Thermochimica Acta, 166 (1990) 357–367
Elsevier Science Publishers B.V., Amsterdam

A TG METHOD OF ANALYSIS FOR USE IN MONITORING THE EFFICIENCY OF FLUIDIZED-BED COAL COMBUSTION PROCESSES *

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(Received 25 July 1989)

ABSTRACT

A TG method developed for the analysis of reaction products in fluidized-bed coal combustion processes in which limestone is added for sulphur capture was modified and further refined. The method is now capable of determining H_2O, $Ca(OH)_2$, $CaCO_3$, carbonaceous materials, $CaSO_4$ and Fe_2O_3 in the samples. The viability and accuracy of the method were verified by analysing reagent grade mixtures and fluidized-bed samples from a pilot-scale fluidized-bed coal combustion process and comparing the results with those of other methods. The TG method may be used to monitor the efficiency of coal combustion and limestone utilization in fluidized-bed processes.

INTRODUCTION

Fluidized-bed coal combustion technology for power generation continues to gain widespread acceptance in many countries owing to its environmental advantages. In this relatively new technology, combustion of coal takes place in fluidized-bed reactors in which limestone ($CaCO_3$) is injected to react with sulphur oxide gases released during the combustion process, before being emitted to the environment.

In the combustion chamber of a fluidized-bed reactor several reactions occur. The major reaction is the combustion of coal with air to form carbon dioxide. At the same time the coal sulphur is oxidized to form sulphur oxide gases, mainly SO_2. Another major reaction is the decomposition of limestone to CaO, which, in the presence of oxygen, reacts with SO_2 to form $CaSO_4$. The latter reaction takes place with the formation of a low-porosity sulphate layer at the surface of the oxide particle, gradually separating the gaseous

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* Presented at the 18th Annual NATAS Conference, San Diego, CA, U.S.A., 24–27 September 1989.

reactants from the reaction interface and halting the progress of sulphation. Besides the sulphate layer, an outer thin layer of coal ash deposit, which may contain a substantial amount of Fe_2O_3, also exists [1,2].

To monitor the efficiency of coal combustion and limestone utilization in fluidized-bed reactors, a reliable and convenient method is required for the analysis of the complex mixture of ash products at different stages of the process. In an earlier stage of this work [3], a method using thermogravimetry (TG) was developed for the analysis of the major components of such products which may contain some or all of the following compounds: $CaSO_4$, $CaCO_3$, CaO, SiO_2, $Ca(OH)_2$, H_2O, carbonaceous materials and coal ash. The method involves the heating of the sample in an O_2/N_2 atmosphere to 750 ° C, during which period successive weight losses corresponding to the evolution of adsorbed H_2O (~ 100 ° C), the dehydroxylation of $Ca(OH)_2$ (~ 400 ° C), the combustion of carbonaceous materials (500–550 ° C) and the decomposition of $CaCO_3$ (600–750 ° C) take place. At 750 ° C, while heating, the oxygen flow is discontinued and at 900 ° C, isothermally, an H_2/N_2 gas mixture is introduced to effect the reduction of $CaSO_4$ to CaS. The method, which was therefore capable of the quantitative determination of H_2O, $Ca(OH)_2$, carbonaceous materials, $CaCO_3$ and $CaSO_4$, was used to analyse numerous samples from a pilot-scale fluidized-bed coal combustion process. The following observations prompted further development of the method.

(1) TG curves of samples with a relatively high $Ca(OH)_2$ content (owing to hydration of the material during cooling in the reactor or during storage) showed a noticeable weight gain, immediately following the dehydroxylation weight loss around 400 ° C, Fig. 1a. The weight gain, which often overlapped with the dehydroxylation weight loss before, and with the weight loss from the combustion of the carbonaceous materials after, did not occur when the samples were heated in an N_2 atmosphere instead of O_2/N_2, Fig. 1b. X-ray diffraction (XRD) analysis of the sample just after the weight gain indicated the disappearance of $Ca(OH)_2$ and an increase in the $CaCO_3$ content. This behaviour may be explained on the basis of the formation of a highly porous CaO on the dehydroxylation of $Ca(OH)_2$. This reactive product, in the presence of carbonaceous materials and an oxidizing atmosphere, may react according to

$$CaO + C + O_2 = CaCO_3 \tag{1}$$

The formation of carbonate by this reaction was also evident from the larger weight loss from the decomposition of $CaCO_3$ in air, Fig. 1a, compared with that in N_2, Fig. 1b.

(2) In some samples examined, the resolution of the two successive weight losses from combustion of carbonaceous materials and decomposition of $CaCO_3$ was incomplete. Various factors such as sample particle size and geometry, heating rate, impurity content and the gaseous atmosphere

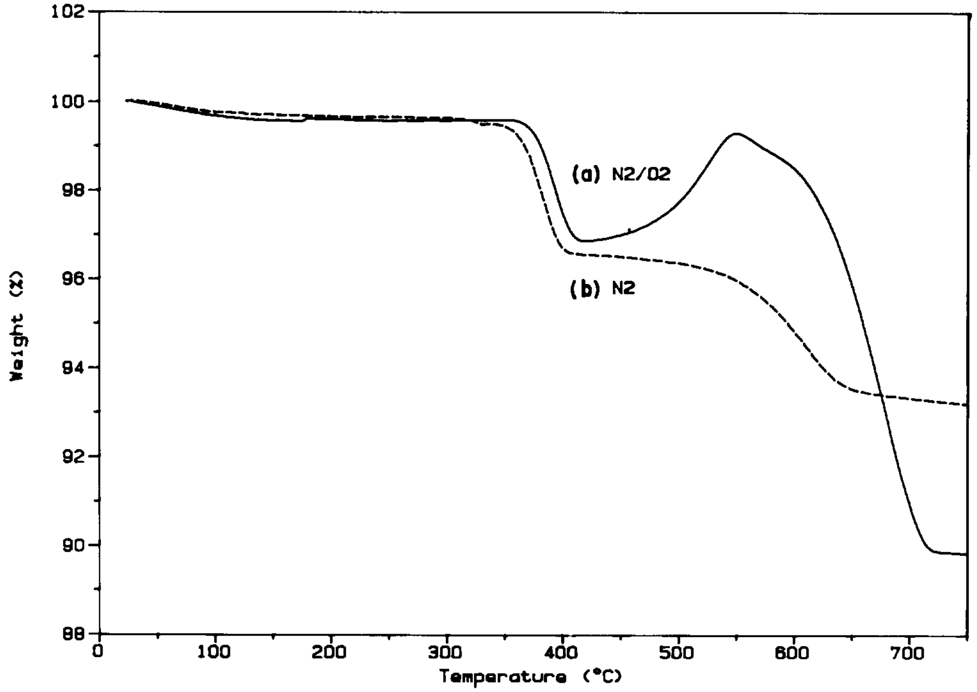

Fig. 1. TG curves for fluidized-bed coal combustion residues in oxidizing (a) and inert (b) atmospheres.

surrounding the particles influence the temperatures at which these reactions commence and terminate.

(3) Quantitative determinations of $CaSO_4$ in many samples by TG seem to result in consistently higher values than those obtained by a variety of other methods. XRD patterns of such samples indicated that iron is present mainly as Fe_2O_3 in the starting material and as metallic iron in the product after the TG analysis. It was therefore evident that the weight loss during the reduction step was not only due to the reduction of $CaSO_4$, but also due to that of iron oxide. The effect will be most severe with coals, such as many eastern Canadian coals, that have ash with a high iron content.

MATERIALS AND EXPERIMENTAL PROCEDURE

Ash samples from a pilot-scale fluidized-bed coal combustor in which limestone is added for sulphur capture were used in the present work. Prepared mixtures of reagent-grade CaO, $CaCO_3$, $CaSO_4$, C, SiO_2 and Fe_2O_3, analysed previously using methods other than thermal analysis, were also used. For the thermal analysis, a Du Pont 9900TA with a 951 TGA module was employed. X-ray diffraction and microscopic examinations were

TABLE 1

A summary of the proposed TG method

Temperature [a]/time programme	Gaseous atmosphere (100 ml min^{-1} total flow rate)	Determination
Heating 20 °C min^{-1} to 750 °C	N_2	H_2O, $Ca(OH)_2$, $CaCO_3$, carbonaceous materials
Isothermal 10 min	60% N_2/40% O_2	
Cooling 20 °C min^{-1} to 550 °C	N_2	
Isothermal 10 min	70% N_2/30% H_2	Fe_2O_3
Heating 20 °C min^{-1} to 875 °C	70% N_2/30% H_2	$CaSO_4$
Isothermal 20 min	70% N_2/30% H_2	

[a] Sample thermocouple temperature.

used as supplementary techniques. The sample thermocouple was protected from potential attack by gaseous products in different atmospheres by a thin coat of alumina paste.

The TG method

The proposed TG method is based on the implementation of some changes and modifications to the above-mentioned method. The first part is similar to that used by earlier investigators in the proximate analysis of coal using thermogravimetry [4,5]. In the present procedure, however, it is assumed that the amount of coal volatiles in the fluidized-bed samples is negligible. The experimental procedure is summarized in Table 1.

RESULTS AND DISCUSSION

During the course of the method, preliminary determinations of sample components listed in Table 1 were based on weight losses corresponding to

$$H_2O(l) = H_2O(g) \quad (2)$$

$$Ca(OH)_2 = CaO + H_2O(g) \quad (3)$$

$$CaCO_3 = CaO + CO_2 \quad (4)$$

$$C + O_2 = CO_2 \quad (5)$$

$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O(g) \quad (6)$$

$$CaSO_4 + 4H_2 = CaS + 4H_2O(g) \quad (7)$$

Reactions (2), (3) and (4) take place as the sample is heated in an inert atmosphere. Reaction (5) occurs in an oxidizing atmosphere and reactions (6) and (7) in a reducing one. In the reduction stage, the modification introduced to separate the reduction of iron oxide from that of $CaSO_4$ was carried out after examining the reduction of the Fe_2O_3 alone and mixed with

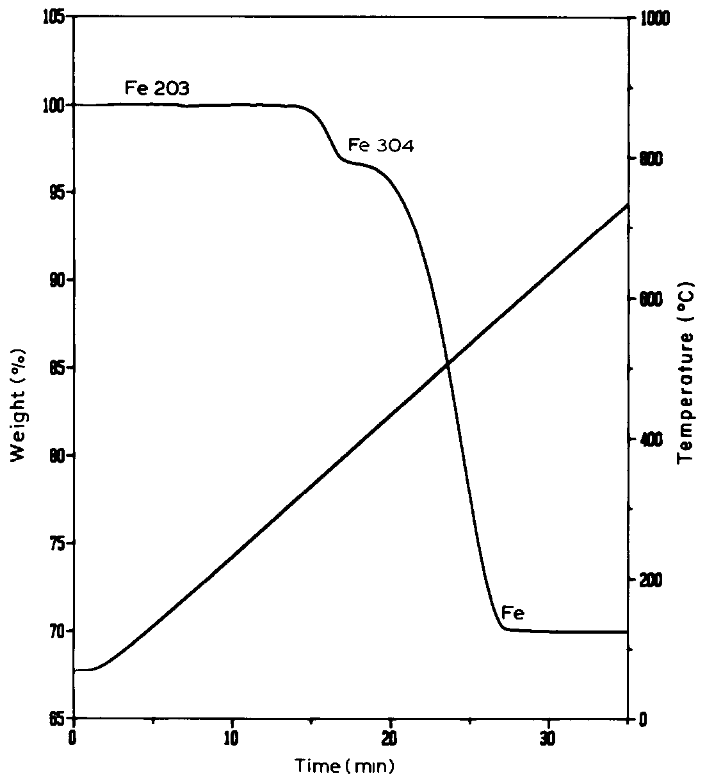

Fig. 2. TG curve for Fe_2O_3 in an N_2/H_2 atmosphere.

$CaSO_4$. The latter was studied in detail earlier [3]. Figure 2 shows a TG curve for the reduction of Fe_2O_3 in an H_2/N_2 atmosphere. The reaction was found to occur stoichiometrically in the temperature range 300–550 °C in two stages with the formation of Fe_3O_4 as an intermediate product. Figure 3 shows a TG curve for a mixture of Fe_2O_3 and $CaSO_4$, indicating that the reduction of the two compounds takes place according to reactions (6) and (7) individually with no detectable interference.

The validity and accuracy of the method was examined by analyzing five different mixtures prepared from reagent grade materials simulating fluidized-bed samples. The mixtures had been previously analyzed in different laboratories by methods other than thermal analysis. TG curves of the mixtures following the proposed TG method are presented in Fig. 4. The quantitative determination of six constituent materials, namely H_2O, $Ca(OH)_2$, $CaCO_3$, C, Fe_2O_3 and $CaSO_4$ were made on the basis of the six steps of weight loss shown on the curves. It is apparent that, by using an inert atmosphere in the first part of the method, the carbonation of CaO according to reaction (1) and the overlap of the decomposition and the combustion and reactions (4) and (5) are avoided. In addition, by modifying

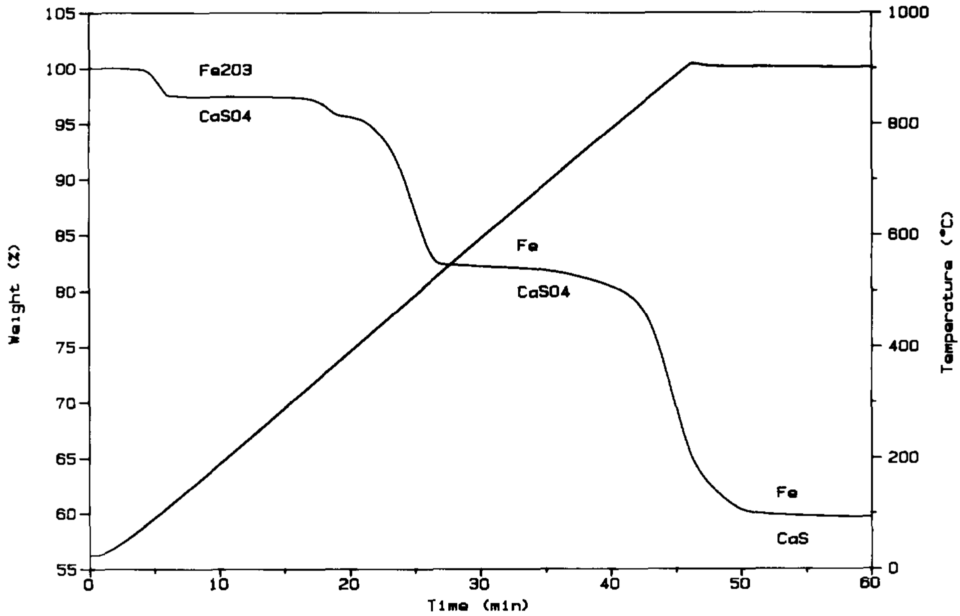

Fig. 3. TG curve for a mixture of Fe_2O_3 and $CaSO_4$ and an N_2/H_2 atmosphere.

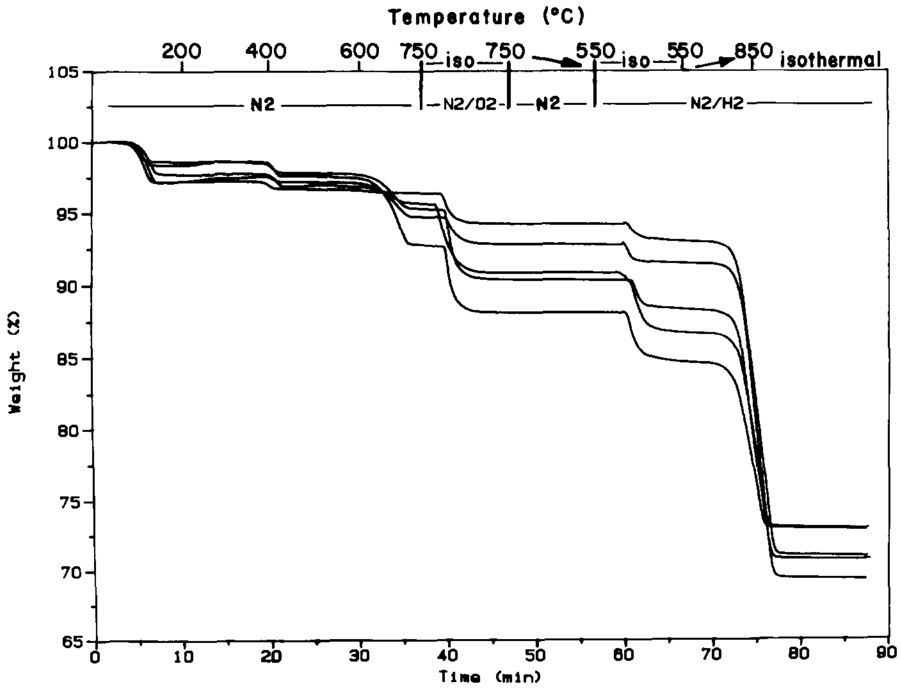

Fig. 4. TG curves for five mixtures of reagent grade materials following the TG method. The curves show six distinct steps of weight loss.

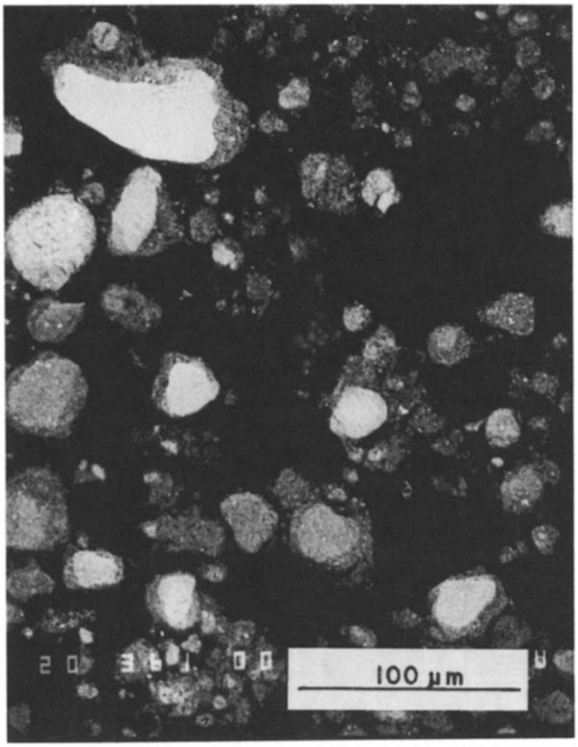

Fig. 5. Photomicrograph of Fe_3O_4 particles with an outer layer of Fe_2O_3.

the temperature profile in the reduction stage, it was possible to separate the reduction of iron oxide from that of $CaSO_4$.

To identify the reaction products at different stages of the analysis, some experiments were interrupted at different temperatures and the samples were examined by XRD. Although the results confirmed the presence of the products of reactions (2)–(7) after each corresponding weight loss, it was noticed that, at 750 °C and before the oxidation step, an appreciable amount of iron oxide (initially added as Fe_2O_3) was found in the form of Fe_3O_4. In the presence of carbon, the following reduction reaction may have taken place in nitrogen

$$3Fe_2O_3 + C = 2Fe_3O_4 + CO \tag{8}$$

No marked weight loss due to reaction (8) was detected, and hence the resulting error in the determination of $Ca(OH)_2$ and $CaCO_3$ is likely to be insignificant. Reaction (8) is expected to occur more extensively in the actual fluidized-bed samples since iron oxide is more intimately mixed with the residual carbonaceous materials in the coal ash.

XRD analysis of the sample after the oxidation step, indicated that Fe_3O_4 did not oxidize back to Fe_2O_3 in any appreciable amount. A photomicrograph of a selected sample, Fig. 5, after the oxidation step indicated that a protective layer of Fe_2O_3 has formed at the surface of the Fe_3O_4 particles preventing further oxidation of the core. On the basis of these findings, the calculation of the initial amount of Fe_2O_3 in the samples was found to be more accurate by correlating the first weight loss during the reduction stage to the reaction

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O \tag{9}$$

and not to reaction (6). Obviously the error introduced by using reaction (9)

TABLE 2

Analyses of prepared mixtures by TG and other methods

Determination	Sample No.	Prepared composition	Concentration (%)				
			TG method	Other methods [a]			
				1	2	3	4
H_2O	1		1.4				
	2		1.8				
	3		2.3				
	4		2.8				
	5		2.8				
$Ca(OH)_2$	1		4.2				
	2		3.2				
	3		3.4				
	4		1.8				
	5		2.1				
$CaCO_3$	1	11.49	11.1	15.73	10.42		13.53
	2	6.51	5.8	10.68	5.93		8.87
	3	3.52	2.7	6.04	2.58		7.39
	4	6.26	5.6	8.61	5.41		8.78
	5	1.52	0.8	2.48	1.03		3.57
C	1	4.95	4.6	4.39	4.02	5.99	5.88
	2	4.95	4.9	4.26	4.64	6.10	5.39
	3	4.95	4.8	4.48	4.24	5.90	4.87
	4	1.98	1.9	1.62	2.30	3.08	2.53
	5	1.98	2.1	1.71	2.14	5.02	2.00
Fe_2O_3	1	14.85	13.3	14.24	13.42	14.18	12.34
	2	14.85	13.8	15.02	13.22	14.80	11.50
	3	9.90	9.7	9.95	9.33	9.29	7.47
	4	4.95	5.2	4.93	5.14	4.72	2.77
	5	4.95	4.7	4.90	4.97	4.62	2.74
$CaSO_4$	1	23.56	24.9	23.58	23.80	23.16	19.47
	2	28.27	29.2	28.14	28.84	27.84	26.56
	3	37.68	37.4	37.27	37.81	35.96	32.77
	4	47.10	47.2	46.39	47.25	44.75	44.54
	5	47.10	47.0	46.76	46.55	44.16	45.26

[a] The numbers refer to the four different laboratories using methods other than TG.

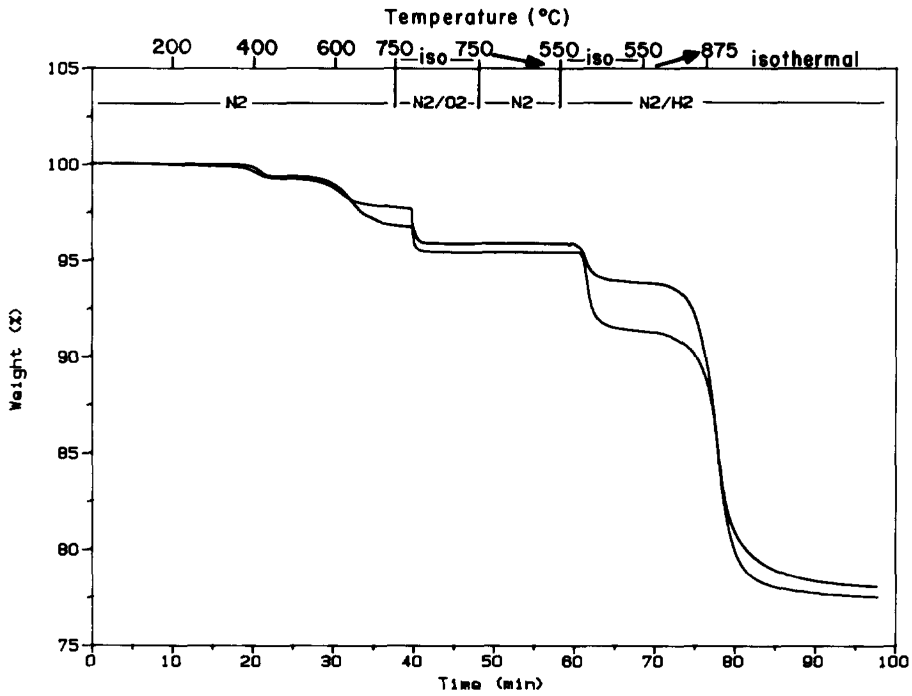

Fig. 6. TG curves for two samples from fluidized-bed coal combustion residues following the TG method.

would be dependent on the extent of the Fe_2O_3-layer formation during the oxidation step.

Table 2 contains a summary of the quantitative analysis of the five mixtures (Fig. 4) together with the starting compositions and the analysis carried out by four different laboratories using methods other than thermal analysis. Some laboratories reported the analyses of CaO and SiO_2 in the samples but these were not included in Table 2.

Besides the speed and convenience of the TG method, its accuracy and reproducibility were demonstrated in the results obtained. The capability of the method to determine H_2O and $Ca(OH)_2$ is important since the neglect of these components can lead to significant errors in the chemical analysis.

The new TG method was used to analyze several samples from the fluidized-bed coal combustion process. Typical TG curves for such samples are shown in Fig. 6. A good resolution between the weight loss from the decomposition of carbonate and that from the combustion of carbonaceous materials is apparent. Separate determination of these two sample components represents one of the main difficulties in the analysis of fluidized-bed residues. Table 3 contains the results of the quantitative analysis of the two samples by thermal analysis and by chemical analysis. The general tendency for reporting higher values for Fe_2O_3 by chemical analysis (calculated from

TABLE 3

Analysis of fluidized-bed coal combustion residues

Determination	Sample No.	Concentration (%)	
		TG method	Chemical analysis
$Ca(OH)_2$	1	2.90	
	2	1.40	
$CaCO_3$	1	3.00	3.73
	2	5.50	5.05
C	1	2.30	2.87
	2	0.83	1.31
Fe_2O_3	1	15.40	16.70
	2	8.20	10.02
$CaSO_4$	1	28.70	26.18
	2	33.80	33.83

the value for total Fe) is probably a result of the assumption that all the iron in the sample is found in the form of uncombined Fe_2O_3. This is not necessarily true since iron can also be present in the form of iron silicates or calcium ferrites.

CONCLUSIONS

A thermal analysis method using thermogravimetry was further developed for the quantitative determination of major components of samples from fluidized-bed coal combustion processes in which limestone is added for sulphur capture. The viability and accuracy of the method were verified by analysing mixtures of reagent grade materials and fluidized-bed ash samples and comparing the results with those obtained by other methods. The method could be used for monitoring the efficiency of coal combustion and limestone utilization in fluidized-bed combustors.

ACKNOWLEDGEMENTS

The authors would like to thank C.A. Hamer for providing the starting materials and the chemical analyses, and the Mineralogy Section of CANMET for the XRD and microprobe analyses. Useful discussions with Dr. A.H. Webster and Dr. P.K. Gallagher are also greatly appreciated.

REFERENCES

1 D.P. Kalmanovich, V.V. Razbin, E.J. Anthony, D.L. Desai and F.D. Friedrich, Division Report ERP/ERL 85-34(OP&J), CANMET, Department of Energy, Mines and Resources, Ottawa, Canada, 1985.

2 C.A. Hamer and D.R. Owens, Division Report MSL 88-81(TR), CANMET, Department of Energy, Mines and Resources, Ottawa, Canada, 1988.
3 S.A. Mikhail, Proc. 16th NATAS Conf., Washington, D.C., U.S.A., Ed. P.J. Kelleghan, pp 502–508 (1987).
4 C.M. Earnest and R.L. Fyans, Proc. 7th ICTA Conf., Kingston, Ontario, Canada, Ed. B. Miller, Vol. 2, pp 1260–1269 (1982).
5 M. Ottaway, Fuel, 61 (1982) 714.