THERMOANALYTICAL INVESTIGATION OF CALCIUM CHROMATE

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ABSTRACT

Thermoanalytical methods have been used to study calcium chromate ($CaCrO_4$) samples. Thermal decomposition temperatures determined by TG in vacuum and by DTA in air could not be successfully used for screening purposes. Other thermogravimetry studies in air indicate that TG can be an effective quality control tool in screening out samples which have an assay value below 97.0% $CaCrO_4$. More complete analyses using TG in an argon atmosphere gave good results for $CaCO_3$ and H_2O content as well as for total $CaCrO_4$. Reliable measurement of $Ca(OH)_2$ was not achieved. Effluent gas analysis—mass spectrometry was used to identify gaseous products as a function of temperature, in order to verify interpretation of TG curves.

Thermogravimetry, differential scanning calorimetry, nuclear magnetic resonance, and mass spectrometry have been used in an effort to explain the unusual weight loss observed between 400 and 600°C for many $CaCrO_4$ samples. $Ca(OH)_2$ decomposition is not the primary cause of this weight loss, as originally suspected, but instead the loss appears to be due to volatilization of H_2O trapped in the $CaCrO_4$ crystal.

INTRODUCTION

Calcium chromate has long been used as the active cathode material in thermally activated voltaic cells (thermal cells) of the type $Ca/LiCl$—KCl, $CaCrO_4/Fe$ [1]. Recent investigations at Sandia Laboratories and at General Electric Neutron Devices Department (GEND) indicate that anhydrous calcium chromate should meet certain standards in order to perform satisfactorily in thermal cells. The most important requirement is a minimum assay value of 97.0% $CaCrO_4$. Included among other requirements are that the samples contain less than 1.0% $Ca(OH)_2$ and less than 1.0% $CaCO_3$.

Methods of analyzing calcium chromate are time consuming, and in some instances, the results are of uncertain accuracy. Approximately 14 h are needed to complete the analytical procedures currently being used. These procedures include: high temperature drying of the sample, iodometric titra-

tion of Cr(VI), EDTA titration of calcium, titration of OH^-, determination of CO_3^{2-} by measuring the volume of CO_2 liberated by acidification, emission spectroscopy, and particle-size analysis using a sedimentation method [2].

In the present work, thermoanalytical techniques have been studied as potential methods for rapidly determining the suitability of calcium chromate samples for use in thermal cells and thermal batteries. Thermal analysis obviously cannot be used to make all of the above determinations, but it might prove useful in evaluating the parameters most critical to use in thermal cells.

EXPERIMENTAL

Calcium chromate samples of various purities and from numerous suppliers were used in this investigation. Some of the samples were intentionally synthesized to be of low purity while others had impurities added to them. Suppliers included: General Electric Neutron Devices Department, Apache Chemical Co., Barium and Chemicals, Inc., BDH Chemicals, Ltd., Mineral Pigments Corp., Var-Lac-Oid Chemical Co., Spex Industries, Inc., and Gallard-Schlesinger Chemical Mfg. Corp. One sample was made at Sandia Laboratories by a method described earlier [3]. In order to avoid possible embarrassment to any manufacturer, each of the $CaCrO_4$ samples was arbitrarily given a code designation. Letters designate the manufacturer and each sample from that supplier is given a different number.

Thermogravimetry curves were obtained using a Cahn electrobalance system previously described [4]. Samples weighed approximately 20 mg and a constant heating rate of $10°C$ min^{-1} was used. Three different atmospheres were employed: static air, argon with a flow rate of 90 ml min^{-1}, and vacuum (10^{-3} torr).

Differential thermal analysis curves were obtained with a Stone differential thermal analysis system employing a technique described earlier [5]. The DTA heating rate was also $10°C$ min^{-1}.

Differential scanning calorimetric determinations were made using a Perkin—Elmer Model DSC-2 with a flowing argon atmosphere, platinum sample pans, and a $10°C$ min^{-1} heating rate.

The effluent gas analysis—mass spectrometry (EGA—MS) apparatus has been described in detail elsewhere [6]. Samples were heated at $5°C$ min^{-1} in an initial vacuum of $\sim5 \times 10^{-8}$ torr. The range of atomic mass units, 0—50, was scanned repeatedly. Peaks were automatically integrated, and computer plots of relative intensity versus temperature were obtained.

Nuclear magnetic resonance (NMR) data were obtained using standard techniques and equipment previously described [7].

Chemical measurements of $CaCrO_4$ purity were made by dissolving the sample in dilute HCl and determining the Cr(VI) using a standard iodometric titration procedure [8]. Total water was determined by heating the samples to $1000°C$, absorbing the volatilized water on $Mg(ClO_4)_2$, and weighing. It was assumed that the only carbon in the samples was in the form of carbonate. The carbonate content was determined simultaneously with the water by heating and absorbing the liberated CO_2 with NaOH on asbestos.

RESULTS AND DISCUSSION

Differential thermal analysis

A survey of the literature concerning the thermal decomposition of calcium chromate [9] indicates that there may be a relationship between purity and thermal stability of $CaCrO_4$ samples. In general, it has been observed that the greater the purity, the higher the thermal decomposition temperature. Differential thermal analysis was used in an attempt to relate purity to thermal decomposition temperature. Typical DTA thermal decomposition peaks are shown in Fig. 1. Although the shapes of these two peaks are different, no correlation was found involving the peak shape.

Figure 2 shows the correlation between DTA decomposition temperature and purity measured chemically. Two samples of high purity showed quite low decomposition temperatures, and in addition, the accuracy in determining the decomposition temperature is rather poor ($\pm 15°C$). Consequently, DTA decomposition temperature does not appear to be a good parameter to use in screening $CaCrO_4$ samples.

Thermogravimetry (vacuum)

Thermogravimetry curves run in a vacuum were also used to measure the thermal decomposition temperature for the various calcium chromate samples. The vacuum was employed to lower the decomposition temperature and bring it within the range of the TG furnace ($\sim 950°C$ max.). A plot of percent $CaCrO_4$ versus the thermal decomposition temperature for 10 samples is shown in Fig. 3. The temperature reported was the temperature at which one-half of the weight loss had occurred in the thermal decomposition step. It is apparent from these data that no useful correlation can be made between $CaCrO_4$ purity and TG thermal decomposition temperature.

Thermogravimetry (air)

A variety of types of TG curves were determined in an air atmosphere for the $CaCrO_4$ samples. Some typical examples of results are shown in Figs. 4

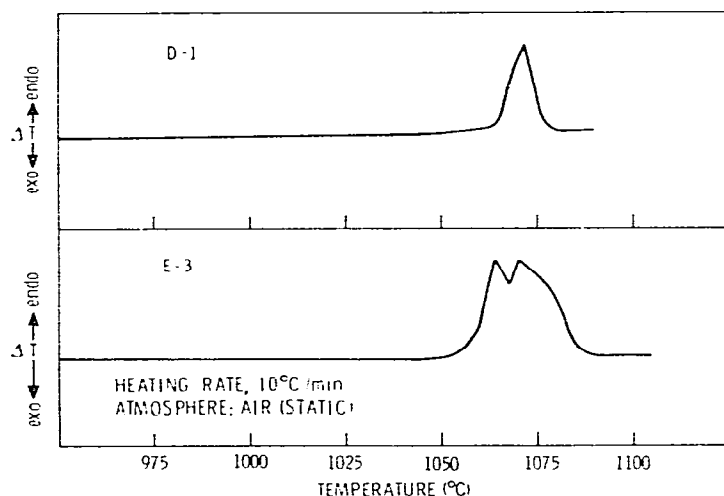Fig. 1. DTA curves for $CaCrO_4$ samples E-3 and D-1.

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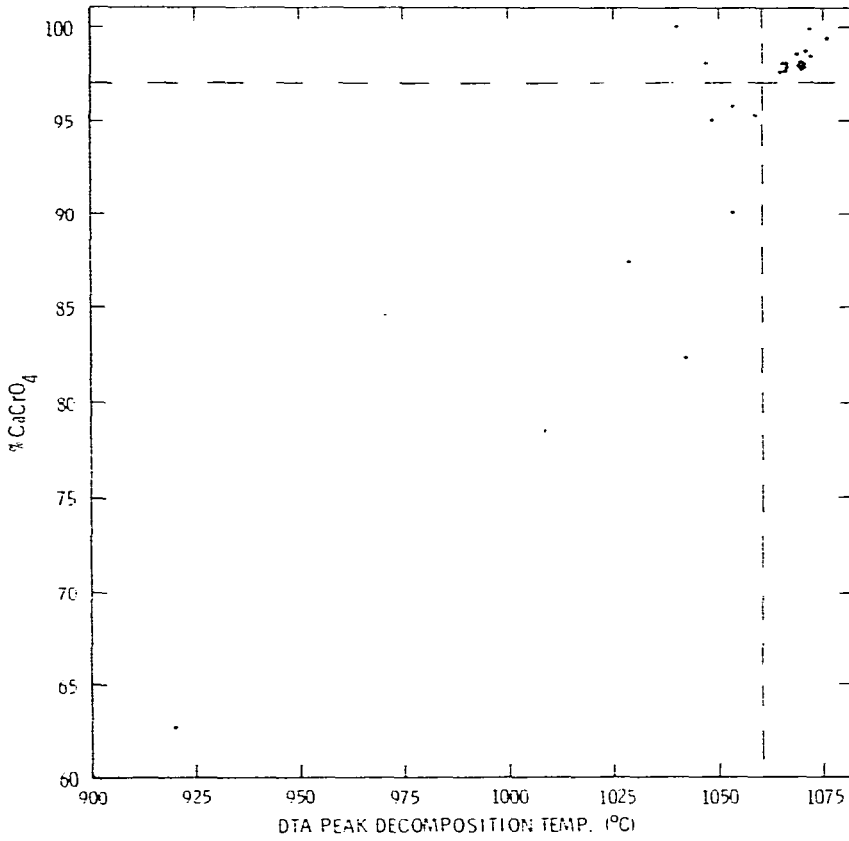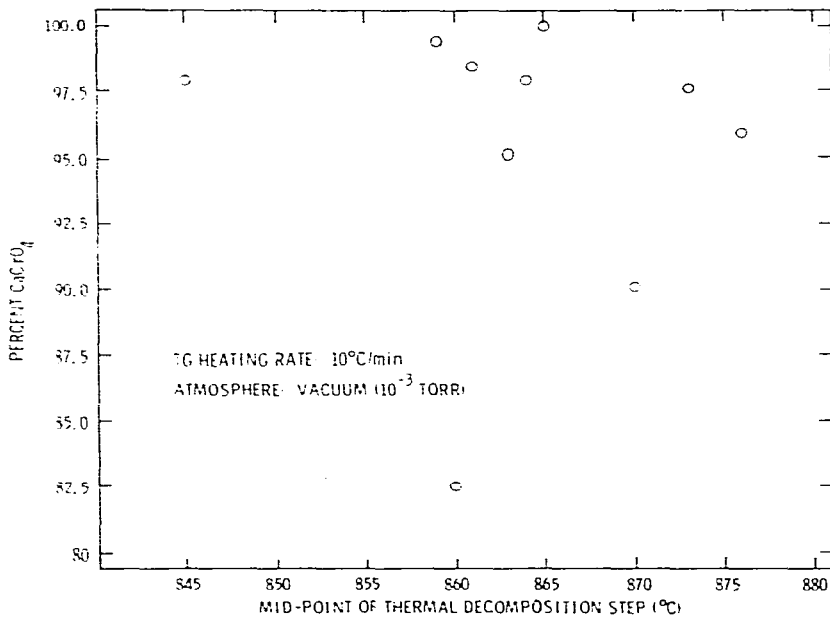Fig. 2. CaCrO$_4$ assay vs. DTA thermal decomposition peak temperatu

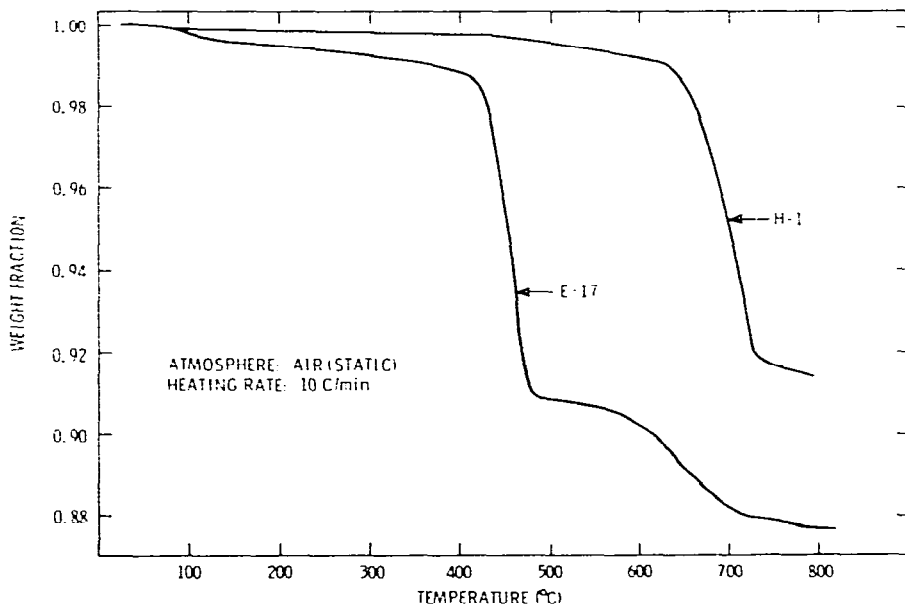
Fig. 3. CaCrO$_4$ assay vs. TG thermal decomposition temperature.

Fig. 4. TG curves for CaCrO₄ samples H-1 and E-17.

and 5. These particular curves show the results for two very impure samples (Fig. 4), some samples of high purity (D-1 and C-1, Fig. 5), and some intermediate purity samples (G-1 and B-1, Fig. 5).

It appears that there is an empirical relationship between the percent $CaCrO_4$ in the samples and the weight loss observed by TG. The TG weight percent at 730°C was chosen as the critical parameter. In Table 1, this parameter is compared with the chemically determined $CaCrO_4$ purity. The
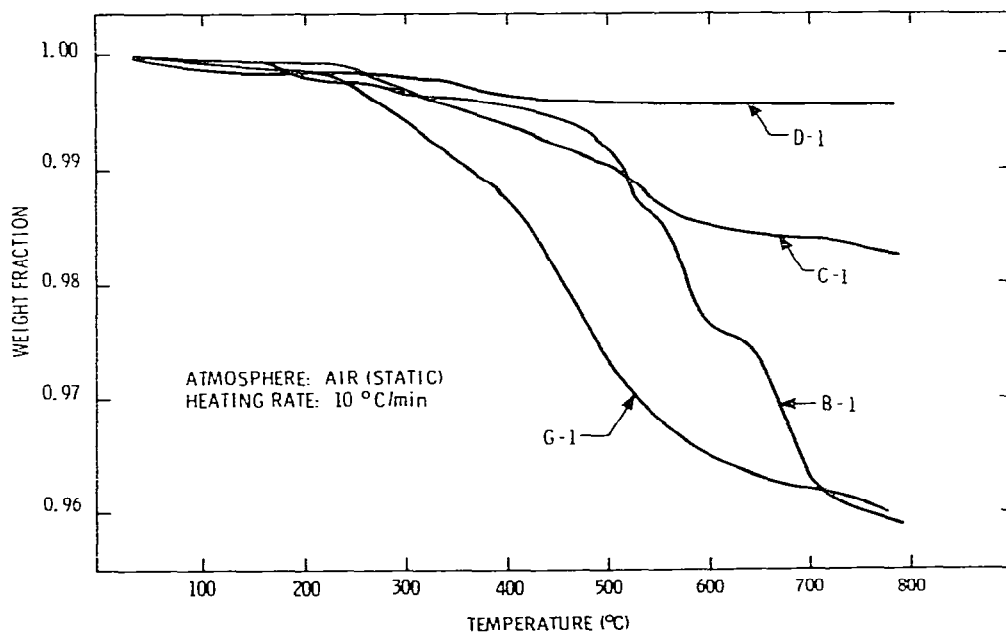
Fig. 5. TG curves for CaCrO₄ samples D-1, C-1, B-1 and G-1.

TABLE 1

Comparison of CaCrO$_4$ assay and TG weight at 730°C

Sample	% CaCrO$_4$	TG wt. % at 730°C
A-1	100.0	98.95
D-1	99.8	99.52
C-1	99.4	98.35
E-3	98.6	97.76
E-5	98.5	97.80
E-4	98.3	97.78
E-11	98.1	97.25
E-8	98.0	97.75
E-6	98.0	97.53
E-14	98.0	97.40
G-2	98.0	97.20
E-7	97.9	97.75
E-9	97.9	97.70
E-16 (W)	97.9	97.36
E-15 (W)	97.9	97.29
E-10	97.7	97.35
E-13	97.7	97.15
E-12	97.6	95.48
E-5 + 2.56 % Ca(OH)$_2$	95.9	96.88
G-1	95.8	96.10
E-2	95.2	95.84
E-1	95.0	95.70
E-5 + 7.8 % Ca(OH)$_2$	90.7	96.08
B-1	90.1	96.05
I-1	87.4	96.03
E-5 + 14.8 % Ca(OH)$_2$	83.7	94.20
H-1	82.4	91.80
E-17	62.7	87.95

agreement between those samples which met the purity specification (min. 97.0% CaCrO$_4$) and those which maintained a TG weight percent of 97.0 or higher is very good. The correlation was poor for only one sample, E-12. There is no apparent explanation for this anomaly. For all other samples, TG weight percent at 730°C could be used to rapidly determine whether a sample would meet the minimum purity requirement.

Samples E-15(W) and E-16(W) have the (W) designation to indicate that they were taken directly from the filter and analyzed while still very wet. The TG curve for E-15(W) is shown in Fig. 6. The sample was maintained at room temperature (25°C) for ~70 min before reaching an equilibrium weight. Upon heating, additional water was lost with the large step ~160—180°C due to the conversion of CaCrO$_4$ · H$_2$O to anhydrous CaCrO$_4$ [10]. The TG curve above 180°C is similar to those observed for most type E-CaCrO$_4$ samples which are normally dried 16 h at 140°C as part of their preparation. This drying is sufficient to convert the material to anhydrous CaCrO$_4$. In order to normalize the TG data for all samples, the TG weight percents listed in Table 1 are based on the TG weight at 180°C as 100%.
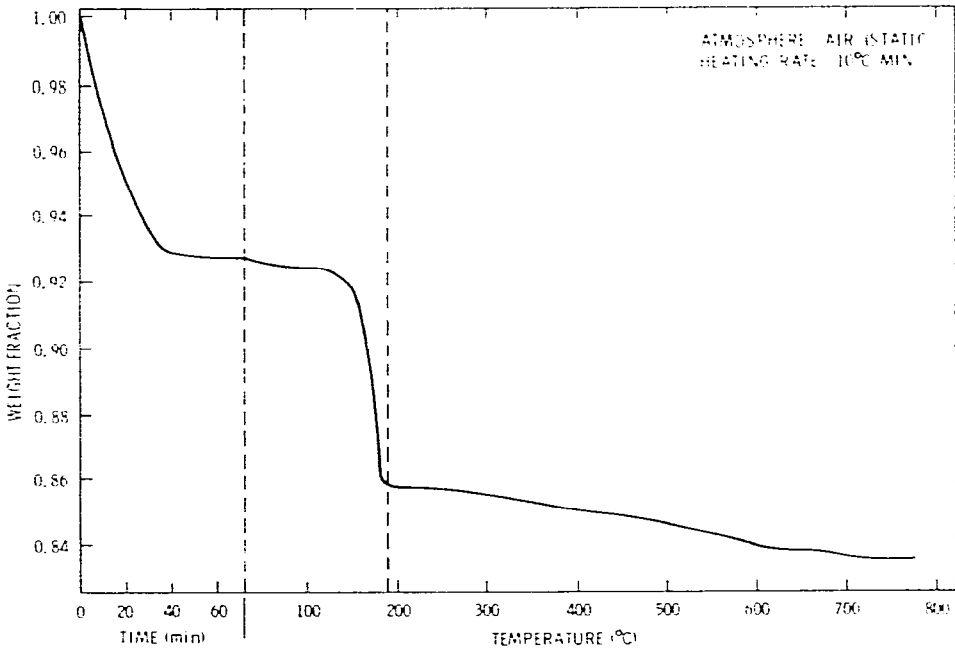
Fig. 6. TG curve for E-15(W) CaCrO$_4$.

These data indicate that it would be possible to remove calcium chromate samples directly from the filter or centrifuge and analyze them immediately via TG to determine if they will meet the purity specification.

Thermogravimetry (argon)

A more complete quantitative analysis of the CaCrO$_4$ was achieved through TG studies in argon. The argon atmosphere was necessary because
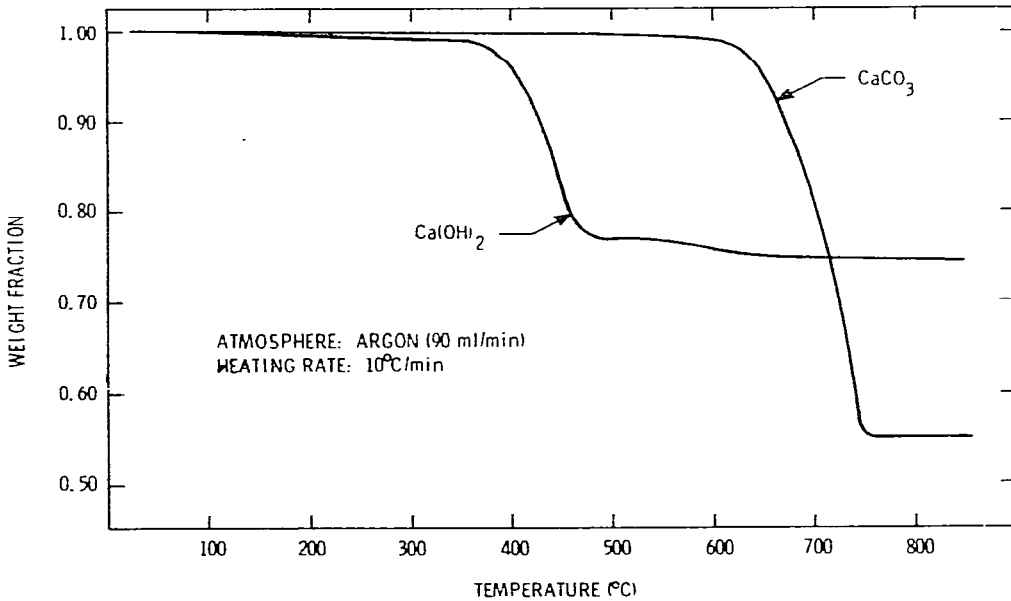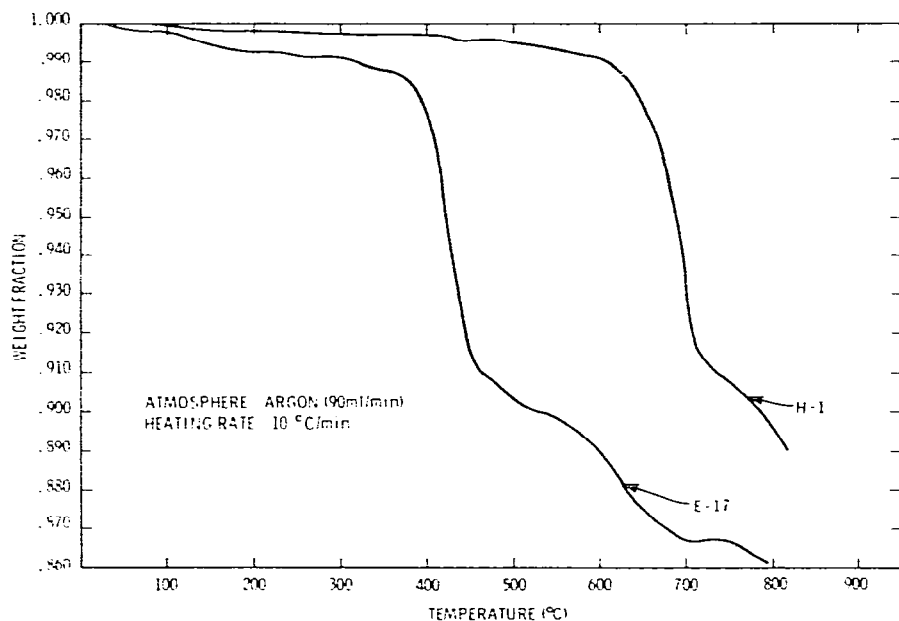

Fig. 7. TG curves for CaCO$_3$ and Ca(OH)$_2$ in argon.

Fig. 8. TG curves for H-1 and E-17 CaCrO₄ samples in argon.

one of the major impurities in $CaCrO_4$ is $Ca(OH)_2$. When heated in air, $Ca(OH)_2$ loses H_2O to form CaO, but some of the CaO reacts with the CO_2 in the air to form $CaCO_3$ [11]. Consequently, the observed weight loss for the $Ca(OH)_2$ decomposition will be too small, and a weight loss attributable to decomposition of the $CaCO_3$ formed will be observed at higher temperatures. The use of a CO_2-free argon atmosphere prohibits this interfering reaction.

Some representative TG curves in argon are shown in Figs. 7–9. Figure 7 shows the curves for two major impurities ($CaCO_3$ and $Ca(OH)_2$) frequently

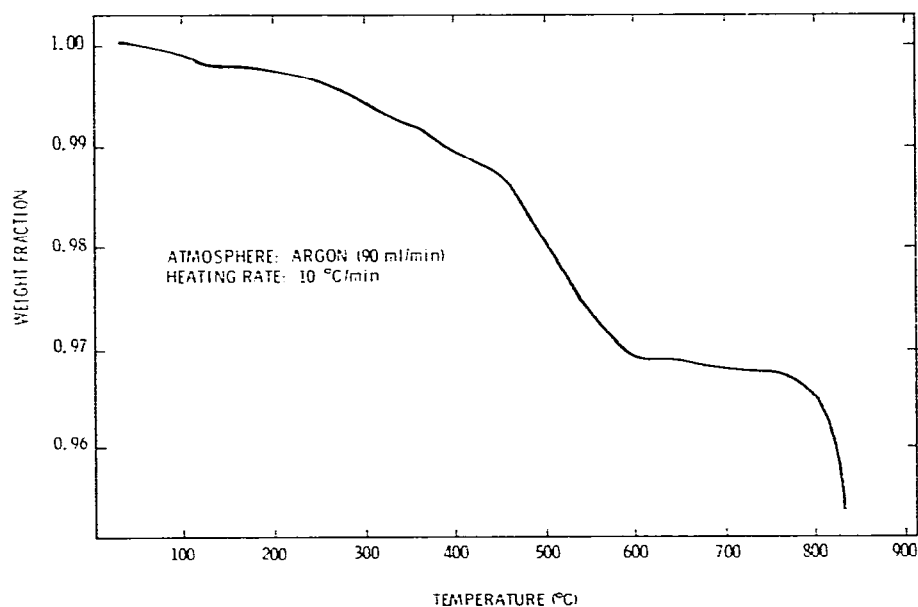Fig. 9. TG curve for E-13 CaCrO₄ in argon.

TABLE 2

Comparison of TG and chemical analyses for $CaCrO_4$

Sample	Analyses from TG in argon						Chemical analyses			
	Total H_2O (%)	H_2O from $Ca(OH)_2$ (%)	CaO at 600°C (%)	CO_2 (%)	$CaCO_3$ at 600°C (%)	$CaCrO_4$ at 600°C (%)	Total H_2O (%)	CO_2 (%)	$CaCO_3$ at 600°C (%)	$CaCrO_4$ at 600°C (%)
E-3	2.2	0.4	1.3	0.0	0.0	98.7	2.8	0.06	0.14	98.6
E-13	3.1	0.4	1.3	0.2	0.5	98.2	3.0	0.3	0.7	97.7
E-12	4.2	0.3	1.0	0.4	0.9	98.1	3.3	0.35	0.8	97.6
G-1	4.0	1.3	4.2	0.2	0.5	95.3	3.9	0.25	0.6	95.8
E-2	4.0	0.6	1.9	0.1	0.9	97.2	4.5	0.2	0.4	95.2
B-1	2.6	0.9	2.9	1.9	4.4	92.7	4.9	1.4	3.3	90.1
I-1	2.0	1.5	4.8	2.2	5.1	90.1	1.7	2.1	4.8	87.4
F-1	5.7	3.4	11.2	1.1	2.7	86.1	6.0	0.9	2.2	86.3
H-1	0.9	0.1	0.3	7.8	17.9	81.8	0.6	7.7	17.6	82.4
E-17	10.5	9.1	31.6	2.6	6.6	61.8	10.6	2.3	5.9	62.7
$CaCO_3$	1.0	0.0	0.0	44.0	101.0	−1.0	1.0	44.1	101.2	0.0
$Ca(OH)_2$	23.1	22.2	89.8	2.6	7.7	2.5	23.3	2.2	6.5	0.0

found in $CaCrO_4$. In Fig. 8, for E-17 $CaCrO_4$, loss of H_2O (absorbed and/or hydrated) is observed up to ~350°C with a large H_2O loss ~425°C due to $Ca(OH)_2$ decomposition. This is followed by a loss of CO_2 from $CaCO_3$ in the 600—700°C range. For H-1 $CaCrO_4$, the major event is a large CO_2 loss indicating high $CaCO_3$ content.

Figure 9 shows a TG curve in argon for $CaCrO_4$ sample E-13. This is representative of behavior of the purer samples and the weight loss steps are not as clearly defined.

Analyses of total H_2O, $Ca(OH)_2$, and $CaCO_3$ content were made from TG curves in argon for 12 samples. CaO content at 600°C was calculated based on the $Ca(OH)_2$ determination. $CaCrO_4$ content at 600°C was then calculated by assuming that the only significant impurities present at room temperature were H_2O, $Ca(OH)_2$, and $CaCO_3$, and that, consequently, only CaO and $CaCO_3$ were present at 600°C. These data are compared with corresponding data based on chemical analyses in Table 2. It will be observed that the agreement is quite good. No values are reported for chemical analyses of $Ca(OH)_2$ since no reliable chemical method of determining OH^- in the small quantities present was found.

The equations used for these calculations are as follows:

$$\% \ CaO_{(600°C)} = \% \ H_2O_{(from \ Ca(OH)_2)} \times \frac{mol. \ wt. \ CaO}{mol. \ wt. \ H_2O} \times \frac{100}{100 - \% \ H_2O_{(total)}}$$

$$\% \ CaCO_{3(600°C)} = \% \ CO_2 \times \frac{mol. \ wt. \ CaCO_3}{mol. \ wt. \ CO_2} \times \frac{100}{100 - \% \ H_2O_{(total)}}$$

$$\% \ CaCrO_{4(600°C)} = 100 - \% \ CaO_{(600°C)} - \% \ CaCO_{3(600°C)}$$

EGA—mass spectrometry studies were used to confirm identification of the weight loss reactions observed in TG. The temperature for any given thermal event will be lower using EGA than with TG, because the EGA data were obtained in vacuum and the TG results were obtained in flowing argon. Agreement between the two methods was excellent recognizing that a 1-to-1 correlation in temperatures will not exist.

Figures 10—13 show the EGA results for four samples. For $CaCrO_4$ H-1 (Fig. 10), a relatively small peak (400—500°C) is observed corresponding to the evolution of principally H_2O. The major EGA peak at 550—600°C is due to loss of CO_2. At higher temperatures (above 650°C), decomposition of the $CaCrO_4$ occurs as evidenced by the very broad O_2^+ peaks in the EGA curve. A trace of SO^+ is also noted which is probably indicative of a small sulfate contamination in the sample. These results correlate well with the TG data for sample H-1 shown previously in Fig. 8. The TG results (Table 2) indicated 0.9% total H_2O and 7.8% CO_2.

Figure 11 shows the EGA data for $CaCrO_4$ B-1. Again, the data correlate well with the TG results. These data indicate that the amount of H_2O was higher and the CO_2 lower for sample B-1 than for $CaCrO_4$ H-1. These indications are confirmed by comparing the data for samples H-1 and B-1 in Table 2. Figure 12 shows the EGA results for $CaCrO_4$ I-1. An interesting feature here is that both Na^+ and Cl^+ were detected, indicating the presence of NaCl
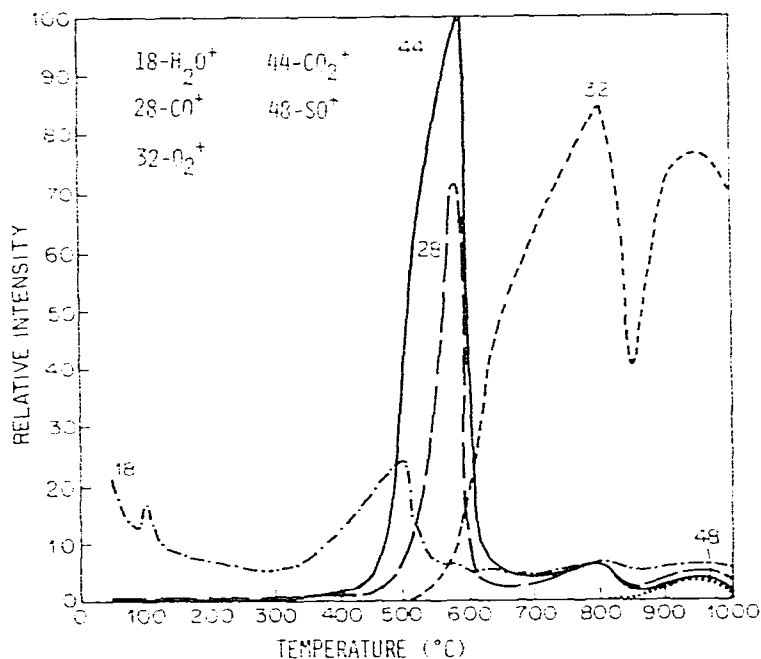
Fig. 10. EGA curves for H-1 CaCrO$_4$.

in the sample. This may have been a side product of the production process which was not thoroughly removed. For example, the CaCrO$_4$ may have been precipitated according to the reaction: CaCl$_2$ + Na$_2$CrO$_4$ → CaCrO$_4$ + 2 NaCl.

Figure 13 is interesting in that it indicates a large H$_2$O loss for CaCrO$_4$ sample E-12 at high temperature (375–575°C). The TG curves for this
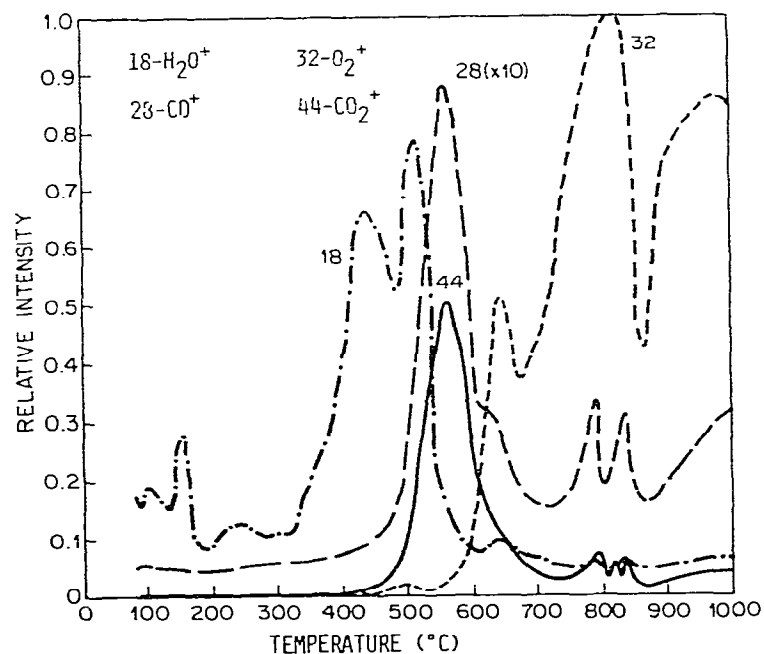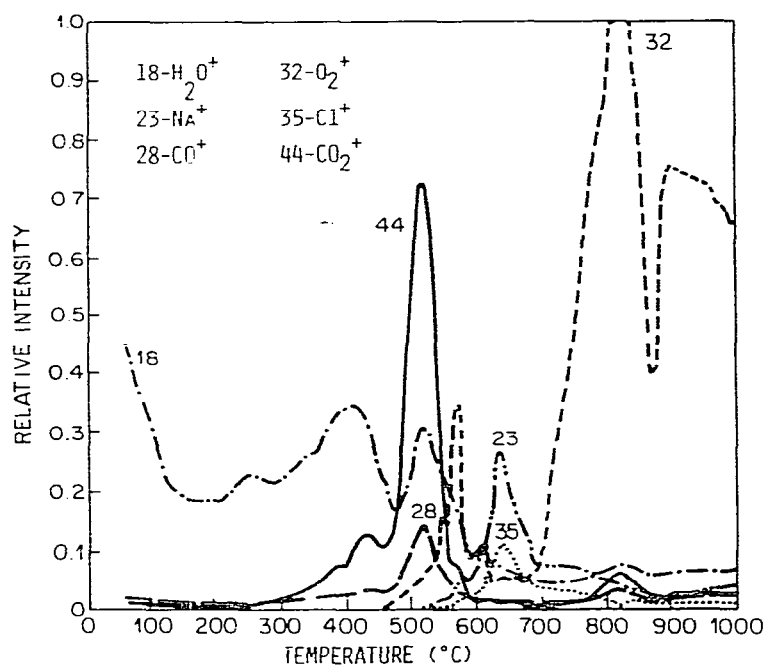

Fig. 11. EGA curves for B-1 CaCrO$_4$.

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Fig. 12. EGA curves for I-1 CaCrO₄.

sample in both air and argon are shown in Fig. 14, and a corresponding large weight loss may be observed in the vicinity 450—550°C. Although good chemical analyses for Ca(OH)₂ were not established, indications were that this sample did not contain sufficient Ca(OH)₂ to account for this weight loss. DSC curves were run for sample E-12 and compared with DSC curves for a sample known to contain large amounts of Ca(OH)₂ impurity and for
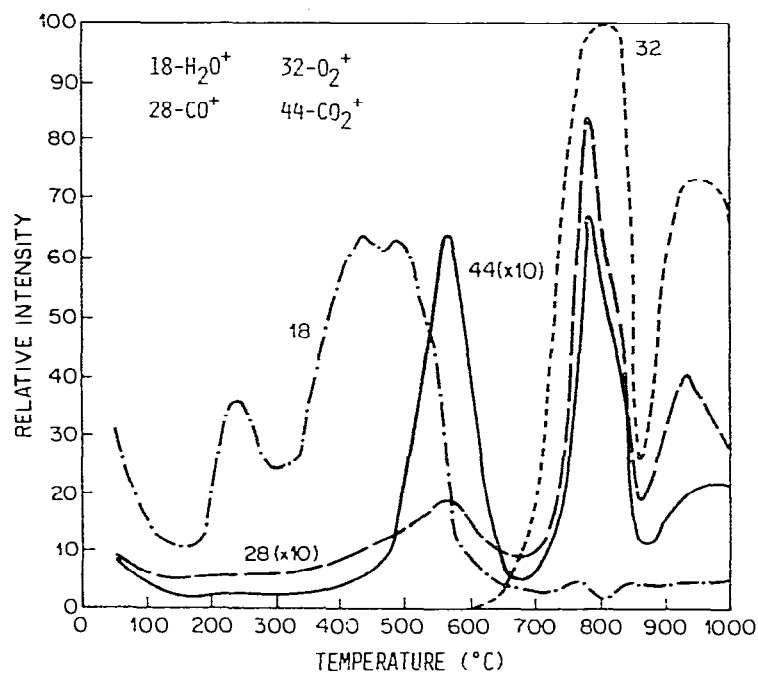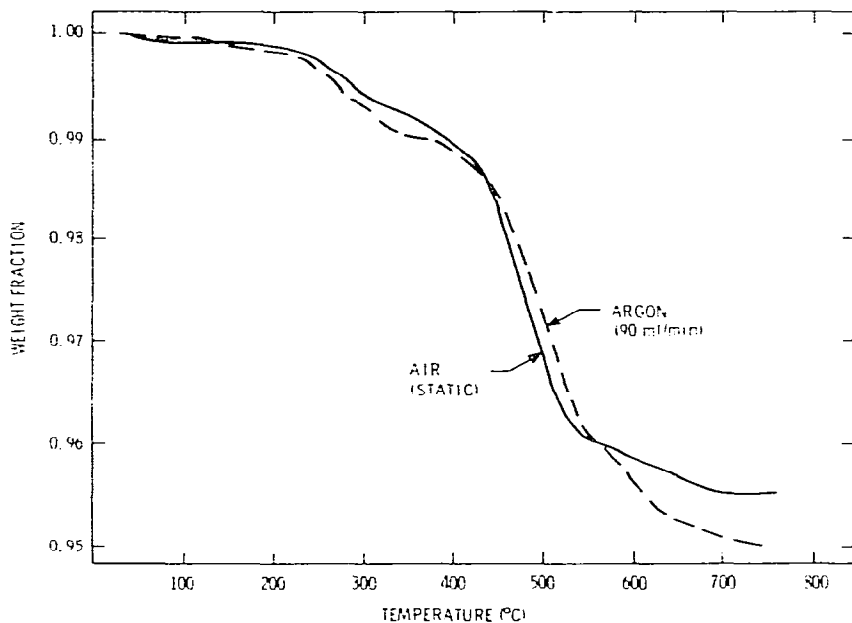

Fig. 13. EGA curves for E-12 CaCrO₄.

Fig. 14. TG curves for E-12 CaCrO$_4$ in air and argon.

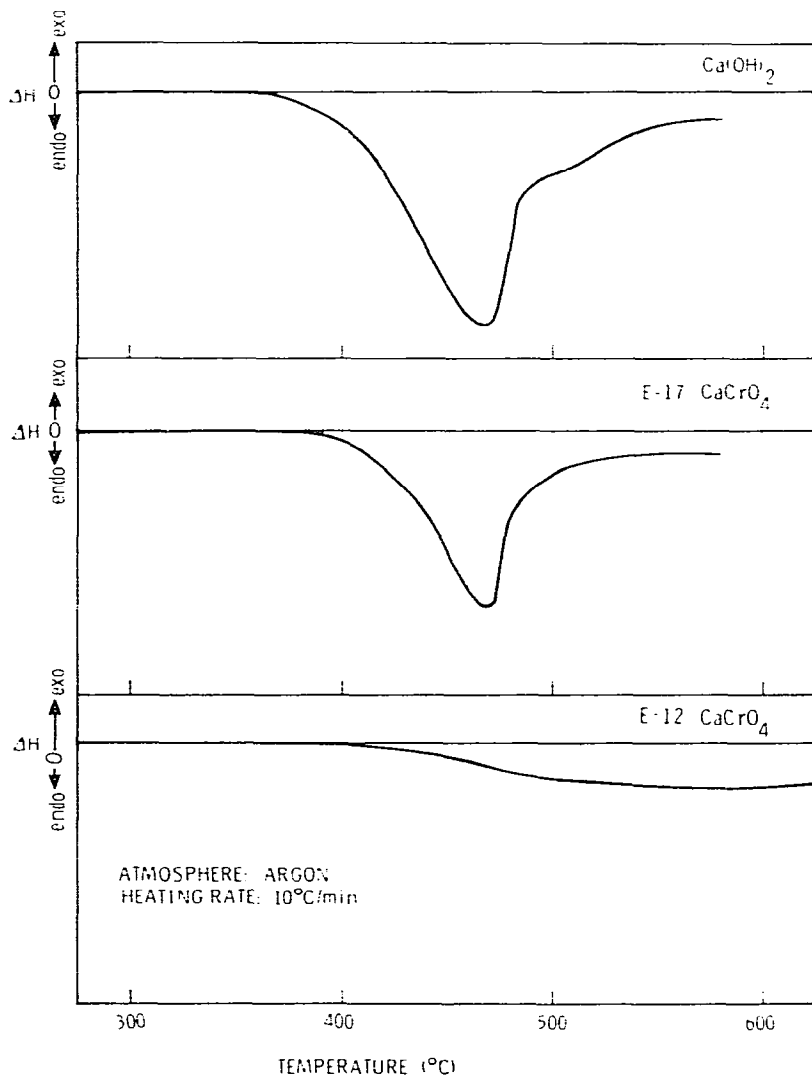Fig. 15. DSC curves for Ca(OH)$_2$, E-17 CaCrO$_4$, and CaCrO$_4$.

Ca(OH)$_2$ itself. These data, which are seen in Fig. 15, indicate that the water released from sample E-12 is not due to Ca(OH)$_2$ impurity.

The belief that this H$_2$O released around 500°C is not from Ca(OH)$_2$ was further supported by NMR studies. The NMR investigations showed that the H$_2$O which remained in the CaCrO$_4$ sample after heating to 400°C was present as water and not as hydroxide. In addition, a sample believed to be very low in Ca(OH)$_2$ content (E-5) was doped with 7.8% Ca(OH)$_2$. A TG curve for that sample (see Fig. 16) was distinctly different from that observed for E-12 (Fig. 14), also indicating that the weight loss for E-12 was due to H$_2$O from a source other than Ca(OH)$_2$.

It was also observed that a great deal of movement occurred in the E-12 CaCrO$_4$ sample at ~500°C during the water loss. On occasion, a significant amount of sample actually jumped out of the TG sample pan. Thus, the water appears to be very tightly bound in the CaCrO$_4$ crystals themselves, leading one to suspect the existence of a hydrated form of calcium chromate. Four hydrates of calcium chromate are known [12]: a hemihydrate, a mono-hydrate, and two different dihydrates. However, all four of these compounds lose their water of hydration at temperatures below 200°C. Mylius and von Wrochem report that, when calcium chromate hydrates are heated, pseudo-morphism can occur, forming materials such as CaCrO$_4$ ·1/4 H$_2$O, and that the expulsion of water from the pseudomorphous material "begins only at considerably higher temperatures" [12]. The same authors also observe that, when these materials are "heated to incandescence, they break up in a very striking way, forming a mealy powder." They state that the water in the pseudomorphous substance is more tightly bound than in the normal hydrates. Thus, it appears that the type E samples in general and, in particu-lar, sample E-12 contain bound water which is not removed until tempera-tures in the vicinity of 550°C are reached. This conclusion is in agreement

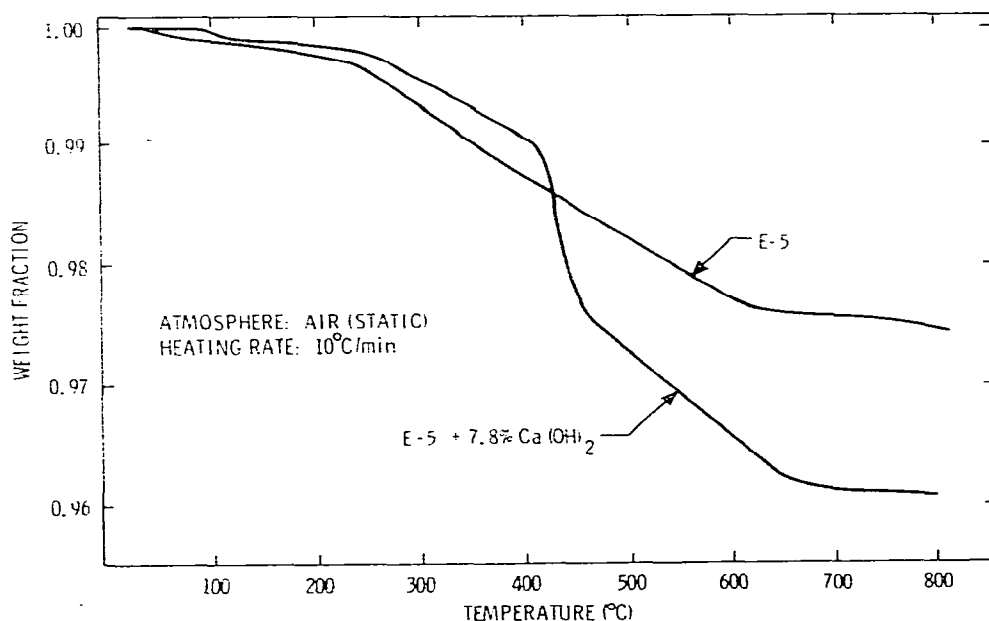Fig. 16. TG curves for E-5 CaCrO$_4$ with and without Ca(OH)$_2$.

with our TG, EGA, and NMR data as well as with the visual observations of the sample during heating.

CONCLUSIONS

Two techniques, DTA in air and TG in vacuum, have been used to determine the thermal decomposition temperature of the $CaCrO_4$ samples. Attempts to establish a quality control screening method by relating the thermal decomposition temperature to $CaCrO_4$ purity have been unsuccessfull. However, it has been shown that TG in air offers promise as a rapid quality control tool for screening $CaCrO_4$ samples for use in thermal batteries. Samples may be screened in this manner even when taken wet from the filter before any drying. The significant parameter appears to be the TG sample weight at 730°C. This weight should not drop below 97.0% (of the weight at 180°C) for acceptable samples.

In addition, when TG data are obtained in an argon atmosphere, values for total H_2O, $CaCO_3$, $Ca(OH)_2$, and $CaCrO_4$ may be determined. Comparison with chemical analyses indicate that the TG results are quite accurate for H_2O, $CaCO_3$, and $CaCrO_4$. No accurate chemical analysis data are available for comparison in the case of low concentrations of $Ca(OH)_2$ impurities.

The final conclusion is that many type E samples contain small amounts of tightly bound H_2O which are released from the calcium chromate crystals in the vicinity of 500—550°C.

ACKNOWLEDGEMENTS

REFERENCES

1 B.H. Van Domelen and R.D. Wehrle, Proc. 9th Intersoc. Energy Conversion Eng. Conf., The American Society of Mechanical Engineers, 1974.
2 W.W. Welbon and R.J. Antepenko, GEND Technical Memorandum GEPP-166, 1975, pp. 31—8.
3 R.P. Clark, R.L. Blucher and H.J. Goldsmith, J. Chem. Eng. Data, 14 (1969) 465.
4 R.P. Clark and F.W. Reinhardt, Thermochim. Acta, 8 (1974) 185.
5 R.P. Clark and F.W. Reinhardt, Thermochim. Acta, 12 (1975) 309.
6 P.K. Gallagher, Thermochim. Acta, 26 (1978) 175.
7 R.A. Assink and G.L. Wilkes, Polym. Eng. Sci., 17 (1977) 606.
8 N.H. Furman (Ed.), Standard Methods of Chemical Analysis, Van Nostrand, New York, NY, 1962, p. 357.
9 R.P. Clark and S.C. Levy, Sandia Laboratories Research Report SC-RR-72-0693, 1973.
10 R.P. Clark, Sandia Laboratories Report SAND77-0647, 1977.
11 G. Liptay (Ed.), Atlas of Thermoanalytical Curves, Heyden, New York, 1973, No. 60.
12 F. Mylius and J. von Wrochem, Abh. Phys. Tech. Reichanst., 3 (1900) 462; Sandia Laboratories Report SAND76-6028, 1976.