

Characterization Study of Electric Arc Furnace Dust Phases

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Electric arc furnace dust (EAFD) is a solid waste generated in the collection of particulate material during steelmaking process in electric arc furnace. The aim of this work is to carry out a chemical and structural characterization of two EAFD samples with different Zn contents. Optical emission spectroscopy via inductively coupled plasma (ICP), X ray diffractometry (XRD) and Mössbauer spectroscopy analysis were carried out in such EAFD samples. From XRD measurements, the samples exhibits the following phases: ZnFe_2O_4 , Fe_3O_4 , MgFe_2O_4 , FeCr_2O_4 , $\text{Ca}_{0.15}\text{Fe}_{2.85}\text{O}_4$, MgO , Mn_3O_4 , SiO_2 and ZnO . The phases detected by Mössbauer spectroscopy were: ZnFe_2O_4 , Fe_3O_4 , $\text{Ca}_{0.15}\text{Fe}_{2.85}\text{O}_4$ and FeCr_2O_4 . Magnesium ferrite (MgFe_2O_4), observed in the XRD patterns as overlapped peaks, was not identified in the Mössbauer spectroscopy analysis.

Keywords: EAFD, characterization, XRD, Mössbauer spectroscopy

1. Introduction

Electric arc furnace dust (EAFD) is a solid waste generated during the steelmaking process. It is classified according to NBR 10004¹ as dangerous solid waste-class I, because Pb and Cd elements leach in water exceeding the maximum limits permitted by the NBR 10005². The State Foundation for Environmental Protection of Rio Grande do Sul – FEPAM – requires that this waste must be stored in an appropriate place, protected from rain. Due to the great generated amount, from 12 to 14 Kg of dust per ton of steel, a study of the steel recycling alternatives is necessary.

In general, and especially in developed countries, the EAFD treatment processes mainly aim the zinc recovering. This is due to the fact that in the last 40 years this element has been used progressively in the galvanizing process of the carbon steel. When these steel scraps are reused, the contained zinc is evaporated during the melting (B. P. 907 °C), passing nearly all to EAFD, remaining very low amount in the steel and in the slag³.

In Brazil, the amount of galvanizing steel recycling is still small to use the major EAFD treatment technologies commercialized all over the world. Besides, there is the zinc ore extraction in Brazil. However, new researches have already been developed in order to recycle the EAFD expecting the increase of zinc in this waste.

As chemical and structural characterization of solid waste is a very important stage to evaluate recycling feasibility, several analytical techniques have been used to study EAFD. Comparing the elementary chemical analysis results, XRD and Mössbauer spectroscopy, it is possible to determine and to quantify the phases present in the EAFD samples studied.

This paper is concerned with chemical and structural characterization of two types of EAFD with different Zn contents.

2. Materials and Methods

Two EAFD samples with different Zn contents were collected from the dust removal system of a steel plant in southern Brazil. This company is characterized by special steel production with a varied chemical composition.

2.1. Chemical characterization

EAFD samples digestion – Brehm⁴ suggested that to get the EAFD complete digestion, the methodology must be done in two stages:

- 1st stage: digestion via electric plate; and
- 2nd stage: alkaline fusion of the insoluble waste from the 1st stage.

To accelerate this procedure, the digestion via microwave oven was used, instead of electric plate (performance time \approx 3 hours). With microwave, the stage performance time is about 45 minutes and the results are the same. A flow diagram of the used methodology is displayed in Figure 1.

Sample 1 was used as a reference to determine the largest possible number of elements in the EAFD, according to the ones involved in the steelmaking in the EAF.

The techniques used for elementary chemical analysis of sample 1 are shown in Table 1.

In sample 2 the major elements (Fe and Zn) were analyzed: these ones are more interesting for the reduction study using carbon reducing agents to get ferrous concentrated⁵. The Ca, Cr, Mg elements were analyzed because they had been identified in the analytical results of structural characterization forming phases like FeOCr_2O_3 , CaFe_2O_4 ⁶ and MgFe_2O_4 ⁷. The analytical results were obtained via ICP.

The silicon amount was not considered in both samples because most of this element evaporates during the 1st stage of the digestion

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method used in the preparation of the samples for chemical analysis via ICP. As a result of that its amount in the dust would be lower. At the same time, its amount was not analyzed via other analytical method because it is known that most of this element appears as SiO₂.

2.2. X ray diffraction

The structural characterization of EAFD was performed through X ray diffraction analysis in a Siemens appliance model D500, in the Physics Institute of the Federal University of Rio Grande do Sul (UFRGS). X ray patterns of samples powdered to 400 mesh were obtained with monochromated Cu K α radiation in the 2 θ -range from 2° to 140° with a scan step of 0.05° 2 θ , and fixed counting time of 1 second for each step. The patterns were analyzed by using the Philips X-Pert Software.

2.3. Mössbauer spectroscopy

Absorbers for Mössbauer spectroscopy measurements were prepared with appropriate amounts of ground (400 mesh) material to satisfy the ideal absorber thickness approximation⁸. The spectra were taken at room temperature using a constant acceleration electromechanical drive system with a multichannel analyzer for collecting and storing the data. The velocity scale was calibrated using a high-purity 6 μ m thick Fe foil. The hyperfine parameters were obtained by a least-squares procedure assuming Lorentzian line shapes constrained to equal halfwidths. ⁵⁷Co in rhodium was used at room temperature as a source, with nominal activity of 10 mCi. Typical errors are \pm 3% on hyperfine parameters and \pm 5% on site occupancies.

3. Results and Discussions

3.1. Elementary chemical analysis

The elementary results for samples 1 and 2 are presented in Tables 2 and 3. The Fe element in sample 1 (42%) is smaller than in sample 2 (48.96%). The contrary is observed for Zn: in sample 1, 12% and in sample 2, 9.24%. According to the literature⁹, about EAFD for carbon steel, the zinc contents are between 11.2% and 26.9%. For the EAFD from stainless steel the contents are between 1.77% and 6.22%. Therefore, Fe and Zn contents found in these EAFD samples are in the intermediate range.

The other elements (for example, Ca, Mg, Cd, Pb, Cr, Mn, and Si) plus O complete the composition. It was decided to use elementary chemical composition because it has been determined in previous works⁴⁻⁶ that the EAF dust does not be constituted by the most stable binary metallic oxides, as it is usually showed by the majority of articles found in the literature^{10,11}.

3.2. X ray diffraction

The X ray diffraction patterns are displayed in Figures 2 and 3, and the obtained oxide phases are summarized in Table 4.

As it can be seen, ZnFe₂O₄, Fe₃O₄, MgFe₂O₄, FeCr₂O₄, Mn₃O₄, MgO, SiO₂, Ca_{0.15}Fe_{2.85}O₄ and ZnO are present in both samples.

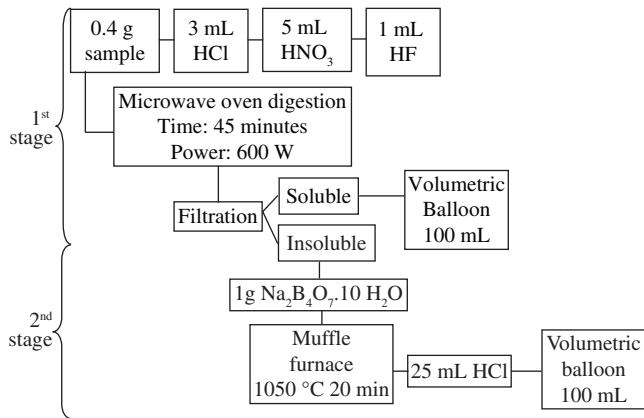


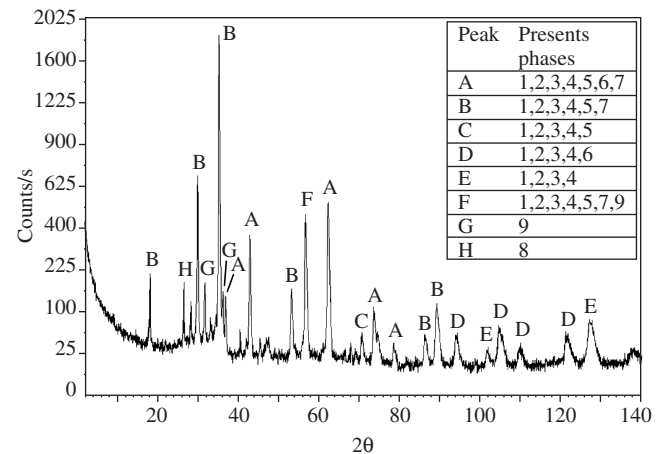
Figure 1. Methodology used for the EAFD samples digestion.

Table 1. Techniques used in the sample 1 elementary chemical analysis.

Elements	Techniques
Al, Cd, Pb, Co, Cu, Cr, Sn, Mg, Mn, Mo, Ni, K, Na, Zn.	Atomic Absorption Spectrometry
Ca	Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).
C, S	Combustion
Fe	Volumetry

Table 2. Elementary results found in sample 1 (wt. (%)).

Element (%)	Fe	Zn	Ca	Cr	Mg	Co	Cu	S	Sn	Al	C	Pb	Mn	Mo	Ni	K	Na	Cd
Sample 1	42	12	4.87	3.20	2.21	0.004	0.36	0.292	0.25	0.36	1.61	1.26	1.65	0.09	0.17	1.32	1.6	0.03



1. Franklinite - ZnFe₂O₄ (PDF: 22-1012);
2. Magnetite - Fe₃O₄ (PDF: 11-0614);
3. Magnesium-ferrite - MgFe₂O₄ (PDF: 17-0465);
4. Chromite - FeCr₂O₄ (PDF: 34-0140);
5. Calcium-magnetite - Ca_{0.15}Fe_{2.85}O₄ (PDF: 46-0291);
6. Periclase - MgO (PDF: 45-0946);
7. Manganese oxide - Mn₃O₄ (PDF: 13-0162);
8. Quartz - SiO₂ (PDF: 05-0490); and
9. Zincite - ZnO (PDF: 36-1451).

Figure 2. X ray diffraction (XRD) pattern of sample 1.

Table 3. Elementary results found in sample 2(wt. (%)).

Element (%)	Fe	Zn	Ca	Cr	Mg
Sample 2	48.96	9.24	3.28	2.90	1.65

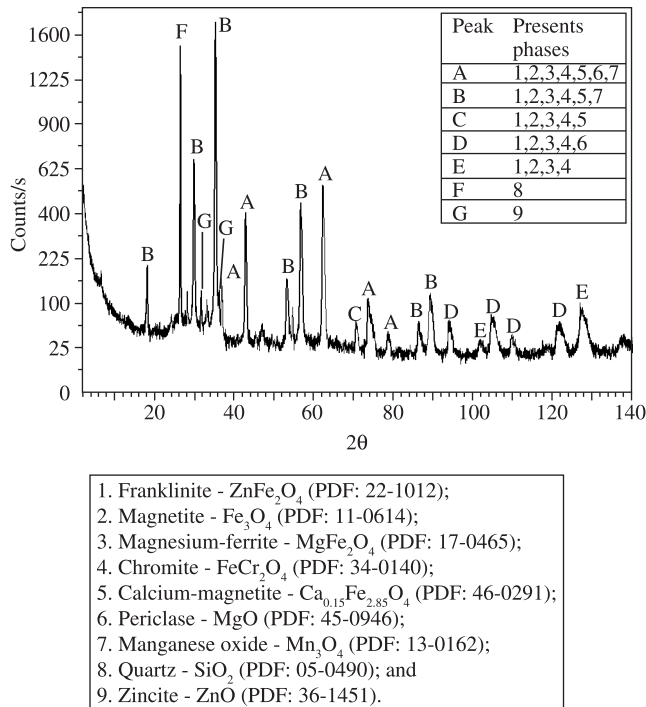


Figure 3. X ray diffraction (XRD) pattern of sample 2.

Table 4. Phases obtained in the XRD analysis of the studied EAFD samples.

Phases	Sample 1	Sample 2
ZnFe_2O_4	X	X
Fe_3O_4	X	X
MgFe_2O_4	X	X
FeCr_2O_4	X	X
Mn_3O_4	X	X
MgO	X	X
ZnO	X	X
SiO_2	X	X
$\text{Ca}_{0.15}\text{Fe}_{2.85}\text{O}_4$	X	X

However, except for SiO_2 and ZnO , the signals from all the phases exhibit overlapping in some extent, as shown in Figures 2 and 3. Because of such overlapping, also observed by Heck⁷, the presence of these phases cannot be unequivocally assured. As it will be shown, to improve the phases identification in EAFD samples it is necessary to use other techniques like, for example, Mössbauer Spectroscopy and Scanning Electron Microscopy with Energy Dispersive Spectroscopy and X ray Mapping Analysis. The Mössbauer Spectroscopy was used for investigation of these ferrous oxide phases ZnFe_2O_4 , Fe_3O_4 , MgFe_2O_4 , FeCr_2O_4 , $\text{Ca}_{0.15}\text{Fe}_{2.85}\text{O}_4$.

3.3. Mössbauer spectroscopy

The Mössbauer spectrum for sample 2 is displayed in Figure 4. It is quite similar to that one obtained for sample 1. The parameters obtained from fitting the spectra are presented in Table 5.

It is interesting to observe that the magnesium-ferrite phase (MgFe_2O_4) identified in samples 1 and 2 through XRD, in overlapped peaks, was not observed in the Mössbauer spectra. Comparing

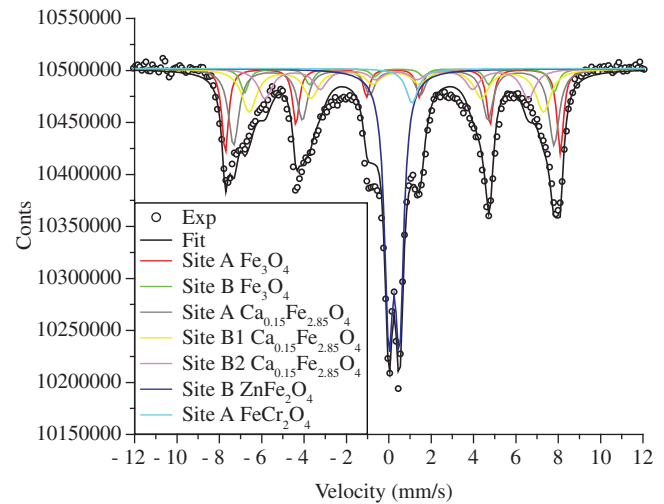


Figure 4. Mössbauer spectrum of sample 2.

Table 5. Mössbauer Parameters* used in the spectra fit of the EAFD samples at room temperature.

Sample	Phase		H_{eff} (kOe)	δ/Fe (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)
1	Fe_3O_4	Site A	489	0.29	-0.01	0.37
		Site B	453	0.55	0.01	0.61
	ZnFe_2O_4	Site A	-	0.35	0.50	0.48
	FeCr_2O_4	Site A	-	-	1.1	0.70
	$\text{Ca}_{0.15}\text{Fe}_{2.85}\text{O}_4$	Site A	470	0.38	-0.06	0.59
Site B		418	0.53	0.01	0.70	
2	Fe_3O_4	Site A	491	0.30	-0.01	0.37
		Site B	453	0.60	0.01	0.47
	ZnFe_2O_4	Site A	-	0.35	0.50	0.47
	FeCr_2O_4	Site A	-	-	1.1	0.70
	$\text{Ca}_{0.15}\text{Fe}_{2.85}\text{O}_4$	Site A	470	0.38	-0.06	0.59
Site B		408	0.47	0.01	0.83	

* H_{eff} , hyperfine field; δ/Fe , isomer shift relative to metallic iron; ΔE_Q , quadrupole shift; and Γ , line width.

Mössbauer results with the Mg amount determined via ICP, it may be suggested that such phase is not present in the dust.

The Mössbauer parameters obtained for Fe_3O_4 , ZnFe_2O_4 and FeCr_2O_4 in both samples are in agreement with those reported in the literature¹²⁻¹⁴.

The hyperfine field for the site assigned as B in $\text{Ca}_{0.15}\text{Fe}_{2.85}\text{O}_4$ is an average between two fitted values, as illustrated in Figure 4. Such a behavior is due to the fact that calcium substitutes iron randomly at the site B, occupying in a disorganized form the iron place in the magnetite B site. The result is that, for each cell, there are different hyperfine interactions and, consequently, there is a hyperfine magnetic field distribution in this site¹⁵.

Values around 0.50 mm/s for the line width are commonly found in the literature. Spectra with wide lines may indicate, among other things, sample disordering¹⁴.

Table 6 shows the ferrous quantification in the oxide phases found in the EAFD according to Mössbauer spectroscopy.

One of the most important characteristics of the Mössbauer Spectroscopy technique is its selectivity. If the emitter Mössbauer

Table 6. Quantification of ferrous in the oxide phases present in the EAFD samples according to the Mössbauer spectroscopy.

Phase		Sample 1 (%)	Sample 2 (%)
Fe ₃ O ₄	Site A	14.80	14.82
	Site B	7.71	5.33
ZnFe ₂ O ₄	Site A	27.01	27.05
FeCr ₂ O ₄	Site A	3.68	2.80
Ca _{0.15} Fe _{2.85} O ₄	Site A	18.59	21.35
	Site B1	16.26	17.39
	Site B2	11.95	11.27

isotope is, for example, ⁵⁷Fe, the resonant absorption may only occur if there are identical nucleus inside the absorbent. In this way, even if the sample shows a great variety of compounds, only the ones which have a Mössbauer nucleus in their constitution, will be detected. Considering that the EAFD does not present only iron in its constitution, the results of the Mössbauer spectroscopy and the ICP analysis (Fe and Zn content) were used to determine the amount of the main oxides phases (Fe₃O₄, ZnFe₂O₄, FeCr₂O₄, Ca_{0.15}Fe_{2.85}O₄ and ZnO). Table 7 shows the analyzed samples composition according to these two techniques. The other oxide compounds with the elements Si, Cd, Pb, Mn, Mg complete the composition.

The amount of ZnO was determined as follows:

1st step: Determination ZnFe₂O₄ amount

$$\%Fe_{ZnFe_2O_4} = \frac{\%Fe_{total(via\ ICP)} \times \%Fe_{ZnFe_2O_4} (via\ Mössbauer)}{100}$$

$$\%ZnFe_2O_4 = \frac{\%Fe_{ZnFe_2O_4} \times \bar{M}_{Fe(ZnFe_2O_4)}}{\bar{M}_{ZnFe_2O_4}}$$

2st step: Determination ZnO amount

$$\%Zn_{ZnFe_2O_4} = \frac{\%ZnFe_2O_4 \times \bar{M}_{Zn}}{\bar{M}_{ZnFe_2O_4}}$$

$$\%Zn_{ZnO} = \%Zn_{total(via\ ICP)} - \%Zn_{ZnFe_2O_4}$$

$$\%ZnO = \frac{\%Zn_{ZnO} \times \bar{M}_{ZnO}}{\bar{M}_{Zn}}$$

Where,

$\%Fe_{ZnFe_2O_4}$: %Fe in ZnFe₂O₄ phase;

$\%Fe_{total(via\ ICP)}$: wt. (%) of total Fe determined via ICP;

$\%Fe_{ZnFe_2O_4} (via\ Mössbauer)$: %Fe in ZnFe₂O₄ phase determined via Mössbauer;

$\%Zn_{ZnFe_2O_4}$: %ZnFe₂O₄ in samples;

$\bar{M}_{Fe(ZnFe_2O_4)}$: molar weight of Fe in ZnFe₂O₄ phase;

$\bar{M}_{ZnFe_2O_4}$: molar weight of ZnFe₂O₄ phase;

$\%Zn_{ZnFe_2O_4}$: %Zn in ZnFe₂O₄ phase;

\bar{M}_{Zn} : molar weight of Zn;

$\%Zn_{ZnO}$: %Zn in ZnO phase;

$\%Zn_{total(via\ ICP)}$: wt. (%) of total Zn determined via ICP;

\bar{M}_{ZnO} : molar weight of ZnO phase; and

$\%ZnO$: %ZnO in samples.

According to Table 7, it is observed that while the EAFD Zn content decreases, the ZnO phase content also decreases and the ZnFe₂O₄ content increases. The relation between the zinc content in these phases is shown in Table 8. The data from this table were calculated considering the amount of Zn in the ZnFe₂O₄ and ZnO phases in both EAFD studied samples.

The results shown in Table 7 and 8 are according to the literature, because for the EAFD with low Zn concentration, most of the Zn

Table 7. Quantification of the mainly oxides phases in the studied EAFD samples.

Phase	Sample 1 (%)	Sample 2 (%)
Fe ₃ O ₄	13	14
ZnFe ₂ O ₄	24	29
FeCr ₂ O ₄	6	6
Ca _{0.15} Fe _{2.85} O ₄	28	35
ZnO	7	2

Table 8. Relation between Zn content in the ZnFe₂O₄ and ZnO phases for EAFD with different Zn contents.

	Sample 1 (12% of Zn)	Sample 2 (9.24% of Zn)
%Zn in ZnFe ₂ O ₄	55	84
%Zn in ZnO	45	16

is in the spinel or ferrite form. While the Zn content increases, the ZnO concentration also increases. However, even with a 28% Zn content, the zinc ferrite is relevant¹⁶. Another author¹⁷ emphasizes that zinc ferrite percentage in the EAFD is directly proportional to the Fe/Zn rate.

4. Conclusion

- ZnFe₂O₄, Fe₃O₄, FeCr₂O₄, Ca_{0.15}Fe_{2.85}O₄, SiO₂ and ZnO phases are present in the studied EAFD samples;
- MgFe₂O₄ phase identified in samples 1 and 2 through the XRD in overlapped peaks, was not observed in the Mössbauer spectra; and
- Concerning Zn compounds, the greater this element concentration is, the greater ZnO content and smaller the ZnFe₂O₄ content are.

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