG trace, especially for the short fibres with high surface area, is not derived from the magnesite decarboxylation, but rather from the chrysotile dehydroxylation. It has also been proved that the magnesite and calcite in asbestos decompose in the same temperature zone as chrysotile, which makes the determination of each of these associated minerals by thermal analysis only approximate. Also, it has been shown that the brucite is often associated with one or more intermediate carbonate species whose thermal stability is less than that of magnesite, which decomposes between 200 and 500°C. The simultaneous use of TG/DTG and EGA/MS thus permits a specific identification of the mineralogical composition of chrysotile asbestos, and consequently an improved quantification of each of its components.

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