



## Study of loss-on-ignition anomalies found in ashes from combustion of iron-rich coal

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### ABSTRACT

Samples of a fly and a bottom ash, each before and after ignition at 960 °C, have been studied by X-ray diffraction, Mössbauer spectroscopy, carbon analysis, and thermogravimetric analysis with the aim to explain an observed negative loss on ignition. Ashes after ignition contain more maghemite resulting from oxidation of newly formed magnetite. Moreover, the fly ash that already contained magnetite exhibited an increase of hematite after ignition. Hercynite present in both ashes transforms to hematite and magnetite after the ignition. All these oxidation processes are responsible for a weight gain which may compensate the loss due to the burning of the remaining carbon in the ashes. Also,  $\alpha$ -Fe is formed after ignition which may have originated from wustite.

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### 1. Introduction

From environmental, economical, and fundamental points of view fly ashes and bottom ashes from coal combustion have been the subject of various studies with respect to their mineralogical composition, their morphology, and their carbon content [1–4]. Particularly, the latter is important, because the remaining carbon content is not only a measure for the efficiency of the combustion process, but is also a necessary parameter for further application of these ashes. Indeed, those ashes are mainly used as additives for cement and concrete and have to meet certain standards. The remaining carbon is usually measured by the loss on ignition (LOI), i.e., the relative loss of mass after heating the ash during a short period at high temperatures (750–960 °C). The LOI for fly ashes used for cement additions must be usually less than 5%, whereas fly ashes of poorer quality (>5% LOI) are then often used in the brick industry.

Although mostly used as a routine measurement, LOI is not always a direct appropriate measure for the remaining carbon content in the ashes. Natural occurring or added limestone (mostly calcite) or dolomite, and the presence of volatile organic compounds, all have a serious impact on the LOI, leading to overestimated unburned carbon contents [5,6]. On the other hand, when the ashes contain a substantial amount of iron minerals, it might

be possible that the weight after ignition changes to a large extent in an opposite way by modification of the Fe-containing components. For instance, oxidation of magnetite to hematite can take place, which would result in a gain of weight.

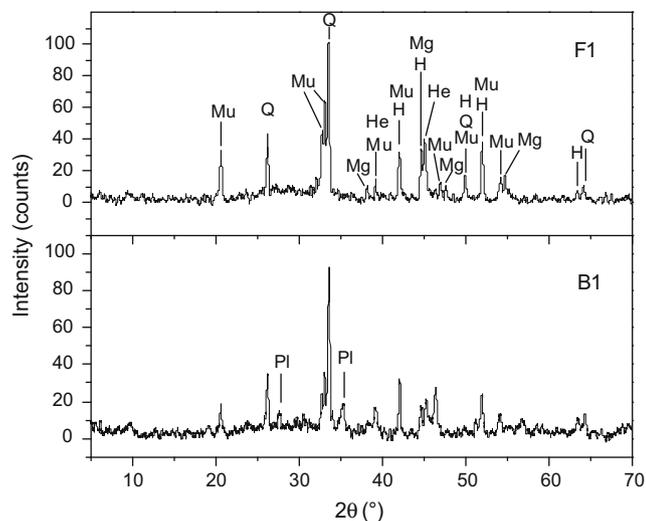
At the Electrabel-Rodenhuize electric generating plant (Desteldonk, Belgium) the quality of the fly and bottom ashes are monitored daily by measuring the LOI after burning the ashes for 30 min at 960 °C. After coal from a new origin was used LOI values for both the fly ash and bottom ash strongly deviated from the usual expected values and even became negative. It was readily suggested that the increased iron content in the new coal played a crucial role in these unexpected LOI results. In order to unravel this problem, a study applying a combination of various techniques was performed to gain information about the character and the behaviour of the Fe-bearing materials in both ashes before and after ignition.

### 2. Experimental

Samples of fly ash (F1 and F2) and bottom ash (B1 and B2), each before and after ignition, respectively, were investigated. X-ray diffractograms (XRD) were recorded on a XRD-6000 Shimadzu diffractometer equipped with a Fe tube and a graphite monochromator. Mössbauer spectra were collected at 295, 140, and 80 K with spectrometers operating at constant acceleration mode with triangular reference signals and using <sup>57</sup>Co(Rh) sources. The spectrometers were calibrated by collecting the spectrum of standard hematite or of a metallic iron foil at room temperature.

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**Fig. 1.** X-ray diffraction patterns of the fly and bottom ashes before ignition (samples F1 and B1, respectively). Mu: mullite; He: hercynite; Q: quartz; H: hematite; Mg: magnetite/maghemite and Pl: plagioclase.

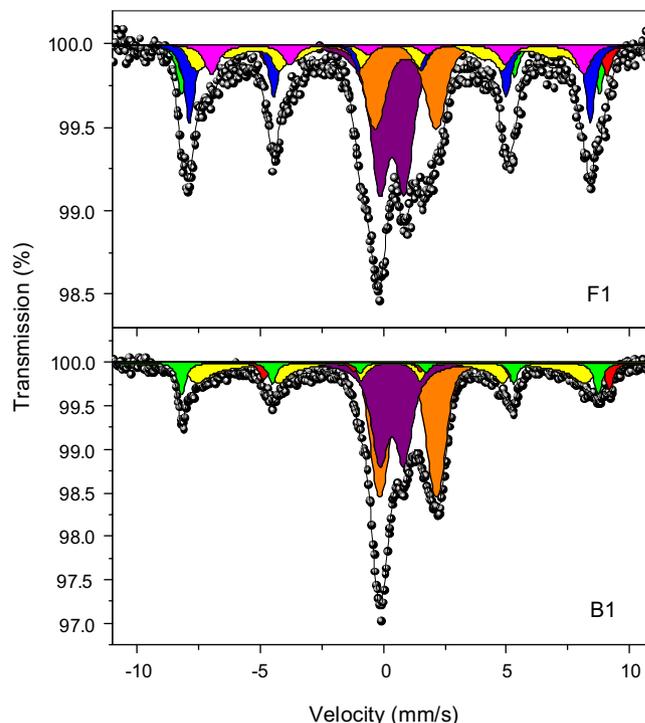
Spectra were analysed using Lorentzian line profiles and considering distributions of hyperfine fields where necessary. Isomer shifts are referenced with respect to  $\alpha$ -Fe at room temperature. The carbon content in the ashes was measured by the flash combustion method with an accuracy of  $\pm 2\%$ . Thermogravimetric measurements between 25 and 1000 °C and under synthetic air (100 ml/min) were carried out on a Du Pont SDT 2960 apparatus applying a heating rate of 5 °C/min.

### 3. Results and discussion

#### 3.1. Fly and bottom ashes before ignition

In the XRD patterns of the fly and bottom ashes before ignition (samples F1 and B1, respectively) characteristic diffraction peaks of quartz ( $\text{SiO}_2$ ), mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ), hercynite ( $\text{FeAl}_2\text{O}_4$ ) and magnetite/maghemite ( $\text{Fe}_3\text{O}_4/\gamma$ - $\text{Fe}_2\text{O}_3$ ) are unambiguously identified (Fig. 1). In the bottom ash, some additional peaks are observed which can be attributed to plagioclase. The mineralogy of sample F1 is typical for the so-called class F fly ashes (ASTM C618) that are obtained from burning high-rank coals [7].

Concerning the iron-bearing compounds, the Mössbauer spectrum at 295 K of the ash F1 shows the two sextets of (oxidized) magnetite, the sextet of weakly ferromagnetic (WF) hematite, and a sextet with zero quadrupole shift  $2\varepsilon_Q$ , pointing to a spinel phase which is most likely maghemite, although the presence of other spinel ferrites cannot be excluded. Therefore, this component will be denoted as a maghemite/ferrite phase. The asymmetrical line shape in the latter is probably due to small-particle morphology as usually observed in such systems and in some cases also from mixed ferrite compounds [8,9]. It is worth to remark at this point that the relative areas (RA) for the magnetite and maghemite/ferrite sextets are not at all accurate due to the strong overlap and possible asymmetric lines for magnetite. Moreover, the broad-lined inner sextet has been fitted with a hyperfine field distribution, which might show some fluctuations in the intensity probabilities. Anyway, this inner sextet is not arising from goethite as claimed by Hinckley et al. [1] in their ashes because well crystallized goethite, being magnetic at room temperature, can only be formed under extreme hydrothermal conditions and is not at all stable at such high temperatures.



**Fig. 2.** Mössbauer spectra at 140 K of the fly and bottom ashes before ignition (samples F1 and B1, respectively). AF hematite (red); WF hematite (green); magnetite  $\text{Fe}^{3+}$  (blue); magnetite  $\text{Fe}^{2.5+}$  (magenta); maghemite/ferrite (yellow);  $\text{Fe}^{3+}$ /mullite (purple); and  $\text{Fe}^{2+}$ /hercynite (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The paramagnetic part of the spectrum consists of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  doublets. Although many doublets of each kind can be expected, the spectrum could only be significantly fitted with one  $\text{Fe}^{2+}$  and one  $\text{Fe}^{3+}$  doublet. The latter doublet, with  $\delta \approx 0.32$  mm/s and  $\Delta E_Q \approx 0.99$  mm/s, is mainly representing an average spectrum for the mullite  $\text{Fe}^{3+}$  doublets. At room temperature, this doublet might also partly represent some superparamagnetic maghemite/ferrite because at lower temperatures the intensity of the  $\text{Fe}^{3+}$  doublet has somewhat decreased. The doublet with  $\delta \approx 1.06$  mm/s and  $\Delta E_Q \approx 2.28$  mm/s is an average for the various  $\text{Fe}^{2+}$  doublets representing the presence of ferrous ions in the structure of hercynite. The Mössbauer spectrum of hercynite at room temperature shows almost complete overlap of the different  $\text{Fe}^{2+}$  doublets [10]. Therefore, no quantitative estimation of the  $\text{Fe}^{2+}$  cation distribution is possible from the 295 K spectrum.

The 295 K Mössbauer spectrum of the bottom ash (sample B1) is similar to the spectrum obtained for the fly ash (sample F1) with the exception that no clear sextets of magnetite were observed. Also, the  $\text{Fe}^{2+}$  doublet contribution is much more pronounced in comparison with the fly ash spectrum.

In these 295 K Mössbauer spectra it is difficult to resolve quantitatively the various sextets due to the expected asymmetrical line shapes arising from small-particle morphology. Spectra were collected at 140 K to determine more accurately the amounts of iron in the various compounds. The latter temperature reduces the asymmetry in the line shape for hematite and maghemite/spinel on the one hand and is situated above the Verwey transition ( $\sim 130$  K for pure magnetite) for the magnetite on the other hand, because the Mössbauer spectrum of magnetite below its Verwey-transition temperature is very complicated [11]. The 140 K spectra of the fly and the bottom ash are shown in Fig. 2 and the hyperfine parameters obtained from the fitted spectra are listed in Table 1.

**Table 1**

Hyperfine parameters derived from the Mössbauer spectra at 140 K of the fly (F1) and bottom (B1) ash before ignition.

Sample	$B_{\text{hf}}$ (T)	$2\epsilon_{\text{Q}}$ (mm/s)	$\delta$ (mm/s)	$\Delta E_{\text{Q}}$ (mm/s)	RA (%)	Assignment
F1	52.6	-0.12	0.46	-	10	Hematite (WF)
	53.4	0.25	0.46	-	7	Hematite (AF)
	50.5	0	0.38	-	17	Magnetite $\text{Fe}^{3+}$
	46.9	0	0.69	-	9	Magnetite $\text{Fe}^{2.5+}$
	48.8	0	0.40	-	15	Maghemite
	-	-	0.47	1.02	26	Mullite
	-	-	1.02	2.56	16	Hercynite
B1	52.5	-0.12	0.45	-	9	Hematite (WF)
	53.9	0.33	0.45	-	8	Hematite (AF)
	49.1	0	0.42	-	17	Maghemite
	-	-	0.46	0.97	28	Mullite
	-	-	1.12	2.33	38	Hercynite
	-	-	-	-	-	-

$B_{\text{hf}}$ : hyperfine field at maximum of the distribution;  $2\epsilon_{\text{Q}}$ : quadrupole shifts;  $\Delta E_{\text{Q}}$ : quadrupole splitting;  $\delta$ : isomer shifts; RA: relative spectral areas. The values of isomer shifts are with reference to metallic iron at room temperature.

For the Mössbauer spectrum of sample F1 the same components as in the 295 K spectrum were considered, but, a sextet due to antiferromagnetic (AF) hematite phase has additionally been taken into account. The coexistence of both magnetic hematite phases (WF and AF) might be explained by either small-particle morphology [12,13] or by the presence of two hematite fractions with an extreme difference in particle sizes or with a distinct difference in aluminium substitution.

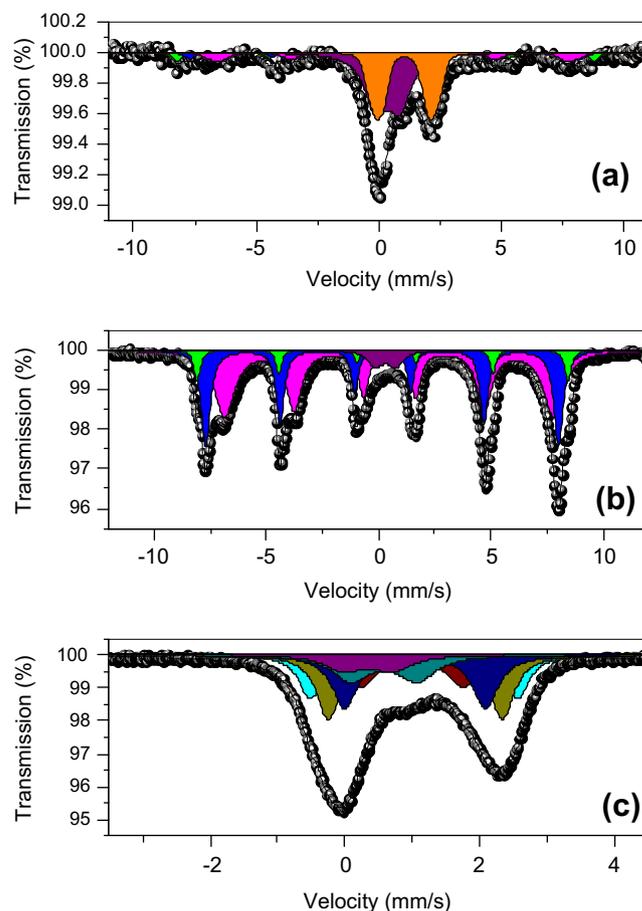
Although no significant amount of magnetite is present in the bottom ash (B1), the Mössbauer spectrum was also measured at 140 K (Fig. 2) to compare with those of the fly ash (F1). The Mössbauer spectrum was fitted using two sextets due to WF and AF hematite, a sextet accounting for maghemite/ferrite/(magnetite), an  $\text{Fe}^{3+}$  doublet and an  $\text{Fe}^{2+}$  doublet (Table 1). Concerning the relative area parameter (RA), the values were found, within experimental error, similar to the ones obtained from the spectrum collected at 295 K, indicating that sample B1 does not show superparamagnetic effects due to small-particle morphology of the iron-bearing oxides.

In order to provide more accurate hyperfine parameters and to obtain a better insight in the iron distribution of the different phases, both samples F1 and B1 were subjected to a magnetic separation resulting in a magnetic and a non-magnetic fraction. An intermediate magnetic fraction was also obtained, however, the obtained Mössbauer results will not be discussed here because the spectra are very similar to the one of the total fraction.

The Mössbauer spectrum at 295 K of the non-magnetic fraction of sample F1 showed only the contribution of the  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  doublets, no magnetic sextets were observed in the spectrum. However, by lowering the temperature to 140 K (Fig. 3a) the spectrum shows, in addition to the  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  doublets, three weak sextets, one due to WF hematite and two from magnetite. This result corroborates the Mössbauer results obtained from the total fraction of sample F1 in which small-particle morphology resulted similarly in a slight decrease of the  $\text{Fe}^{3+}$  doublet at lower temperature. The spectrum at 295 K of the magnetic fraction of sample F1 shows four components: a WF hematite sextet, the two magnetite sextets, and a weak  $\text{Fe}^{3+}$  doublet (Fig. 3b). The broad-lined sextet due to maghemite/ferrite is not clearly observed in this fraction, but might be somewhat hidden by the inner magnetite sextet.

The spectrum collected at 80 K of the non-magnetic fraction of sample B1 (Fig. 3c) does not show any sextet contribution, confirming the absence of superparamagnetic effects in the bottom ash sample. The Mössbauer spectrum was fitted with four  $\text{Fe}^{2+}$  doublets characteristic for hercynite, a weak  $\text{Fe}^{3+}$  doublet that is considered as an average for the three mullite doublets, and another  $\text{Fe}^{3+}$  doublet with quadrupole splitting of 0.98 mm/s and isomer shift of 0.69 mm/s (Table 2). The identification of the precise

nature of the latter iron phase on the basis of the adjusted hyperfine parameters is not possible because of the strong overlap between the various doublet lines in the central part of the spectrum. However, it is not unreasonable to suggest that the doublet may be due to wustite ( $\text{Fe}_{1-x}\text{O}$ ) that may indeed be present in a small amount in the bottom ash. The Mössbauer spectrum of the



**Fig. 3.** Mössbauer spectra of the magnetic and non-magnetic fractions of the fly and bottom ash samples. (a) non-magnetic fraction of the fly ash measured at 140 K; (b) magnetic fraction of the fly ash measured at 295 K; (c) non-magnetic fraction of the bottom ash measured at 80 K. WF hematite (green); magnetite  $\text{Fe}^{3+}$  (blue); magnetite  $\text{Fe}^{2.5+}$  (magenta);  $\text{Fe}^{3+}$ /mullite (purple); average for the  $\text{Fe}^{2+}$  doublets in hercynite (orange); and  $\text{Fe}^{2+}$ /hercynite (cyan, dark yellow, navy and brown). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 2**  
Hyperfine parameters derived from the Mössbauer spectra at 140 K of the non-magnetic fraction and at 295 K of the magnetic fraction of the fly (F1) ash sample, and at 80 K of the non-magnetic fraction of the bottom (B1) ash sample.

Temperature (K)	Sample	$B_{\text{hf}}$ (T)	$2\varepsilon_{\text{Q}}$ (mm/s)	$\delta$ (mm/s)	$\Delta E_{\text{Q}}$ (mm/s)	Assignment
140	F1 non-magnetic fraction	52.6*	-0.12*	0.46*	-	Hematite (WF)
		49.4	0	0.38*	-	Magnetite Fe <sup>3+</sup>
		43.4	0	0.69*	-	Magnetite Fe <sup>2.5+</sup>
		-	-	0.48	0.97	Mullite
		-	-	1.17	2.11	Hercynite
295	F1 magnetic fraction	51.1	-0.15	0.37	-	Hematite (WF)
		48.6	0	0.28	-	Magnetite Fe <sup>3+</sup>
		45.4	0	0.59	-	Magnetite Fe <sup>2.5+</sup>
		-	-	0.40	0.91	Mullite
		-	-	0.45	0.72	Mullite
80	B1 non-magnetic fraction	-	-	1.13	3.07	Hercynite
		-	-	1.15	2.57	Hercynite
		-	-	1.10	1.52	Hercynite
		-	-	1.15	2.08	Hercynite
		-	-	0.69	0.98	Iron phase
		-	-	-	-	-
		-	-	-	-	-

$B_{\text{hf}}$ : hyperfine field at maximum of the distribution;  $2\varepsilon_{\text{Q}}$ : quadrupole shifts;  $\Delta E_{\text{Q}}$ : quadrupole splitting;  $\delta$ : isomer shifts. The values of isomer shifts are with reference to metallic iron at room temperature.

\* Fixed parameters.

magnetic fraction of sample B1 is very similar to the total fraction spectrum.

### 3.2. Fly and bottom ash after ignition

The Mössbauer spectrum at 140 K of the fly ash after ignition (sample F2) shows also the two hematite sextets (WF and AF phases), the distributed maghemite/ferrite sextet and the mullite doublet (Fig. 4). However, magnetite is absent and the Fe<sup>2+</sup>/hercynite doublet has nearly completely disappeared. On the other hand, the characteristic sextet of  $\alpha$ -Fe is clearly observed.

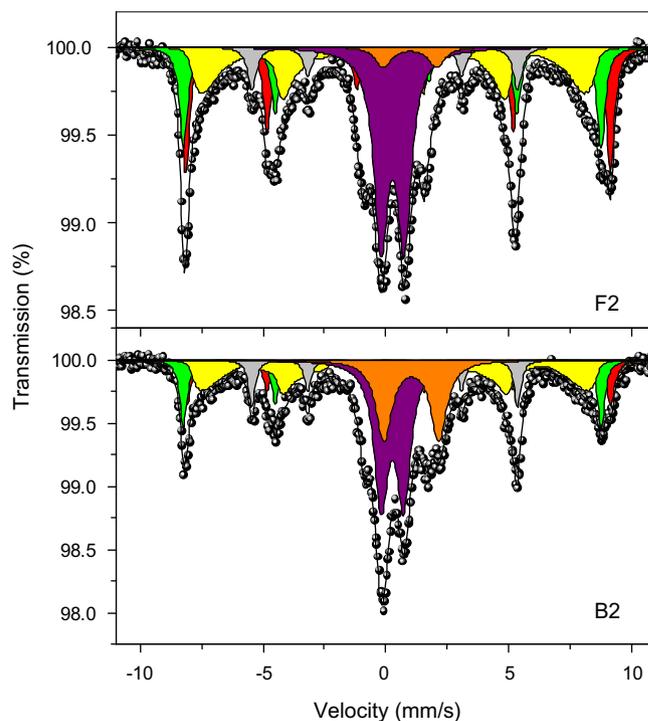
Considering the relative area values of the subspectra of the various components observed in the fly ash before (Table 1, sample F1) and after ignition (Table 3, sample F2), one can readily observe that besides the formation of metallic iron, the contribution of hematite as well as maghemite/(ferrite) increased considerably after ignition. The contribution of the Fe<sup>3+</sup> doublet did not change, confirming the previous assignment of this doublet to mullite, which is indeed stable up to very high temperatures. On the contrary, magnetite has completely vanished whereas the doublet attributed to Fe<sup>2+</sup>/hercynite is also strongly reduced. The formation of  $\alpha$ -Fe after ignition in air could be explained by the following reaction:



which could, for instance, be the final result of the decomposition of siderite (FeCO<sub>3</sub>) [14]. However, siderite is only present in the coal and transforms during combustion to hematite or magnetite. The latter is usually formed in the higher temperature regions of the furnace, which is the reason for being solely present in the fly ash. Moreover, the hyperfine parameters of the siderite doublet are quite different of those observed for the Fe<sup>2+</sup> doublets in the Mössbauer spectra. As already suggested, one of the doublets appearing in the spectra of the non-magnetic fraction of the bottom ash sample before ignition could be assigned to wustite, the presence of this phase resulting in the formation of  $\alpha$ -Fe after ignition. Therefore, it is not excluded that wustite may also be present in the fly ash before ignition, although its spectral contribution could not be directly resolved in the Mössbauer spectrum of the non-magnetic fraction of the sample due to the overlap with the inner lines of the sextets (Fig. 3a).

From the changes in the relative areas of the subspectra, it can be suggested that magnetite and hematite are formed from oxidation of hercynite. In order to verify this oxidation process, a syn-

thetic hercynite sample was subjected to a heat treatment at 960 °C for 30 min in air, which are the same conditions used in the routine LOI measurements. The Mössbauer spectrum at 295 K of the obtained product is shown in Fig. 5. The spectrum is composed of a WF hematite sextet, two magnetite sextets, an Fe<sup>3+</sup> doublet with hyperfine parameters typical for iron in the structure of corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), and a weak Fe<sup>2+</sup>/hercynite doublet. The latter one is most probably the result of the non-complete transformation of the hercynite during the short heating. From this experiment, it is clear that magnetite and hematite are the main iron-bearing oxidation products from hercynite, which can be roughly represented by the following reaction



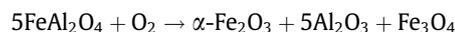
**Fig. 4.** Mössbauer spectra at 140 K of the fly and bottom ashes after ignition (samples F2 and B2, respectively). AF hematite (red); WF hematite (green); maghemite/ferrite (yellow); Fe<sup>3+</sup>/mullite (purple); Fe<sup>2+</sup>/hercynite (orange); and  $\alpha$ -Fe (light-gray). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 3**

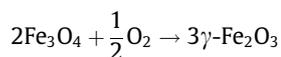
Hyperfine parameters derived from the Mössbauer spectra at 140 K of the fly (F2) and bottom (B2) ash after ignition.

Sample	$B_{\text{hf}}$ (T)	$2e_Q$ (mm/s)	$\delta$ (mm/s)	$\Delta E_Q$ (mm/s)	RA (%)	Assignment
F2	52.7	-0.15	0.45	-	17	Hematite (WF)
	53.6	0.31	0.45	-	21	Hematite (AF)
	48.5	0	0.43	-	24	Maghemite
	33.5	0	0.07	-	8	$\alpha$ -Fe
	-	-	0.38	0.94	27	Mullite
	-	-	1.08	2.16	3	Hercynite
B2	52.7	-0.16	0.45	-	13	Hematite (WF)
	53.5	0.36	0.45	-	10	Hematite (AF)
	48.8	0	0.47	-	23	Maghemite
	33.5	0	0.07	-	9	$\alpha$ -Fe
	-	-	0.37	0.91	27	Mullite
	-	-	1.14	2.23	18	Hercynite

$B_{\text{hf}}$ : hyperfine field at maximum of the distribution;  $2e_Q$ : quadrupole shifts;  $\Delta E_Q$ : quadrupole splitting;  $\delta$ : isomer shifts; RA: relative spectral areas. The values of isomer shifts are with reference to metallic iron at room temperature.



The presence of maghemite instead of magnetite in the burned ashes might be explained by the newly formed magnetite from both hercynite and wustite, which afterwards oxidizes to maghemite according to

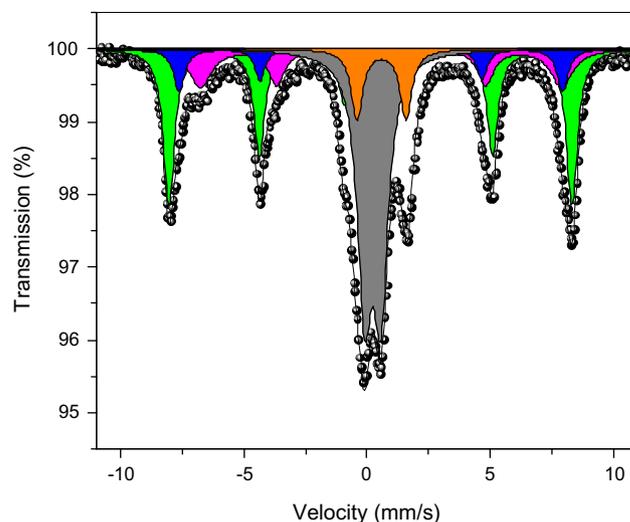


On the other hand, the magnetite that was already present in the fly ash oxidizes completely to hematite after ignition.

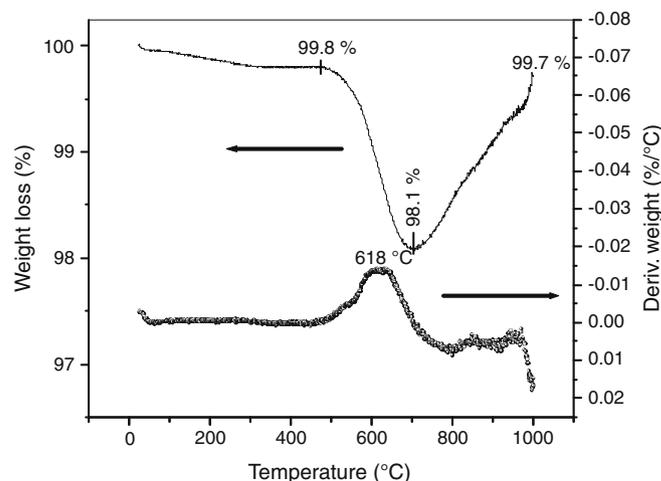
The spectrum at 140 K of the bottom ash after ignition (B2) shows two sextets of hematite, a maghemite/ferrite sextet, a  $\text{Fe}^{3+}$ /mullite doublet, a  $\text{Fe}^{2+}$ /hercynite doublet, and in addition, a sextet of  $\alpha$ -Fe. Comparing the relative areas of the bottom ash before and after ignition (Tables 1 and 3, respectively), it can be observed that the hematite and maghemite contribution increases at the expense of the hercynite phase after ignition. It is not excluded that the remaining doublet attributed to hercynite may also represent other  $\text{Fe}^{2+}$ -containing components such as glasses. Finally, as suggested  $\alpha$ -Fe is formed from the wustite after the ignition.

The observed negative LOI can now be explained by the different oxidation processes involving the formation of magnetite, maghemite, and hematite, which is responsible for a weight gain and compensates the loss due to the burning of the remaining carbon in both samples fly (F1) and bottom (B1) ash before ignition. The unburned carbon has been directly measured by carbon analysis. The carbon content was found to be 2.31 wt.% for sample F1 and 1.09 wt.% for sample B1.

The various processes resulting in weight changes can normally be observed from thermogravimetric analysis (TGA). The TGA curve and the corresponding derivative curve of sample F1 are represented in Fig. 6. A minor weight loss (0.2%) that could account for the release of adsorbed water is observed between 25 and 280 °C. At higher temperatures, in the range 500–700 °C with a maximum at 618 °C, a loss in weight is clearly noticed. This weight loss can be mainly ascribed to release of the remaining unburned carbon in the sample as  $\text{CO}_2$ . At temperatures beyond 700 °C, a gain in weight takes place and is still not completed at temperatures up to 1000 °C. The weight gain is clearly associated with the aforementioned oxidation processes resulting in the formation of hematite, magnetite, and maghemite. Precise results on the amount of unburned carbon in the fly ash sample cannot be derived from the TGA analysis, but it is nevertheless clear that the weight gain can compensate the loss due to unburned carbon.



**Fig. 5.** Mössbauer spectra at 295 K of a pure hercynite sample heated in air at 960 °C during 30 min. WF hematite (green); magnetite  $\text{Fe}^{3+}$  (blue); magnetite  $\text{Fe}^{2.5+}$  (magenta);  $\text{Fe}^{3+}/\text{Al}_2\text{O}_3$  (gray); and  $\text{Fe}^{2+}$ /hercynite (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 6.** Thermogravimetric curve (solid line) and its respective derivative (dotted line) of the fly ash before ignition (sample F1).

#### 4. Conclusions

From the present study on a fly and a bottom ash, before and after ignition, it follows that a hercynite phase is present which transforms to hematite and magnetite. In the short time of the ignition experiment at 960 °C, the magnetite is not converted to hematite but oxidizes rather (probably afterwards) to maghemite. The magnetite which was already present in the fly ash is converted completely to hematite after ignition. All those oxidation processes lead to a weight gain that can offset the weight loss due to the burning of the remaining carbon. Therefore, negative LOI values cannot be excluded in this type of iron-rich ashes when the ignition is performed at relatively high temperatures (960 °C). In order to avoid such anomalies, LOI should only be measured after ignition at moderate temperatures (~750 °C) at which, at least, hercynite remains stable [15].

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