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THERMOGRAVIMETRIC METHODS FOR DETERMINING CARBON CONTENT IN FLY ASHES

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ABSTRACT

Unburnt carbon content in fly ashes was determined using thermogravimetry. After being heated in an inert atmosphere, carbon reacts towards iron oxide components in fly ash, and after it is heated in an oxidizing environment, carbon oxidation process overlaps carbonate decomposition. A thermogravimetric method combining inert and oxidizing atmospheres was designed, in such a way that hydrated lime, calcium carbonate, and unburnt carbon contents for several fly ashes were determined. Carbon content in fly ash-sized fractions also was determined, with highest carbon content found in the coarsest fractions. © *1998 Elsevier Science Ltd*

Introduction

The carbon content in fly ashes from thermoelectric power plants depends on the efficiency on the combustion process. A generally accepted test method for estimating the quality of a fly ash is the determination of its loss on ignition, or LOI (1). LOI values for high-calcium fly ashes are usually very low (less than 1%), whereas LOI values for low-calcium fly ashes are usually higher, especially for those produced by older and more inefficient thermoelectric power plants (LOI values up to 10%) (2).

However, in the LOI test method, a fly ash sample is ignited in a muffle furnace at 750–950°C, and the weight loss is not only related to the presence of unburnt carbon in fly ash, but also to carbonates and combined water present in hydrated lime or residual clay minerals (3). Moreover, the presence of sulphides, sulphur, and some iron minerals will decrease the LOI value due to gain in weight because of oxidation. However, it seems that carbon is, generally, the substance most responsible for ignition loss.

The presence of unburnt carbon in fly ashes has several important effects on their uses. The color of the mortars and concretes incorporating fly ashes (4), may appear black or dark grey (5). The water requirement of fly ash-cement pastes and the rheological properties of mortars and concrete (6) is affected because the water/cement + fly ash ratio needed to obtain a paste of normal consistency is greater for fly ashes with high carbon content. Dhir et al. (7) found

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a good correlation between slump or water reduction in concrete, and the product of fly ash fineness (as 45 μm sieve retention) and the LOI value. In general, poor water requirement properties have been found for high-carbon-content fly ashes. A decrease in air entrained in mortar or concrete was found due to the presence of carbon in fly ashes (8). Apparently, porous carbon particles adsorb organic compounds, which cancels their role as air-entraining substances. A beneficial effect on mechanical strength was found by Hornain et al. (9) when high-LOI fly ash was used. The dosage of air-entraining agents (AEA) in concretes incorporating fly ashes (10,11) is affected by carbon in fly ash. Gebler and Klieger (12) established a good correlation between AEA requirement and carbon content, showing an increase of AEA requirement with organic matter content, carbon content and LOI. Recently, Hill et al. (13) studied the importance of optically isotropic amorphous carbon on the adsorption of AEA. The chloride migration and the effective diffusion coefficients are also affected (14).

This is why standard specifications in many countries (15) limit LOI values (to the 5–12% range), assuming this parameter provides a good estimation of carbon content.

Carbon content may be determined by elemental analysis (e.g., a dry combustion-based analyzer) but organic and inorganic carbon can not be distinguished. Test samples may be previously treated to remove inorganic carbon (carbonates) using acid treatment, decomposing the carbonates and absorbing the resulting carbon dioxide in an absorbent. Such procedures have been described for coal (16) and water (17) samples. Total carbon from elemental analysis, less inorganic carbon determined as evolved CO_2 due to acid treatment, yields organic carbon content in the sample. Thermogravimetry for compositional analysis also could be applied (18) as in coal, polymers, and oils. Indirectly, carbon content also could be determined from calorific value, but this procedure becomes very difficult as the proportion of fuel is too low for obtaining accurated values (19).

The scope of this investigation is to develop thermal analysis methods for determining carbon content in fly ashes. Distribution in size of carbon particles and morphology of carbon particles will be also studied.

Experimental

Thermal Analysis

Thermal analyses were carried out in a Mettler-Toledo TGA850 module, equipped with an ultramicro balance (resolution of the balance: 0.1 μg), with a horizontal furnace. The sample temperature sensor is placed under the platinum sample holder, guaranteeing a sample near measurement of the sample temperature. There were two purge gas inlets to the furnace chamber, one of them for conducting nitrogen, and another for dry air. For evaluating data, Mettler-Toledo Star Software was used. This software permits one to evaluate weight changes for a sample (thermogravimetric curve) and Single Differential Thermal Analysis curve (obtained in absence of reference sample by difference of the sample temperature and calculated reference temperature with a mathematical model). Thermal methods designed will be indicated for each experiment when necessary. Exothermic events are given as downward peaks.

A JEOL JSM-6300 was used for scanning electron microscopy studies, operated at a 15 kV accelerating voltage.

Fly Ashes, Fly Ash-Sized Fractions, and Nomenclature

Fly ashes studied in this research were from the following Spanish themoelectric power plants: Andorra-Teruel (F1), Avilés-Asturias (F2), Puentenuevo-Córdoba (F3), Pasajes-Pais Vasco (F4) Los Barrios-Cádiz (F5) and Carboneras-Almería (F6). Fly ashes were sieved and several fly ash fractions obtained: fraction retained on 80 μm sieve (FX+80 samples, FX being the corresponding original fly ash); fraction passed through 80 μm-sieve and retained on 63 μm sieve (FX+63); fraction passed through 63 μm sieve and retained on 50 μm sieve (FX+50); and, finally, fraction not retained on 50 μm sieve (FX-50). The coarsest fractions, FX+80, FX+63 and FX+50 were crushed and homogenized in an agate mortar before thermal analysis.

Results and Discussion

Morphology of Carbon Particles in Fly Ashes

Morphology of carbon particles was analyzed by means of electron microscopy. Figure 1 shows several views of carbon particles. The typical vesicular structure due to the volatilization process of the low molecular weight fraction from the original coal particles is observed. Unaltered coal particles were not found in the studied samples, suggesting that incomplete combustion of coal particles due to insufficient oxygen concentration (20) was not the problem, but that the high temperature environment causes the volatilization of part of carbon particles, and remaining carbon becomes coke (19). Plates 1c and 1d show spherical inorganic fly ash particles adhering to carbon particles. Diamond suggested (20) that in the combustion process, unburnt carbon particles were in a high temperature environment for melting inorganic impurities and embedded inorganic particles could appear, but only adhering fine inorganic fly ash particles were found in this work.

Thermogravimetric Analysis in an Oxidising Atmosphere

Thermogravimetric analysis can be carried out in different environmental atmospheres. When a fly ash is heated in an oxidising environment (e.g., air), the thermogravimetric curve (TG) shows a weight loss in 500–740°C range (see Fig. 2). This loss is attributed to carbon oxidation and calcium carbonate decomposition according to the following chemical reactions:

$$2C + xO_2 \rightarrow 2CO_x \ (x = 1, 2)$$

$$CaCO_3 \rightarrow CaO + CO_2$$

Another small weight loss is observed at 450°C due to water loss from hydrated lime. The differential thermogravimetric curve (DTG) shows two peaks in the 500–740°C range, indicating an overlap of two different processes. Finally, The Single Differential Thermal Analysis curve (SDTA) shows a strong exothermic peak (due to combustion of carbon) which has a shoulder at about 700°C (due to endothermic calcium carbonate decomposition).

Because carbonate decomposition overlaps carbon oxidation, alternative thermal analysis methods need to be developed for distinguishing both reactions. Through heating in an inert

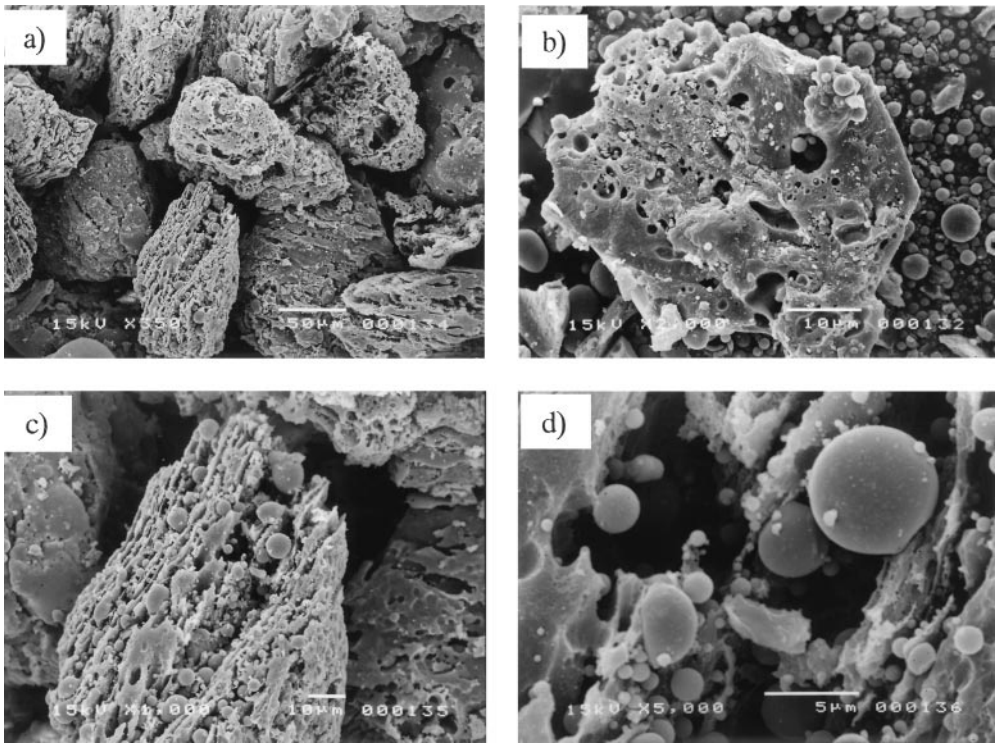

FIG. 1.
Scanning electronic microscopy micrographs for carbon particles in fly ash samples: *a*) General view for a sample with high carbon content (F4−80); *b*) vesicular carbon particle; *c*) carbon particle with adhering inorganic fly ash microspheres; *d*) surface detail of a carbon particle.

environment (e.g., N_2), oxidation of carbon by gaseous oxygen O_2 would be hindered and carbonate content could be determined; subsequently, the sample could be heated in an oxidising atmosphere and carbon oxidation would take place.

Thermogravimetric Analysis in an Inert Atmosphere

Obviously, in an inert environment, carbon oxidation does not take place; in these experimental conditions, when samples are heated, volatilization of organic matter, carbonate decomposition, and water release from hydrated compounds will occur. However, when a fly ash is heated in nitrogen atmosphere, a significant loss of weight was observed in the 750–1000°C range (see Fig. 3); moreover, loss due to water released from hydrated lime (450°C) was observed, and no volatilization of organic matter was detected. The weight loss at high temperature was not detected whenfly ash sample was heated in an oxidising atmosphere, suggesting different reaction mechanisms under each type of environment.

It is well-known that coal can reduce some minerals (oxides, sulphides, . . .); the most important case is the chemical reduction of iron oxides by coke in a blast-furnace (21). Thermochemical data (22) concerning the reduction of iron oxides with carbon are repre-

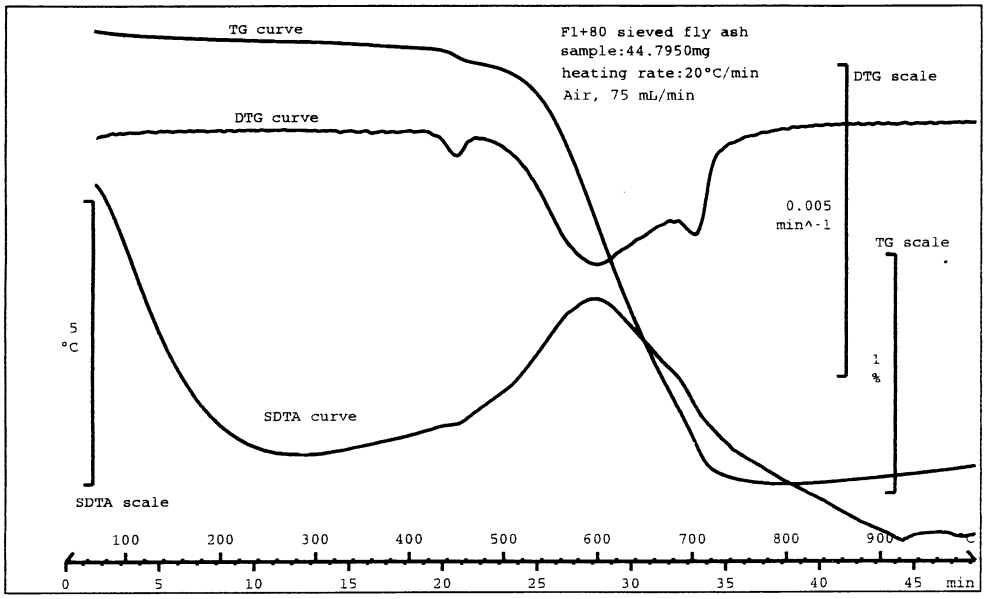

FIG. 2.

Thermogravimetric (TG and its derivative DTG) and differential thermal analysis (DTA) curves for F1+80 fly ash in an oxidizing atmosphere.

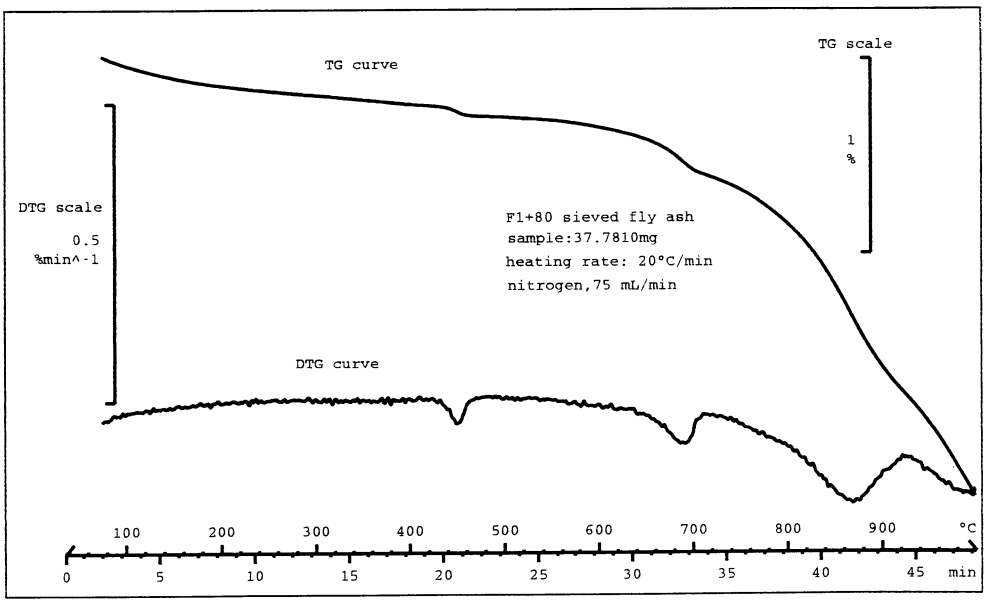

FIG. 3.

Thermogravimetric (TG and its derivative DTG) curves for F1+80 fly ash in an inert atmosphere.

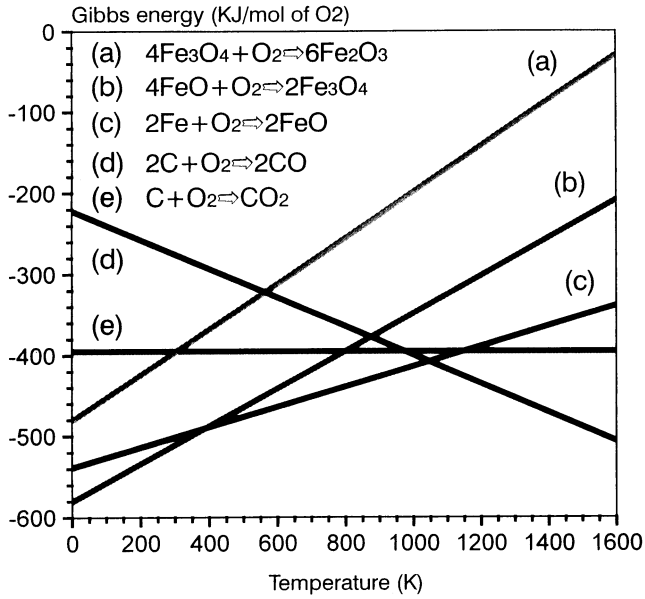

FIG. 4.
Ellingham's diagram for carbon and iron oxides.

sented using a ΔG-T diagram (also known as Ellingham′s diagram). Figure 4 plots ΔG for the following oxidation reactions versus temperature:

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$2C + O_2 \rightarrow 2CO \quad (2)$$

$$2Fe + O_2 \rightarrow 2FeO \quad (3)$$

$$6FeO + O_2 \rightarrow 2Fe_3O_4 \quad (4)$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \quad (5)$$

From this diagram, two observations are relevant here. Firstly, the reduction of iron oxides with carbon is thermochemically feasible: Fe_2O_3 may be reduced starting at 304 K, Fe_3O_4 at 798 K and FeO at 1045 K. And secondly, the carbon oxidation product for temperatures less than 973 K (700°C) will be carbon dioxide, CO_2, whereas carbon monoxide will be produced for temperatures higher than 973 K. That is the reason when fly ash is heated in an inert atmosphere, an important weight loss is observed: the unburnt carbon reacts towards iron oxides present in fly ashes (generally as hematite or magnetite). It seems that this oxidation reaction is kinetically slow and only occurs at high temperatures, yielding carbon monoxide as carbon oxidation product. Tests were carried out by heating mixtures of hematite or magnetite with active carbon (Fig. 5) in an inert atmosphere. In both cases, thermogravimetric analyses showed important looses in the range 700-1100°C, indicating the occurrence of oxidation-reduction processes. Additional tests showed that the ratio carbon/iron oxide controlled the weight loss value.

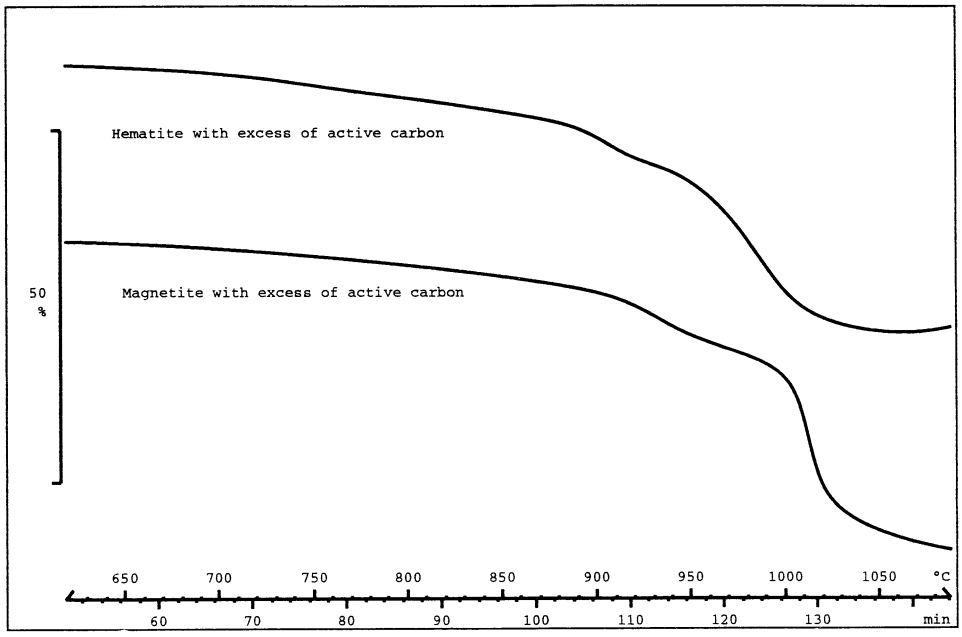

FIG. 5.
Thermogravimetric (TG) curves for carbon/magnetite (10:1 molar ratio) and carbon/hematite (5:1) molar ratio in an inert atmosphere.

Thus, the transformation of carbon to carbon monoxide could be incomplete if amount of available iron oxide is low, or alternately, if contact between carbon and iron oxide particles is restricted.

In order to evaluate correctly the carbon content a new thermal method has been designed.

Thermogravimetric Analysis Combining Inert/Oxidising Atmospheres

The developed method takes into account that in inert atmosphere the sample may be not heated over 750°C because of iron oxide reduction by unburnt carbon. Covered crucibles were not used in order to facilitate switching from an inert to an oxidizing atmosphere. The proposed thermal method was designed as follows:

1. Loss of moisture: heating from 35 to 100°C (heating rate 10°C/min.) in a nitrogen atmosphere (75 mL/min.);
2. Removing reactive oxygen: hold at 100°C for 15 min.; purging gas nitrogen (75 mL/min.);
3. Heating in inert atmosphere: from 100 to 750°C (heating rate 20°C/min.), nitrogen flowing gas (75 mL/min.);
4. Cooling period: from 750 to 100°C (cooling rate −20°C/min.) with nitrogen flowing gas (75 mL/min.);
5. Changing from inert to reactive environment: isothermal temperature process at 100°C for 5 min., air as flowing gas (75 mL/min.);

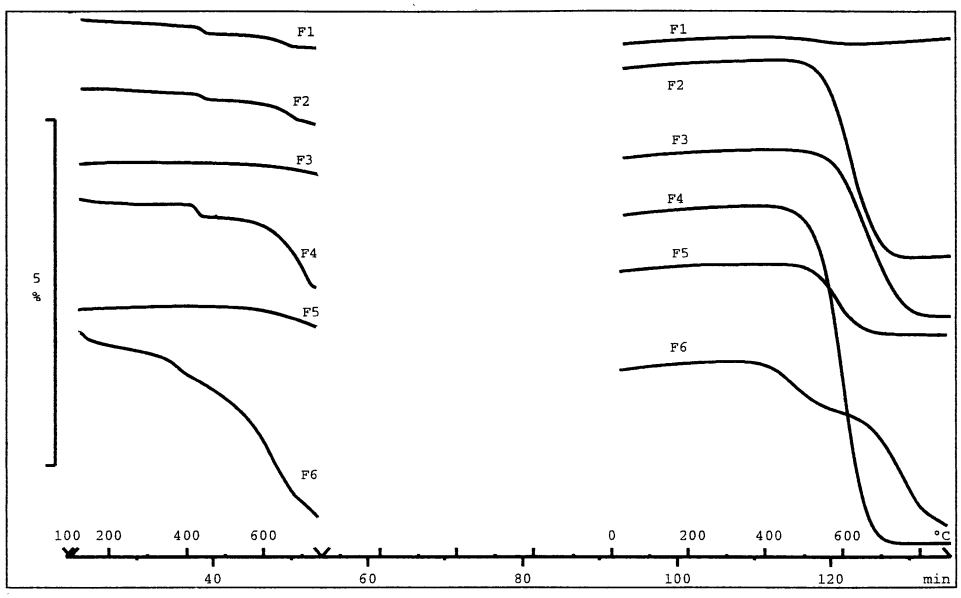

FIG. 6.
Thermogravimetric (TG) curves for F1 to F6 fly ashes in inert/oxidizing atmospheres (only heating curve sections are depicted for clarity).

6. Heating in reactive atmosphere: from 100 to 1000°C (heating rate 20°C/min.) in air (75 mL/min.).

Figure 6 plots thermogravimetric curves for F1 to F6 fly ashes (only heating curve sections are shown for clarity). Only F1, F2, F5, and F6 fly ashes showed a weight loss about 400–450°C (inert environment curve section), attributed to water release from hydrated lime. For all fly ashes, calcium carbonate decomposition in the 600–750°C range (inert environment curve section) was detected. Hydrated lime and calcium carbonate contents are summarised in Table 1. From the oxidising environment curve sections, significant weight losses were observed for all fly ashes, which was attributed to carbon oxidation. Carbon contents for

TABLE 1
Hydrated lime, calcium carbonate, and unburnt carbon contents for FX fly ashes.

Fly ash	Hydrated lime content (%)	Calcium carbonate content (%)	Unburnt carbon content (%)
F1	0.48	0.40	0.09
F2	0.16	0.81	2.83
F3	-	0.37	2.39
F4	-	0.75	4.86
F5	0.76	2.26	1.01
F6	1.37	3.19	0.70

TABLE 2
Hydrated lime, calcium carbonate, and unburnt carbon contents for FX+80, FX+63, FX+50 and FX−50 fly ash fractions.

Fly ash Fraction	Hydrated lime content (%)	Calcium carbonate content (%)	Unburnt carbon content (%)
F1+80	0.28	1.38	2.85
F1+63	0.44	0.55	0.19
F1+50	0.44	0.38	0.08
F1−50	0.48	0.45	-
F2+80	-	0.57	6.41
F2+63	0.02	0.33	2.18
F2+50	0.63	0.65	2.02
F2−50	0.60	0.76	0.87
F3+80	-	0.01	4.22
F3+63	-	0.01	2.94
F3+50	-	0.23	2.32
F3−50	-	0.30	1.07
F4+80	-	1.27	31.39
F4+63	-	0.51	15.10
F4+50	-	0.39	8.42
F4−50	-	0.01	1.79
F5+80	1.19	3.26	7.50
F5+63	0.83	1.88	0.67
F5+50	1.17	2.66	0.37
F5−50	1.18	2.67	0.36
F6+80	2.26	6.56	1.74
F6+63	1.89	4.81	0.37
F6+50	1.55	3.52	0.60
F6−50	1.18	5.61	0.68

fly ashes also are summarised in Table 1. The highest carbon content was found for F4 fly ash and lowest carbon content for F1 fly ash. Sample F6 showed a second weight loss step, but attempts at identifying the source of this loss were unsuccessful. Probably this weight loss was due to hydroxo-silicate decomposition or later contamination of fly ash.

Thermogravimetric Carbon Content Determination for Fly Ash-Sized Fractions

In order to study in depth the influence of carbon content and the carbon particle size on thermogravimetric curve, fly ashes were sieved and four fractions (FX+80, FX+63, FX+50, and FX-50) were prepared from each original FX fly ash. Hydrated lime, calcium carbonate, and carbon contents for these fly ash sized fractions are summarised in Table 2. Figure 7 shows thermogravimetric curves (carbon oxidation section) for F4 fly ash fractions. From these data, several observations can be emphasized: 1) hydrated lime was not detected for F3 and F4 fly ash-sized fractions and for F2+80; 2) except for F6 fly ash, highest hydrated lime content was found for finest fractions (FX+50 and FX-50); 3) calcium carbonate was detected in all samples, but in this case an obvious correlation with particle size cannot be

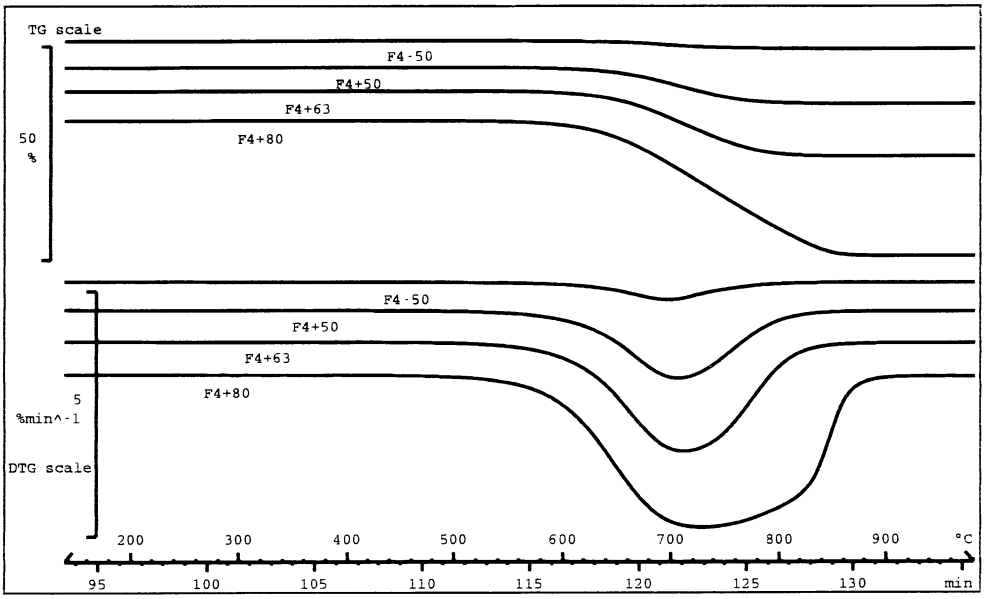

FIG. 7.
Thermogravimetric (TG and its derivative DTG) curves for F4 fly ash-sized fractions in inert/oxidizing atmosphere.

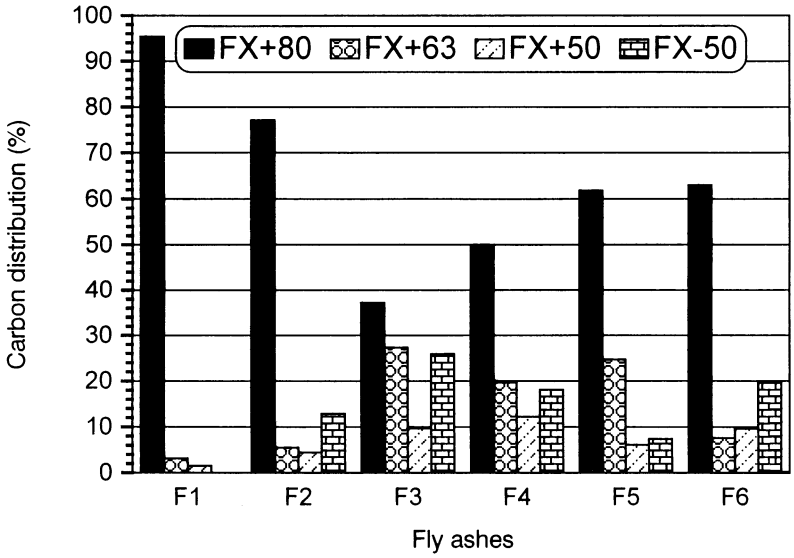

FIG. 8.
Carbon distribution in fly ashes.

established. Finally, unburnt carbon was determined for all the samples except for F1–50; measured carbon contents were in the 31.39% to 0.08% range, with the highest carbon contents observed for the coarsest fractions FX+80. In general, unburnt carbon decreases as fineness increasese, suggesting that carbon content separation accompanies separation of the fly ashes by sieving. Figure 8 plots the distribution of total unburnt carbon with fineness, showing that for F1, F2, F5, and F6 samples, unburnt carbon appeared at percentages higher than 60% in thecoarsest fraction, FX+80

Conclusions

1. Carbon particles in the studied fly ashes showed typical vesicular structure, suggesting volatilization of the low molecular weight fraction during combustion.
2. When fly ash samples were heated in an oxidizing environment, thermogravimetric curves showed an overlap of carbon oxidation and calcium carbonate decomposition.
3. When fly ash was heated in inert atmosphere, thermogravimetric curves showed an important weight loss in 750–1000 °C range, which has been attributed to an oxidation-reduction process between carbon and iron oxide in fly ashes.
4. A thermogravimetric method combining inert/oxidizing atmospheres has been designed, permitting one to determine hydrated lime, calcium carbonate, and unburnt carbon contents in fly ashes.
5. No correlation was established between calcium carbonate content and finenes, but, generally, highest hydrated lime content was found for the finest fractions of fly ash.
6. Measured carbon content in fly ash sieved fractions were ranged from 31.39 to 0.08%, with the highest carbon content for fly ash fractions containing particles greater than 80 μm in diameter.

Acknowledgment

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