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Environment

STUDIES OF FLY ASH USING THERMAL ANALYSIS TECHNIQUES

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Abstract

Improved thermoanalytical methods have been developed that are capable of quantitative identification of various components of fly ash from a laboratory-scale fluidized bed combustion system. The thermogravimetric procedure developed can determine quantities of H_2O, $Ca(OH)_2$, $CaCO_3$, $CaSO_4$ and carbonaceous matter in fly ash with accuracy comparable to more time-consuming ASTM methods. This procedure is a modification of the Mikhail-Turcotte methods that can accurately analyze bed ash, with higher accuracy regarding the greater amount of carbonaceous matter in fly ash. In addition, in conjunction with FTIR and SEM/EDS analyses, the reduction mechanism of $CaSO_4$ as $CaSO_4+4H_2 \leftrightarrow CaS + 4H_2O$ has been confirmed in this study. This mechanism is important in analyzing and evaluating sulfur capture in fluidized-bed combustion systems.

Keywords: AFBC, fly ash, TG/FTIR

Introduction

An atmospheric fluidized-bed combustor (AFBC) uses atmospheric pressure to effectively fluidize the bed, which allows for hotter (and therefore more efficient) burning of coal [1]. The results of AFBC combustion are gases, mostly CO_2 and some sulfur-bearing gas, heat, and two kinds of ash: bed ash and fly ash. Bed ash is that ash which remains in the bed for the duration of combustion. It is subjected to high temperatures (in excess of 1500°F) for an extended amount of time, burns hotter, and is relatively devoid of carbon. Fly ash, on the other hand, is ash which was removed from the bed by negative air pressure passing over the bed. As this ash was originally at the top of the bed and escaped the bed during combustion, it burns cooler and for a shorter period of time, making it comparatively carbon-rich. Since

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carbonaceous matter is a major constituent of fly ash, it is important that techniques to analyze fly ash are accurate with regard to carbon.

Any $CaCO_3$ present in the FBC fly ash is simply limestone that failed to break down into CaO, while the H_2O and carbonaceous materials are results of combustion. Other substances, such as $Ca(OH)_2$ and $CaSO_4$, form from reactions between CaO (degeneration of limestone) and gases evolved in combustion, generally SO_2 and $H_2O(g)$. These types of reactions are particularly beneficial, as they prevent pollutants from reaching the atmosphere (up to 50% reduction in SO_2), and allow TG analysis to determine the relative amounts of sulfur and other compounds present in the fly ash [2, 3].

There are two key differences between the Mikhail-Turcotte method [4] and the modified procedure. Firstly the Mikhail-Turcotte method causes $CaCO_3$ to decompose (in N_2) before the carbon combusts (in N_2 and O_2), whereas the modified method burns the carbon first. In the Mikhail-Turcotte method, this results in some of the carbon pyrolyzing, a process that is assisted by oxygen in the carbonaceous material. As a result, the apparent percentage of carbon present will be lower than the actual percentage using the Mikhail-Turcotte method. Since the modified method burns the carbon first, at a temperature not high enough to decompose $CaCO_3$, the carbon and $CaCO_3$ are effectively separated, while there is some overlap in the Mikhail-Turcotte method.

The second difference is that the modified procedure converts CaO into $CaCO_3$ before combusting the carbon. The advantage of this is that there will essentially be no CaO left to absorb CO_2 produced by carbon when it is pyrolyzed. Were this not so, there would be another stage of overlap where the CaO gains mass while the carbon was being combusted. While this mass loss is rather insignificant when analyzing bed ash, for which the Mikhail-Turcotte method was developed, it makes a considerable difference when analyzing carbon-rich fly ash.

In analyzing ash using either TG method, the amount of each constituent of the ash present can be determined by forcing each to decompose at a different stage of the run. This way, any significant mass loss can be attributed to one particular compound with reasonable certainty. Three of these compounds, H_2O, $CaCO_3$, and $Ca(OH)_2$ will decompose regardless of the atmosphere they are in, and care must be taken to isolate their decompositions from each other and from decomposition of other compounds. $CaSO_4$ is easier to separate, as it is dependent upon an atmosphere of H_2/N_2 (5/95), the carbonaceous material must have O_2 in order to oxidize, and CaO must be in the presence of CO_2, to form $CaCO_3$.

By pyrolyzing H_2O, $Ca(OH)_2$, and $CaCO_3$ in N_2, the other two compounds, carbonaceous materials and $CaSO_4$, can be prevented from reacting to any appreciable degree when the first three compounds are decomposing. It would also be desirable that no CaO is present when the carbon is pyrolyzing, due to the overlap of CaO mass gain and carbon mass loss. Also, the carbon should have combusted completely before the $CaCO_3$ is allowed to decompose.

Once the mass gain or loss due to each component of ash has been determined, the actual mass percentage of each component must be found. While mass change is proportional to the mass percentage of each substance, they are not equal. Only a portion of the mass of each compound is gained or lost in combustion, corresponding to the mass of the gas evolved or absorbed during the reaction. The mass of each substance present is related to its mass change as shown in Table 1.

Table 1 Conversion between mass loss and mass of substance

Reaction	Actual mass substance/ mass change shown
$H_2O(l) \leftrightarrow H_2O(g)$	1 g/g
$Ca(OH)_2 \leftrightarrow CaO+H_2O(g)$	78 g/18 g
$C+O_2 \leftrightarrow CO_2$	1 g/1 g
$CaCO_3 \leftrightarrow CaO+CO_2(g)$	100 g/44 g
$CaSO_4+4H_2 \leftrightarrow CaS+4H_2O(g)$	136 g/64 g

The actual percent mass for each of these compounds can be found by finding the mass change on its representative curve and multiplying by the corresponding factor. For $CaCO_3$ alone, however, one must then determine the source of the $CaCO_3$. Some may be created from the CaO present after decomposition of $Ca(OH)_2$, and some may be present from combustion. By first finding the amount of $Ca(OH)_2$ present, the amount of $CaCO_3$ generated from $Ca(OH)_2$ can be found and subtracted from the total mass of $CaCO_3$-found during combustion, leaving the original amount of $CaCO_3$ as the result.

To determine the reduction mechanism for $CaSO_4$, the products of reduction must be ascertained with certainty. Three mechanisms are possible:

$$CaSO_4+4H_2 \leftrightarrow CaS+4H_2O \tag{1}$$

$$CaSO_4+H_2 \leftrightarrow CaO+SO_2+H_2O \tag{2}$$

$$CaSO_4 \leftrightarrow CaO+SO_3 \tag{3}$$

The first reaction is the one predicted by the Mikhail-Turcotte method, but the other two are also feasible. By using standard thermodynamic information, FTIR scans of $CaSO_4$ and fly ash, and TG runs of $CaSO_4$, it can be determined conclusively what products are present. One can therefore confirm whether the mechanism mentioned in the Mikhail-Turcotte method is in fact correct.

Experimental

A TA2960 Simultaneous Differential Thermal Analysis system was used for analysis of the fly ash samples, using both the modified method and a variation of the Mikhail-Turcotte method. ASTM method D 5016 was used to find the percentage of sulfur to the greatest accuracy possible, D 5373 for carbon, and D 5142 for moisture and ash determination. The other constituents, such as $CaCO_3$ and $Ca(OH)_2$ were not analyzed using ASTM methods. These ASTM results were used

Table 2 Previous TG method conditions – slight variation on Mikhail-Turcotte method

Step	Conditions	Holding period	Gas
1	20°C min^{-1} to 200°C	10 min	N_2
2	20°C min^{-1} to 450°C	10 min	N_2
3	20°C min^{-1} to 850°C	15 min	N_2
4	Isothermal	15 min	Air
5	20°C min^{-1} to 1000°C	15 min	N_2/H_2 (95/5)
6	Isothermal	15 min	N_2/H_2 (95/5)

Table 3 Modified TG method conditions[A]

Step	Conditions	Holding period	Gas
1	20°C min^{-1} to 200°C	10 min	N_2
2	20°C min^{-1} to 450°C	10 min	N_2
3	20°C min^{-1} to 550°C	30 min	CO_2
4	Isothermal	30 min	Air
5	20°C min^{-1} to 850°C	–	N_2
6	20°C min^{-1} to 1000°C	15 min	N_2/H_2 (95/5)

[A] Sample size=50 mg, purge gas is 150 mL min^{-1}.

Table 4 FTIR method for fly ash and $CaSO_4$

Step	Conditions	Holding period	Gas
1	20°C min^{-1} to 550°C	–	N_2
2	Isothermal	30 min	Air
3	20°C min^{-1} to 1000°C	–	N_2
4	Isothermal	10 min	N_2/H_2 (95/5)

Table 5 SEM method for fly ash and $CaSO_4$

Analysis conditions	
Quant. method: XPP/ASAP	Acquisition time 300 s
Normalization factor: 100.00	
Sample conditions	
kV: 20.0	Beam current: 57.0 picoAmps
Working distance: 15.0 mm	Tilt angle: 0.0°
Take off angle: 25.0°	Solid angle·beam current: 0.2

as a baseline for comparison of the two TG methods. The fly ash samples were from a 12-inch AFBC system at Western Kentucky University, and each method was used on each sample. To analyze the reduction mechanism, a 1600 Series Perkin-Elmer FTIR was used to determine the gases evolved from reduction of $CaSO_4$, and a JEOL JSM-5400 SEM with EDX was used for analysis of reduction products. Tables 2–5 list the analysis conditions for the various experiments performed.

Results

The individual mass loss or gain for each material can be seen on the TG curve, each occurring at a different temperature, as shown in Fig. 1. The percent mass change that each compound is responsible for is found by measuring a vertical line from the top of the curve to the bottom. The weight change in the sample due to each compound, having been found, must be multiplied by the percent mass change factor (Table 1) to find the percent mass of each compound.

H_2O is removed at a temperature around 100°C, $Ca(OH)_2$ decomposes at approximately 400°C, and $CaCO_3$ breaks down between 600 and 750°C. CaO, a product of $Ca(OH)_2$, reacts in a CO_2 atmosphere to form $CaCO_3$ at 550°C. At 650–750°C, the $CaCO_3$ decomposes into CaO and CO_2. It is important to realize that a significant portion of this $CaCO_3$ was not present in the fly ash originally, but is the result of a reaction between CaO (resulting from $Ca(OH)_2$ decomposition) and CO_2. It is necessary to determine how much $CaCO_3$ was formed from the CaO, and to subtract this from the total $CaCO_3$ present after analysis to find the amount of $CaCO_3$ originally in the ash. After the $CaCO_3$ has sufficiently decomposed, at tem-

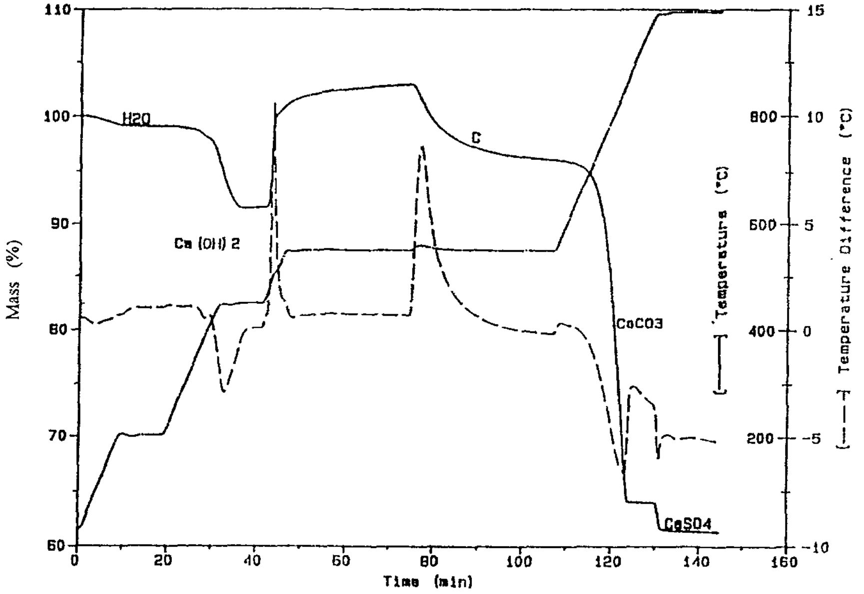

Fig. 1 TG curve of fly ash using the modified method

peratures near 1000°C, $CaSO_4$ is reduced in the presence of N_2/H_2 purge gas. This produces CaS and $H_2O(g)$, as determined by the correct reaction mechanism.

$CaCO_3$ formation dictates the accuracy with regard to carbon. If it is performed before the carbonaceous material is pyrolyzed, some of the carbon will combust during the $CaCO_3$ stage, which results in mass loss. This is clearly illustrated in Fig. 2, where there are two peaks on the DTG curve in the $CaCO_3$ range. $CaCO_3$ should be the only substance reacting.

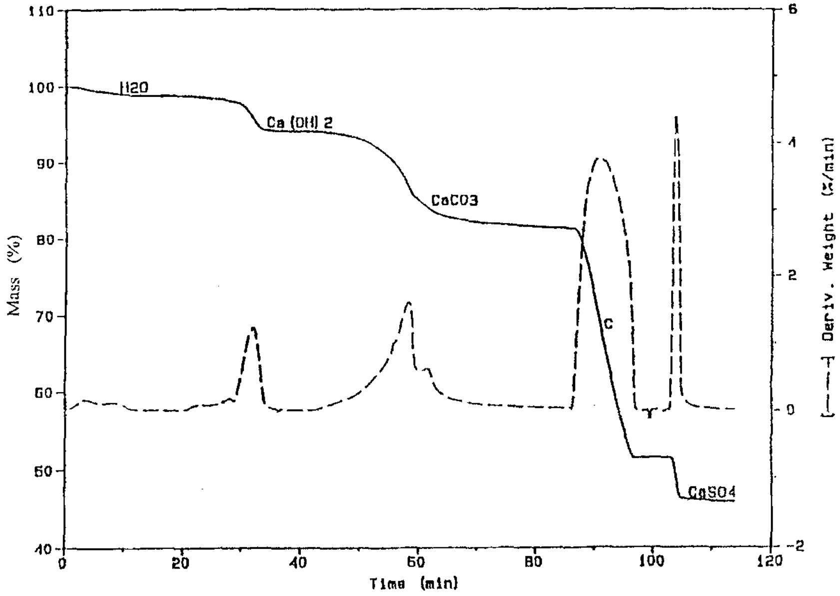

Fig. 2 TG curve of fly ash using a variation of the Mikhail-Turcotte method

Results of the TG analysis using this new procedure were found to correspond closely to results from ASTM methods using the same samples. The results show close agreement between the TG results and ASTM results for sulfur, carbon, and ash. Ash contents were nearly identical for the ASTM and TG methods. Sulfur contents, while quite close to those obtained by ASTM, were consistently higher than that from ASTM methods by an average of 0.3%, and no larger than 0.6%. The carbon results, on the other hand, were low by an average of 0.4%, reaching an error of 0.8% on one occasion. Since the differences between TG and ASTM results for sulfur and carbon are rather consistent, the results could be corrected slightly to yield results that correspond even more closely to the ASTM results.

The differential temperature curve in Fig. 1 shows the relative ΔH for each step in the run. The reduction of $CaSO_4$ is endothermic, as evidenced in Fig. 1 and corroborated by standard heats of formation for all three reactions [5]. Since there is a correlation between ΔG and ΔH (assuming ΔS to be relatively similar for comparison) the most favored reaction thermodynamically is likely to be the reaction that is closest to being exothermic (negative ΔH). The second reaction is endothermic by

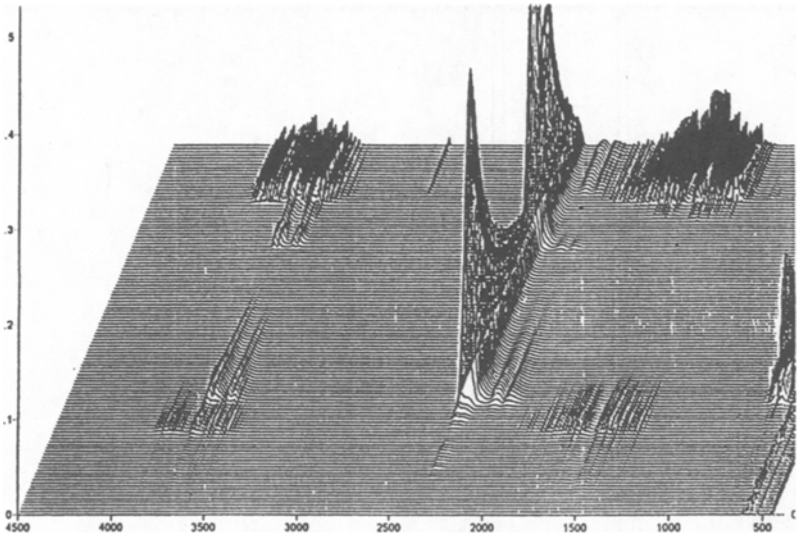

Fig. 3 FTIR profile of fly ash

109 kJ, while the third reaction is endothermic by 308 kJ [5]. These numbers seem to point toward the first mechanism, which is endothermic by only 26 kJ.

The FTIR gas analysis curve for fly ash shows peaks for H_2O and CO_2, two for each gas, as is illustrated in Fig. 3. The peaks for CO_2 are first from the combustion of carbon, then from the decomposition of $CaCO_3$. The water comes from the decomposition of $Ca(OH)_2$ first, and then shows another peak at what can only be the reduction of $CaSO_4$. These peaks correspond to water, implying that H_2O is a product of reduction. However, missing are peaks for either SO_2 or SO_3, ruling out either sulfur-bearing gas as a product of $CaSO_4$ reduction.

SEM/EDS results also point conclusively to the first mechanism. A SEM scan of the residue $CaSO_4$ reduction residue shows peaks for two elements, a double peak from about 3.675 and 4.245 keV that corresponds to calcium and one from 2.245 to 2.495 keV characteristic of sulfur. This indicates that the product of reaction (non-gaseous) is CaS. The peak for oxygen is quite minimal, indicating an al-

Table 6 SEM/EDS analysis of fly ash and $CaSO_4$ reaction residue

Fly ash	Element	Mass %	Atomic %	Counts/s
	S	71.19	75.54	434.90
	Ca	28.81	24.46	103.53
	S/Ca ratio	2.47	3.09	4.20
$CaSO_4$	S	69.41	73.93	171.47
	Ca	30.59	26.07	44.88
	S/Ca ratio	2.27	2.84	3.82

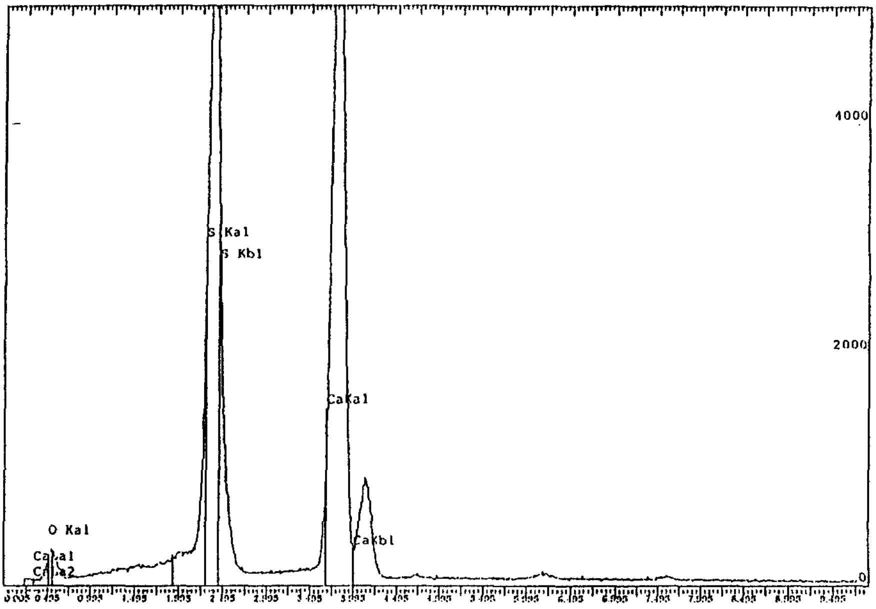

Fig. 4 SEM scan spectrum of fly ash

most complete lack of oxygen. What oxygen did remain in the sample likely resulted from $CaSO_4$ that failed to be reduced. A scan for fly ash using the same method shows very similar results as illustrated in Fig. 4. Peaks occur in the same places for both scans, with large calcium and sulfur peaks and minute traces of oxygen.

Quantitative results of the same scans show the results of sample contents after heating in H_2/N_2 at 1000°C. The results of fly ash and $CaSO_4$ sample residue are shown in the following table (Table 6).

These results show consistent S/Ca ratios, with fly ash greater by a factor of only 1.10, indicating that the fly ash residue has an only slightly greater content of sulfur as compared to the $CaSO_4$. This confirms, as the TG data indicated, that the only solid product of $CaSO_4$ reduction is CaS. Considering the data from FTIR, TG, thermodynamic properties, and SEM, the most probable mechanism is $CaSO_4+4H_2 \leftrightarrow CaS+4H_2O$.

Conclusions

The improved TG techniques are capable of simultaneously determining the content of fly ash with regard to six key components. The analytical results of the fly ash using improved TG techniques are very close to those obtained by ASTM methods. In addition to analyzing the fly ash, four different methods have also been able to determine conclusively the reduction mechanism of $CaSO_4$ as resulting in H_2O and CaS. As these improved techniques have greater speed and comparable accuracy to ASTM methods, they would be preferable in all situations but those where increased accuracy is more important than added speed and convenience.

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