THERMAL ANALYSIS OF HECTORITE. PART I. THERMOGRAVIMETRY

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(Received 6 October 1982)

ABSTRACT

Several hectorite specimens representing both raw carbonate bearing ores and processed hectorite (carbonate-cleaned) specimens were analyzed by the computerized thermogravimetric techniques of TG and DTG. The results of these thermogravimetric investigations combined with the results of automated acid evolved carbonate determinations and plasma emission spectroscopy were employed to gain new insights to both the composition and thermal behavior of both raw hectorite ores and carbonate-cleaned hectorite clay mineral specimens.

INTRODUCTION

Hectorite is a trioctahedral member of the smectite clay minerals group. Unlike the dioctahedral members of this group, hectorite contains no aluminum ions in the silicate structure. In hectorite all possible octahedral positions, originally containing Al^{3+}, have been substituted by Mg^{2+} and Li^+ ions [1]. The formula suggested for hectorite by Ross and Hendricks [2] is

$$(OH)_4 Si_8 \left(\underset{\underset{Na_{0.66}}{\downarrow}}{Mg_{5.34} Li_{0.66}} \right) O_{20} \cdot n \, H_2O$$
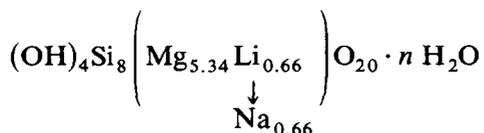
where $n \, H_2O$ represents interlayer water. As is shown by the formula, the structural lattice charge results from a substitution of Li^+ for Mg^{2+}. The charge balancing cation, located external to the silicate layer, is sodium. Although not indicated by the formula of Ross and Hendricks, hectorite is known to contain fluorine atoms. In another formula calculated from chemical analysis data by Kerr et al. [3], the gram atoms of fluorine are equal in number to that of the $-OH$ groups in the silicate structure. In a more recent compilation [4], the chemical analysis of the SHCa-1 hectorite specimen (carbonate-contaminated) of the Clay Mineral Society Source

Clays Collection was found to contain 2.75% fluorine in the raw hectorite ore.

Hectorite finds important uses in the ceramic industry as a suspending agent in glazes, as a plasticizing agent for non-plastic formulations such as high alumina or zirconium bodies, and as a non-migrating binder in extruded bodies. Due to its ability to gel water [5], it finds many uses in both the paints and cosmetics industries. It is also used as a clarifier for beverages. Organo-clays derived from hectorite are used as oil drilling fluids and more recently [6] as stereo-specific catalysts.

Most hectorite ore specimens in the United States are limited to those found in southeastern California (near Hector, CA), and are always found associated with large proportions of calcite and, in some cases, varying amounts of dolomite. Thus, the hectorite ores are commercially processed to remove most of the carbonate component prior to use.

In this study, an attempt is made to resolve several existing questions regarding the thermal behavior of hectorite. First, when we speak of the thermal behavior of hectorite, should we make a distinction between the raw (carbonate bearing) clay specimen and the uncontaminated clay mineral specimen? As will be seen in the total study which follows, the thermal behavior is markedly different for the raw hectorite ore specimens and those in which a large percentage of the carbonate component has been removed. Second, the issue of how much of the thermal activity observed in the ca. 550–850°C temperature range is actually due to dehydroxylation of the clay mineral component and how much is associated with the decomposition of the carbonate mineral component is addressed experimentally. Third, experiments were performed to establish the high temperature behavior as well as those factors which affect the thermal curves obtained from the technique of differential thermal analysis.

Since the objectives were several and the solution to the problems are not in all cases directly obtained by the thermal analysis techniques of DTA, TG, and DTG alone, a variety of analytical techniques were employed. These include X-ray diffraction, acid evolved carbon dioxide determinations, plasma emission spectroscopy, and, in some cases, optical microscopy. Due to the extensive nature of this study, the results will, therefore, be presented in two parts.

In the first part the techniques of thermogravimetry (TG) and derivative thermogravimetry (DTG) will be used to study both raw hectorite ores as well as processed (carbonate cleaned) hectorite specimens. The technique of automated acid evolved carbon dioxide determination will also be used to determine the total carbonate content of the specimens of this study. The results of inductively coupled plasma emission spectroscopy of the dilute acid soluble carbonate component will also be presented. The combined results of these studies will be used to offer new insights to both the composition and thermal behavior of hectorite.

EXPERIMENTAL

Hectorite specimens of this study

Four different hectorite specimens were used in this study. Two of these specimens were raw hectorite ores containing a large carbonate component. One of these was the well studied SHCa-1 hectorite specimen (San Bernadino County, CA) obtained from the Source Clays Collection of the Clay Minerals Society. The other raw hectorite ore was obtained from the R.T. Vanderbilt Co. (Norwalk, CT). Two industrially processed (carbonate-cleaned) hectorite ore specimens containing different amounts of residual carbonate components were also studied. It should also be noted that the physical form of the raw hectorite specimens was that of a fine clay powder (< -100 mesh) and that of the processed hectorite specimens was of low density flakes (thin laths).

Instrumentation and special techniques

All results of thermogravimetry were obtained using the Perkin-Elmer TGS-2 thermogravimetric analysis system along with the System 4 Microcomputer Controller, Perkin-Elmer Thermal Analysis Data Station (TADS), and the TADS printer/plotter, shown in Fig. 1. All TG and DTG thermal curves given in this study are hard copy printouts from the TADS printer/plotter.

The temperature axes of the TG thermal curves were calibrated using Curie point standards and horseshoe magnet which are standard items supplied with the instrument. For the purpose of sample temperature calibration, the Curie point standards were buried in a sample of the SHCa-1 hectorite specimen which had previously been heated to 1000°C prior to TG experiments leading to adjustment of the temperature axis.

Due to the nature of the hectorite specimens, the technique previously used by Gallagher and Warne [7] in which a fine meshed platinum gauze was placed over the TG sample to prevent loss of mass not associated with thermal decomposition or evolution was employed. Obviously, the mass of such a Pt gauze must normally be electronically nulled prior to loading the TG sample. When using the TADS Data Station, however, this is not necessary since a press of the "zero" key on the TADS keyboard establishes the mass of the Pt gauze as the new reference zero value of the balance. The sample is then loaded and the Pt gauze is again placed over the sample.

All inorganic (carbonate) carbon determinations reported in this study were performed by an automated method which was developed by Culmo [8] in our laboratories. In this method, a Perkin-Elmer Model 240C elemental analyzer, shown in Fig. 2 along with the Perkin-Elmer 240DS Data Station, is used in conjunction with an acid evolved carbonate kit. A descriptive
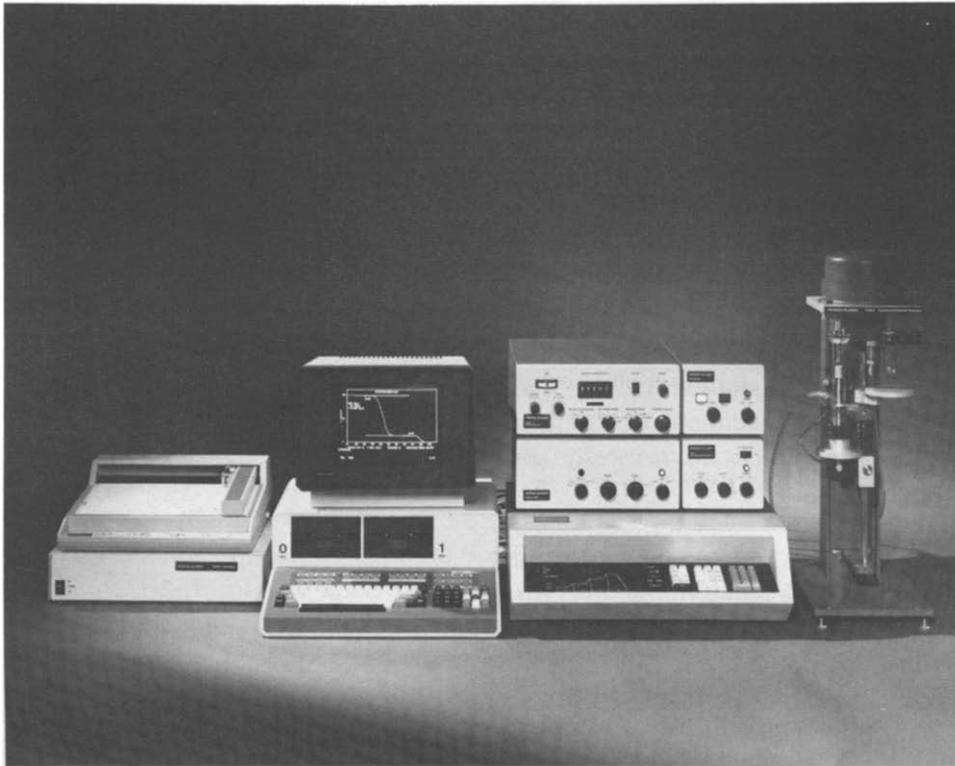
Fig. 1. Perkin-Elmer TGS-2 thermogravimetric analysis system, system 4 microcomputer controller, thermal analysis data station, and TADS printer plotter.

diagram of the carbonate kit is given in Fig. 3. As is shown in the diagram, a phosphoric acid bath which is thermostated at 110°C is used. The weighed sample is encapsulated into a platinum vial and sealed with an alumina wool plug. The vial is delivered to the acid bath via a ladle. The evolved carbon dioxide is subsequently measured by thermal conductivity using a difference signal obtained from measurements made before and after CO_2 scrubbing. A stream of high purity helium was used as the carrier gas. The carbon bridge of the 240C elemental analyzer was calibrated using primary standard calcium carbonate with the acid-evolved carbonate kit.

RESULTS AND DISCUSSION

Figure 4 shows the TADS hard copy TG and DTG thermal curves for the SHCa-1 hectorite source clay specimen obtained in dynamic nitrogen purge using a heating rate of 10°C min^{-1}. As can be seen from the thermal curves, there appear to be three distinct decompositions in the temperature range of
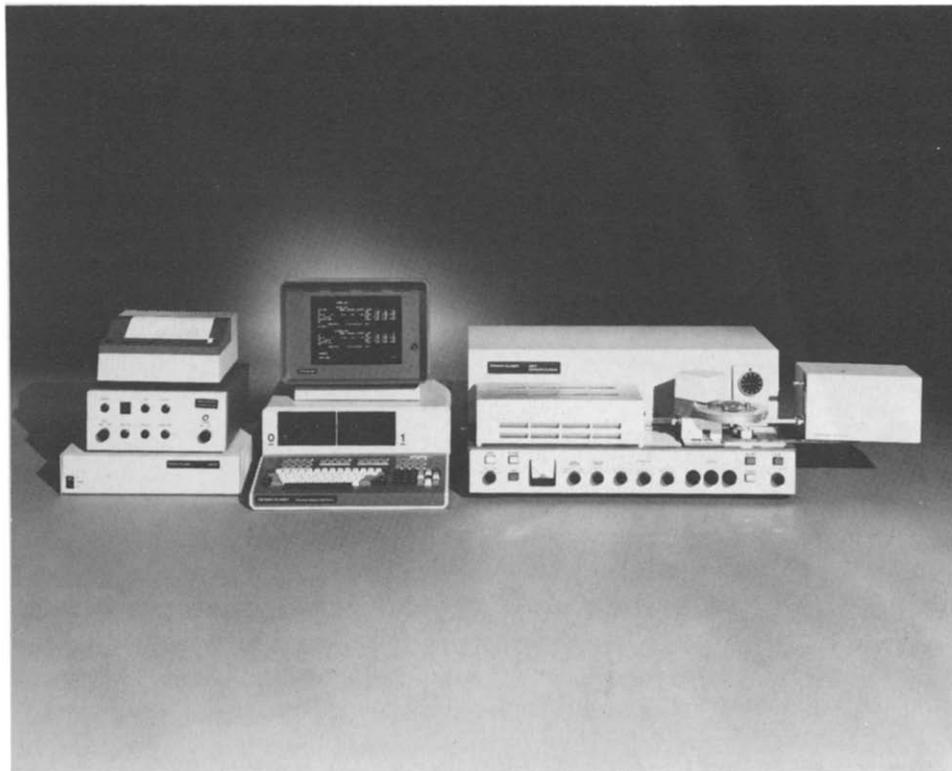
Fig. 2. Perkin-Elmer Model 240C elemental analyzer with 240DS data station.

study. The lower temperature weight loss is due to the loss of interlayer water from the trioctahedral smectite clay mineral component of this natural specimen. The double decomposition event occurring between ca. 550 and 850°C is believed by most to be due to the decomposition of the carbonate component as well as dehydroxylation of the clay mineral component. One will also note that a slight but continuous bleed is observed in the weight loss (TG) curve between the temperature region of the interlayer water loss and the major carbonate/dehydroxylation decomposition region.

Figure 5 describes the procedure used by the TADS in this study for assignment of weight losses between any two temperatures of interest. This procedure may be achieved by use of the TADS CRT screen cursor to divide the entire thermal curve into weight loss regions. Alternately, the temperature region of interest may be entered via the TADS keyboard. Regardless of which option is used, the weight loss assignments are automatically stored for any sequence of determinations and may be cumulatively recalled to the CRT screen by a push of a "RESULTS" key.

Figure 6 shows the plotting of these results for the weight loss assignment for the three temperature regions of interest, along with the TG thermal
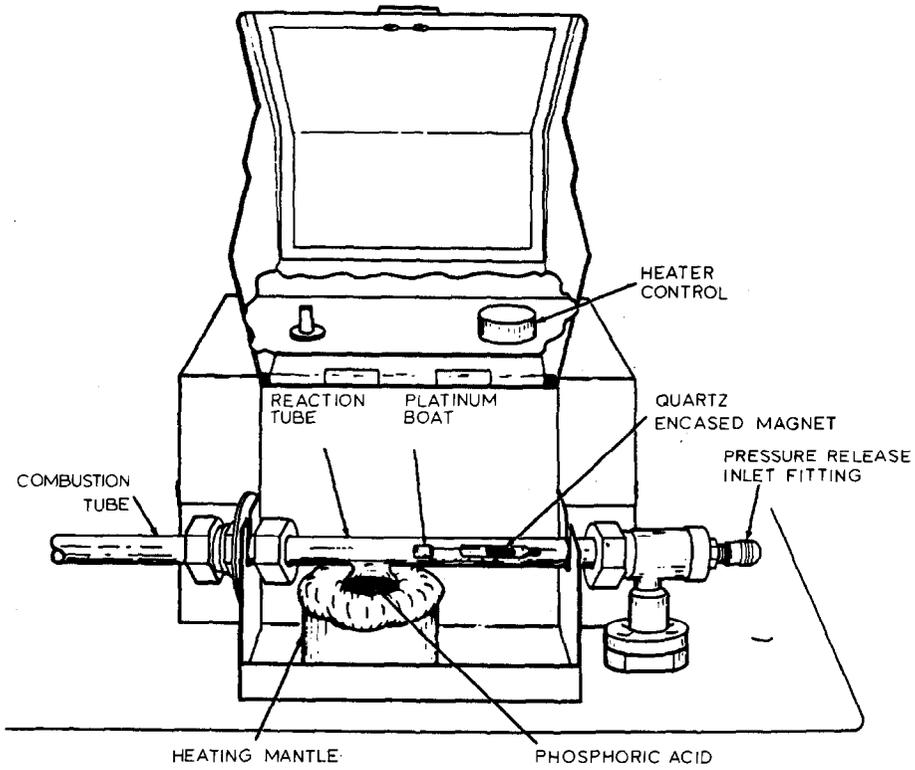
Fig. 3. Descriptive drawing of carbonate kit used with the 240C elemental analyzer.
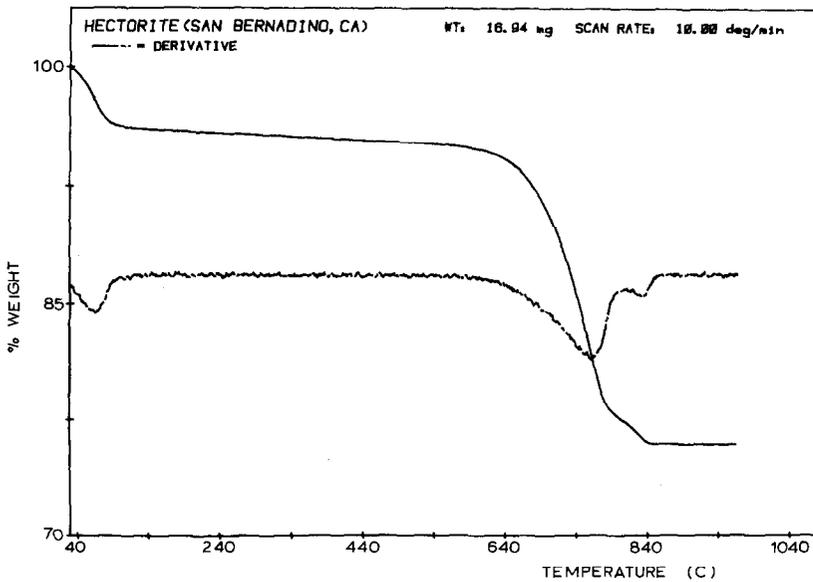
Fig. 4. TG and DTG thermal curves for the SHCa-1 source clay hectorite specimen.
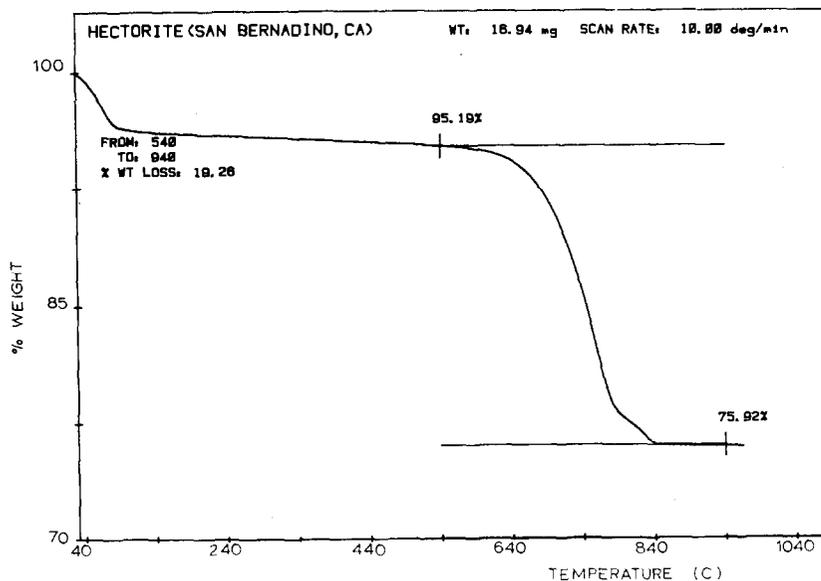
Fig. 5. TG weight loss assignment using the thermal analysis data station.

curve, for the SHCa-1 hectorite source clay specimen. As can be seen in the Fig., the temperature regions from 30 to 240°C, 240 to 540°C, and 540 to 940°C were chosen to describe the weight loss profile of the SHCa-1 specimen. It should be stated that the magnitude of weight loss due to loss of
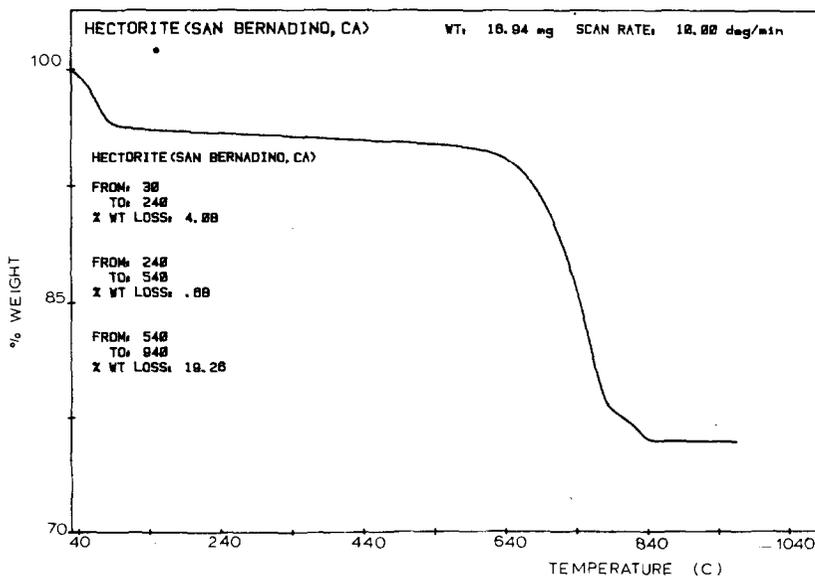
Fig. 6. Simultaneous hard copy display of TG thermal curve and weight loss assignments for SHCa-1 hectorite specimen.

TABLE 1

TG data summary for hectorite specimens in this study

	wt. loss (%)			
	30–240°C	240–540°C	540–940°C	Total
SHCa-1 hectorite	4.12	0.68	19.26	24.06
Processed hectorite ore	7.78	0.84	3.47	12.09
Veegum T	7.09	0.65	5.57	13.31

interlayer water will be affected by the P_{H_2O} to which the clay is exposed prior to analysis. Thus, for comparing absolute values of percentage weight loss for the total thermal curve, the specimens should be exposed to the same relative humidity. MacKenzie and Caillere [9] recommend equilibration in vacuo over a saturated solution of $Mg(NO_3)_2 \cdot 6 H_2O$ (55% relative humidity).

One will observe fromt the TG data summary given in Table 1 that the SHCa-1 hectorite source clay exhibits a total weight loss of 24.06% of the original sample weight on heating from 30 to 940°C. MacKenzie and Caillere [9] report the thermogravimetric determination of the interlayer water and combined dehydroxylation/carbonate dehydroxylation region for this same source clay specimen. Since it is not certain as to what upper temperature was used in their work for the assignment of the total interlayer water loss, the best comparison of data is made with the values for the major carbonate/dehydroxylation decomposition. MacKenzie and Caillere [9] report a value of 20.28% weight loss based on the weight of the sample "at a point just prior to dehydroxylation on the TG curve". When the same is done here using the weight loss value based on the percentage of sample weight at 540°C (see Table 2), a value of 20.23% is assigned for the carbonate/dehydroxylation decomposition. The excellent agreement in these values implies that the SHCa-1 specimen is quite homogeneous since the

TABLE 2

TG weight loss as a percentage of sample weight at 540°C

	wt. loss (%) (540–940°C)
SHCa-1 hectorite	20.23
Hectorite ore	22.23
Veegum T	6.04
Processed hectorite ore	3.80
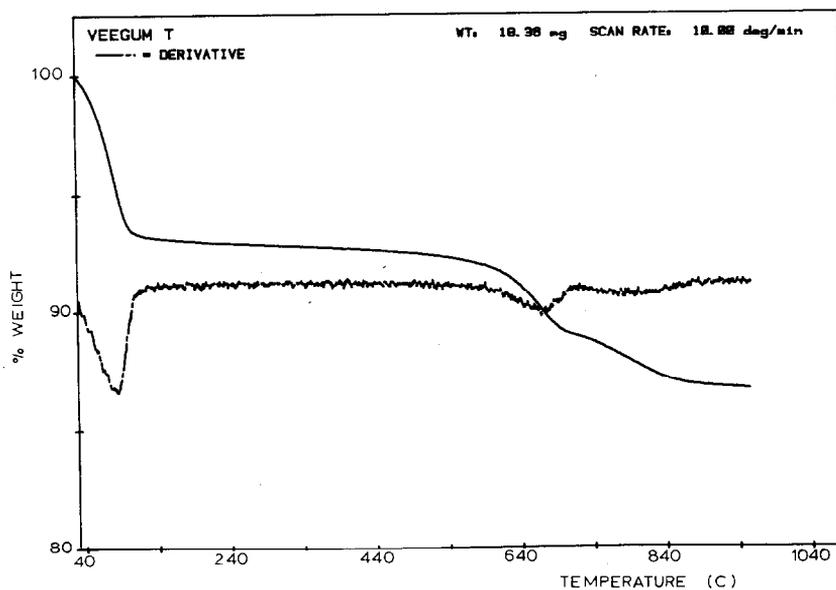
Fig. 7. TG and DTG thermal curves for Veegum T hectorite specimen.

MacKenzie–Caillere value was obtained with a 469.3 mg sample and that of this study employed only 16.94 mg of TG sample. Also, the agreement speaks well of the representative specimens issued from the Source Clays Collection by the Clay Minerals Society.
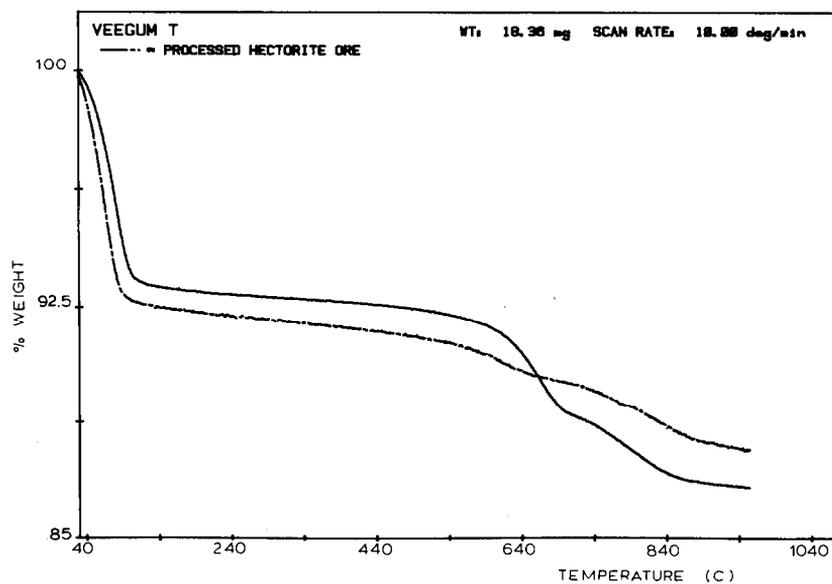
Fig. 8. TG thermal curves for Veegum T and processed hectorite ore specimens.

Processed hectorite specimens

As mentioned earlier, the natural hectorite ore specimens are processed for the removal of much of the carbonate contaminant prior to use. This is generally achieved on a density basis with the lighter colloidal flakes of cleaned hectorite removed at the top of the tank. Figure 7 shows the TG and DTG thermal curves for a commercial hectorite (Veegum T) sold primarily for use in the ceramics industry. One will note that the removal of much of the carbonate component leads to a greater percentage weight loss due to loss of interlayer water and a decrease in the percentage weight loss in the carbonate/dehydroxylation decomposition region.

Figure 8 shows the simultaneous display by the TADS of the Veegum T hectorite along with another processed hectorite ore which is even cleaner than the Veegum T. Again, one will note the increase in interlayer water and decrease in the magnitude of the weight loss in the carbonate/dehydroxylation region with increase in carbonate removal.

This observed trend implies that, for specimens which are exposed to the same relative humidity prior to analysis, both the percentage weight loss associated with the loss of interlayer water and the magnitude of the percentage weight loss in the carbonate/dehydroxylation region may serve as an indication of the "cleanliness" of the hectorite clay mineral.

Figure 9 shows the TG thermal curves for both a raw hectorite ore specimen and an industrially processed hectorite specimen. Assuming that these two specimens represent the actual before and after batch processing
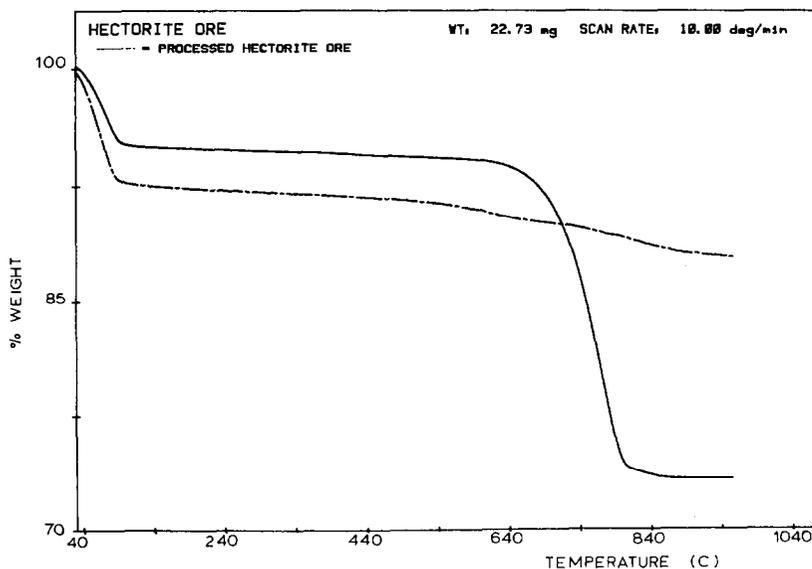
Fig. 9. TG thermal curves for a raw hectorite ore specimen and a processed hectorite ore.

TABLE 3

Results of inorganic carbon determinations by acid decarbonation–elemental analysis

	% C_i	% CO_2	% CO_3^{2-}
SHCa-1 hectorite	5.03	18.44	25.15
Hectorite ore	6.05	22.18	30.25
Veegum T	1.00	3.67	5.00
Processed hectorite ore	0.46	1.69	2.30

materials, comparison of the two TG thermal curves could serve as an indication of the efficiency of the cleaning process. Of the two major weight loss regions, the interlayer water loss should provide the most direct comparative data by thermogravimetry. The values for the 540–940°C weight losses, given in Table 2, could also serve as a first approximation of the efficiency. However, one must remember that there are more than one independent weight loss events occurring in this temperature region.

For this reason, the best comparison of carbonate levels in the two specimens is made using the automated acid-evolved carbon dioxide determination using the Model 240C elemental analyzer. Table 3 gives the results of this determination for all four specimens of this study. As is seen from the Table, the instrument gives the results in percentage inorganic carbon. For the purpose of comparison with TG data, these results have also been expressed as both % CO_2 and % CO_3^{2-} using the appropriate stoichiometric factors.

Some interesting conclusions may be made using these results. First, the efficiency of carbonate removal by the industrial processing of the raw hectorite ore specimen may be calculated by the expression

$$\% \text{ efficiency} = \frac{\left(\text{total } CO_3^{2-}\right) - \left(\text{residual } CO_3^{2-}\right)}{\left(\text{total } CO_3^{2-}\right)} \times 100$$

where the total CO_3^{2-} is the percentage carbonate anion in the raw hectorite ore and residual CO_3^{2-} is the percentage carbonate anion in the processed hectorite ore. On insertion of these values from Table 3, one obtains an efficiency assignment for this industrial batch processing of 92.4%.

Another interesting assignment which may be made using this acid-evolved carbon dioxide determination is the percentage carbonate in the SHCa-1 source clay specimen. As is seen in Table 3, the total % CO_3^{2-} is observed to be 25.15%. An intelligent estimation was made by McKenzie and Caillere [9] using thermogravimetry in dynamic nitrogen atmosphere. In their estimation, the "weight loss above 810°C was allocated to calcite" and an approximation of 27% calcite was made. When the % CO_3^{2-} value obtained by acid-evolved CO_2 in this study is expressed as % calcite ($CaCO_3$), a value of 42.00% is obtained.

Since this value is based on $CO_2(g)$ evolution, a further check was made by dissolving a weighed quantity of the SHCa-1 specimen in a 2% hydrochloric acid solution, filtering, and bringing the total volume to 100 cm^3. The percentage Ca^{2+} ion was then determined using a Perkin-Elmer Model 5500 sequential scanning inductively coupled plasma emission spectrographic system. Thus, the acid soluble Ca^{2+} component was determined to be 16.0% by weight of raw SHCa-1 clay specimen. Assuming that all of the Ca^{2+} ions arrive via the acid reaction with the basic CO_3^{2-} anion of calcite, the percentage calcite may be calculated from this datum to be 40.0% calcite. The difference in this value and that for the calculation based on $CO_2(g)$ evolution can be explained as due to the presence of other carbonate species in the SHCa-1 specimen as well as any differences which might arise from the use of two different instrumental techniques.

The final, and possibly the most important, point to be made here involves the comparison of the TG data for the two cleanest hectorite specimens (Veegum T and "processed hectorite ore") and the acid evolved $CO_2(g)$ determinations. Since the acid evolved $CO_2(g)$ data were obtained on undried samples which were exposed to the same humidity environment as those in the thermogravimetry, the % CO_2 values in Table 3 may be compared to the percentage weight loss values for the 540–940°C temperature region given in Table 1. The difference in these two values for each of the carbonate-cleaned specimens may be used to determine that portion of percentage weight loss in the 540–940°C region which is not associated with carbonate decomposition. When this is done, the Veegum T and "processed hectorite ore" give weight loss values of 1.90% and 1.78%, respectively, in excess of that due to $CO_2(g)$ evolution. Since these two specimens contain different amounts of interlayer water, for comparative reasons these values should be adjusted to represent percentage weight loss based on the weight of sample at 540°C. When expressed in this manner, the Veegum T loses 2.06% and the "processed hectorite ore" specimen loses 1.95%.

Thus, the average percentage weight loss for these two industrially cleaned hectorite specimens which could possibly be assigned to the dehydroxylation of hectorite clay mineral in the 540–940°C, is 2.00%. This value is much lower than that predicted from the empirical formula of Ross and Hendricks [2] given earlier in this work. In the absence of interlayer water, and using the stoichiometry 4 $(-OH) \rightarrow 2$ $H_2O(g)$, the empirical formula predicts a weight loss of 4.72% for the hectorite clay mineral. Obviously, raw hectorite ores containing large quantities of carbonate component will give even smaller values than that observed for the Veegum T and "processed hectorite ore" of this study due to the contribution of the contaminant to the total weight of the sample.

These findings raise further questions regarding both the rate of dehydroxylation and temperature range of the dehydroxylation of hectorite clay mineral. They do, however, ascertain that the strong thermal events, ex-

hibited in the thermal curves of raw hectorite ores by TG, DTG, and DTA, in this temperature region are primarily due to the decomposition of carbonate component(s).

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