Metallurgy and materials

Carbothermic reduction of Electric Arc Furnace Dust via thermogravimetry

Abstract

Electric Arc Furnace Dust (EAFD) is a solid waste originated from electric steel-making furnaces. Currently, according to some authors, there is an estimated generation of 15 to 25 kg of dust per ton of steel produced. The formation of the dust is related to the following steps of the process: furnace charge, metal volatilization, iron vaporization under the arc, drag of solid particles and, mainly by the collapse of CO bubbles from metallic bath decarburization. The dust has metals that are harmful to the environment. Otherwise, it is mostly composed of the elements iron, zinc and oxygen. Due to increasing costs for disposal and because it is considered a hazardous waste, industry is looking at the possibility of returning the dust to the steelmaking process. One of the alternatives is by reintroducing the waste in an electric melting shop using self-reducing agglomerates as part of the furnace burden. In this study, self-reducing mixtures are prepared with EAFD and petroleum coke (PET), presenting chemical and physical characterizations. An evaluation about the behavior of the mixtures is carried out in thermobalance, regarding the possibility of use in measuring accurate PET content in self-reducing pellets. As results it could be stated that the elements of economic interest, Zn and Fe, represent, respectively, 34.23 and 22.80%, in weight. These elements are present in chemical species frankilinite, zincite and magnetite and the reducible oxygen was estimated as 17.90%. Also, it was concluded the optimal content of petroleum coke in the mixtures varies from 10 to 15%, in weight. Therefore, the utilization potential of the thermogravimetric technique in the industrial field for adjustment of carbon content in batches of self-reducing pellets is satisfactory.

Keywords: electric arc furnace dust; characterization; thermo-balance.

1. Introduction

According to a sustainability report posted by Instituto Aço Brasil in 2015, 8% of coproducts and wastes generated from the steel industry are dust and fines. Among these residues, there is a material called Electric Arc Furnace Dust (EAFD). The production of steel by Electric Arc Furnace (EAF) increased about 12% in Brazil and 15% in the world, from 2005 to 2014. Therefore, the amount of EAFD generation has probably increased. According to some authors, the estimation of dust generation per ton of steel produced is around 15-25 kg (Machado, 2004; Alves et al., 2009; Guézenec et al., 2005). The formation of the dust in the steelworks is associated with the following points: furnace loading; metal volatilization, such as zinc; iron vaporization under the arc or drag of solid particles and mainly, CO bubble collapse, which occurs from decarburization in the metallic bath (Guézenec et al., 2005). The EAFD is mainly composed of Fe and Zn, in different kinds of metallic oxides, like ZnO, ZnFe₂O₄, Fe₃O₄ (Pickles, 2009). For dust with low concentrations of zinc, the major part is present in the form of spinels and ferrites. Thermodynamically, the phase zincite, appears in EAFD when Zn/(Fe+Zn) is higher than 0.37 in mass (Buzin, 2009). The higher the Zn content, the higher the ZnO content (Machado, 2004). The chemical composition of EAFD depends fundamentally on raw materials, type of steel produced and alloys used (Machado, 2004). It can vary, suffering changes from heat to heat in the same steel plant (Guézenec et al., 2005).

From an environmental point of view, according to (ABNT) NBR 10004-2004, the EAFD is classified as a waste class 1, hazardous. That is why plants avoid its destination in landfills, and look for alternative methods to disposal through recycling or returning it to the steel production process. These alternatives are based on the metallic content recuperation of the dust (Fe and Zn) as well as a search for sustainable...
improvements and costs reductions of the environmental destinations of this waste. In view of steel plants being semi-integrated, there are no reduction reactors, making it difficult to recycle EAFD.

The disposal or treatment of the dust is expensive and is the focus of increased attention in recent years. Some of the EAF dust is being disposed of in hazardous waste landfill sites, but because appropriate storage sites are lacking and placed more distant from the generation point, increasing pressure is being placed on steelmakers to adopt some method for the treatment of the dust (Mantovani and Takano, 2000).

The self-reduction technology consists of an intimate mixture, between the metal oxide, and the carbon material that intends to extract the element of value. The iron oxides and the reductant might be close to each other, in the same compact agglomerate, with a great surface area available for the necessary reduction reactions. This intimate contact is due to the fine granulometry of the constituents (Buzin, 2009; Bagatini, 2011), usually with an auxiliary binder. Decreasing the particle size of the reductant is also responsible for an increased rate of iron oxide reduction at a given temperature. This is due to specific surface increase, which potentiates the Boudouard reaction, due to the fact that the carbon particles have a greater surface for reaction with CO$_2$ (Nogueira, 2010). In the specific case of EAFD, use of self-reduction agglomerates can make it possible for metallic iron content recycling as well as generating a new dust enriched with zinc content, as the process conditions for this metal tend to accumulate again in EAFD. Dusts with higher zinc content can be more attractive for commercialization as a coproduct.

In view of the increasing interest in EAFD recycling in semi-integrated steel plants, the objective of this paper was divided in the following topics: dust chemical, phases, morphology and physical characterization; Petroleum coke (PET) chemical and physical characterization; Self-reduction of EAFD and PET mixtures, as well as the evaluation of carbothermic reduction behavior of the materials via thermogravimetry.

2. Materials and methods

2.1 EAFD chemical, phases, morphology and physical characterization

Electric Arc Furnace Dust (EAFD) was collected in a semi-integrated steel plant in the state of Rio Grande do Sul, Brazil. Chemical characterization was conducted via Inductively Coupled Plasma (ICP), X Ray Diffraction (XRD) and Mössbauer spectroscopy. Room Temperature Mössbauer spectra of powder samples was obtained in constant acceleration mode, using a source of 57 Co in Rh matrix with initial nominal activity of 50 mCi. Analysis of the experimental spectra was done by least-square fitting assuming Lorentzian line shapes. A high purity α-Fe foil was used for velocity-scale calibration. The isomer shift is relative to α-Fe. For the XRD, source materials: Cu K$_{αα}$; goniometry speed and interval 0.02º/25s – 10 to 70º 2theta; time 25 s per step and acceleration of 40 kV/25 mA.

The carbon content of the dust was determined via dry combustion in an elemental analyzer CNHS.

Physical characterization was also carried out through size particle distribution by laser diffraction, surface area by BET (Brunauer, Emmet and Teller) method, along with Scanning Electron Microscopy (SEM).

2.2 Petroleum coke (PET) chemical and physical characterization

PET sample was obtained in the same plant as the EAFD. Due to the coarseness of the sample (50% > 0.5mm), for the aim of this study (future pellets production), a granulometric adequation was carried out using a ball mill. After material grinding, the PET was characterized using approximate analysis and size particle distribution by laser diffraction.

2.3 Thermogravimetric EAFD/PET assays

Thermobalance tests were carried out with mixtures containing EAFD and PET, as follows in Table 1.

<table>
<thead>
<tr>
<th>Composition</th>
<th>EAFD (97)</th>
<th>EAFD (96)</th>
<th>EAFD (95)</th>
<th>EAFD (92)</th>
<th>EAFD (90)</th>
<th>EAFD (95)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET (3)</td>
<td>4</td>
<td>5</td>
<td>8</td>
<td>10</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

The tests were conducted in a Netzsch thermobalance, model 409 PC Luxx. Mixtures, with a mass of 250 mg, were introduced into an alumina cylinder crucible (37x54mm), being slightly compacted by an instrument for hand manipulation (Figure 1).

![Figure 1](image-url)

a) Thermobalance (LaSid – UFRGS) and b) Crucible used for the tests.
The samples were heated in a 30°C/min rate until a temperature of 600°C, and kept at this temperature for 20 minutes. This first isothermal step aimed to eliminate moisture and a greater part of reductant volatile matter from the samples, avoiding in this way, mass losses due to oxide reduction from the EAFD. After this devolatilization step, the samples were heated at a 30°C/min rate until 1100°C and kept at this temperature for 20 minutes. A 100ml/min nitrogen flux was introduced in the furnace during the entire experiment.

3. Results and discussion

3.1 EAFD chemical, phases, morphology and physical characterization

Table 2 shows the elemental composition of the dust, obtained by ICP and dry combustion in an elemental analyzer CNHS.

<table>
<thead>
<tr>
<th>Elemental Composition of the Dust (% wt)</th>
<th>Zn</th>
<th>Fe</th>
<th>Mn</th>
<th>Ca</th>
<th>Mg</th>
<th>Pb</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.97</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Elements Zn (32.23%) and Fe (22.80%) represent the majority of the waste. According to literature (Machado, 2004), zinc concentration in dusts originated in steelmaking may vary between 11.12 and 26.90%. The reason for a more elevated content herein could be associated with greater utilization of galvanized scrap in the production of the steel in the plant where the EAFD was sampled. The carbon content of EAFD is 0.91%. Other elements shown in Table 2 are inside the usual ranges found in literature (Machado, 2004; Nyrienda, 1991). Non-analyzed elements, among them oxygen, complete the characterization of the EAFD and total 31.53% of the EAFD.

Phase composition determination was conducted by X Ray Diffraction (SIEMENS-Bruker-AXS D500, with a Cu tube equipment, in 40kV/25mA). The XRD diffractogram, in Figure 2, shows the crystalline species identified in EAFD.

The analysis indicates, mainly, the presence of franklinite (ZnFe₂O₄), zincite (ZnO) and magnetite (Fe₃O₄). These mineralogical phases match with what was expected in a typical EAFD composition from the literature. According to several authors (Machado, 2004; Silva et al., 2008; Telles et al., 2010), the result for this characterization technique was very similar.

In order to support ferrous phase characterization, a Mössbauer spectroscopy analysis was carried out and the results are in Table 3.

<table>
<thead>
<tr>
<th>Iron phases distribution</th>
<th>ZnFe₂O₄</th>
<th>Fe₃O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>(% wt)</td>
<td>75</td>
<td>25</td>
</tr>
</tbody>
</table>

Mössbauer spectroscopy, as a complementary analysis to XRD, because of its quantitative factor. From the elemental composition of EAFD indicated in Table 2 and the ferrous phases quantified in Table 3, the majority of oxide phase content present in the waste can be estimated (ZnO, ZnFe₂O₄, Fe₃O₄) (Table 4).
Table 4

<table>
<thead>
<tr>
<th>EAFD Composition</th>
<th>$\text{ZnFe}_2\text{O}_4$</th>
<th>ZnO</th>
<th>$\text{Fe}_3\text{O}_4$</th>
<th>Other phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%) wt</td>
<td>36.9</td>
<td>30.2</td>
<td>7.9</td>
<td>25.1</td>
</tr>
</tbody>
</table>

This estimation was conducted according to a procedure described by Machado et al (2006).

Franklinite (36.8%), zincite (30.2%) and magnetite (7.9%) represent the majority of compounds found within the EAFD. According to Takano et al (1999), the zincite content was higher in dusts rich in zinc; as much zinc is identified in the waste, more zincite will appear in the character. Other compounds without Zn and Fe presence totaled 25.1%. Using the estimation in Table 4, we calculated the reducible oxygen content associated to all those phases according to Equation 1:

$$O_{\text{reducible}} = \%\text{ZnFe}_2\text{O}_4 \cdot \frac{M_O}{M_{\text{ZnFe}_2\text{O}_4}} + \%\text{ZnO} \cdot \frac{M_O}{M_{\text{ZnO}}} + \%\text{Fe}_3\text{O}_4 \cdot \frac{M_O}{M_{\text{Fe}_3\text{O}_4}} \quad (1)$$

Where, the reducible oxygen corresponds to the sum of the oxygen weight percentage of each phase shown above ($\text{ZnFe}_2\text{O}_4$, ZnO and $\text{Fe}_3\text{O}_4$). Thereby, the reducible oxygen in the EAFD, content is 17.9%. With this number, it was possible to measure the minimal carbon content necessary for consumption of this percentage of oxygen, in mass.

Particle size distribution was conducted by laser diffraction size analysis to determine granulometric characterization (Figure 3).

In terms of granulometry, over 80% of the particles of EAFD, have a size of less than 5 µm.

The surface area (BET) was 3.93 m²/g, a value found to be consistent with the range described in literature (Nyrienda, 1991).

The spherical shape of the EAFD is shown in Figure 4, an image taken by SEM.

The bubble burst at the surface of the steel bath is responsible for the shape formation of an upward liquid jet from which some visible droplets can be ejected and give the spherical shape. The SEM analysis was conducted in order to compare the sample used in this study in terms of particle shapes to a typical EAFD also found in literature (Mantovani et al., 2002).
3.2 Petroleum coke chemical and physical characterization

PET composition is shown in Table 5.

Table 5
PET Approximate analysis.

<table>
<thead>
<tr>
<th>Fixed Carbon</th>
<th>Volatile Matter</th>
<th>Ashes</th>
</tr>
</thead>
<tbody>
<tr>
<td>(% wt)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>89.4</td>
<td>10.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The reductant has a low content of inorganic contaminants (0.6%) and a high content of fixed carbon. Utilization of a carbon source with a low ash content could be attractive for use in furnaces, as the generation of slag might be reduced.

Figure 5 shows the granulometric distribution of the PET.

![Granulometric distribution of the PET.](image)

The PET was grinded to a level where 50% of its particles were below 100 µm in diameter.

3.3 Thermogravimetric EAFD/PET assays

During the first step of the weight losses observed (until 600 °C), the curves are related to moisture evaporation from raw materials, as well as partial PET devolatization (Figure 6).

With heating, it was observed that the samples showed a sharp weight loss (Figure 6), which begins in temperatures close to 900 °C and goes on until the maximum temperature of the test (1100 °C). The behavior of the samples in temperatures above 900 °C was related to the reduction of metallic oxides containing reducible oxygen - reactions (2) and (3) -, gasification of fixed carbon (4) in petroleum coke and mainly because of zinc expelled out the system in the gas form (3).

![Thermogravimetric assays for the mixtures of dust and PET.](image)
Mixtures of 10 and 15% PET were verified to have similar weight losses. The weight loss due to zinc volatilization was caused by reduction/vaporization of this metal, since after reduction, the metallic zinc is immediately vaporized (907°C) (Rosenqvist, 1973).

Mixtures compositions, the estimated and total weight loss in thermogravimetric tests, can be seen in Table 6.

\[
\begin{align*}
\text{Fe}_x\text{O}_{y}\text{(s)} + \text{CO}\text{(g)} & = \text{Fe}_x\text{O}_{y}\text{-1(s)} + \text{CO}_2\text{(g)} \\
\text{ZnO}\text{(s)} + \text{CO}\text{(g)} & = \text{Zn}\text{(g)} + \text{CO}_2\text{(g)} \\
\text{C}(s) + \text{CO}_2\text{(g)} & = 2\text{CO}\text{(g)}
\end{align*}
\]

The maximum estimated weight loss calculated is the sum of reducible oxygen, zinc and carbon content. It is remarkable that it does not consider moisture, volatile matter and volatile elements like lead and cadmium.

This equation establishes a mass carbon/oxygen ratio equal to 0.75 for total reduction of iron and zinc oxides present in EAFD. Thus, the behavior of weight loss of the different samples in Table 6 could be explained by evaluating the C/O reducible ratio of each mixture. The weight loss increases as this ratio gets close to 0.75. However, it was verified that mixtures of 10 and 15% PET had similar weight losses. Thus, for mixtures with smaller C/O reducible ratios, the carbon percentage was not enough to achieve the total reduction of iron and zinc oxides. Therefore, the verified weight loss of 3 to 8% of the petroleum coke, is inferior to the estimated maximum weight loss. On the other hand, for mixtures with 10 and 15%, the verified PET losses are close to the estimated maximum weight loss (Table 6). In the same way the difference between the total loss of the test regarding the C/O reducible ratio could be explained.

The weight loss compared to the estimated maximum weight loss for the sample with 10% PET indicates, possibly, the total reduction of iron and zinc oxides present in EAFD, even with a C/O reducible inferior to 0.75. This could be due to mixed CO/CO\(_2\) formation, i.e., with lower carbon consumption than reaction (5) predicts.

While the iron and zinc oxide reduction reactions occur together, the slowest step controls the global process of the agglomerate reduction. According to several studies (Carvalho et al., 1994; Fruehan, 1977; Moon and Sahajwalla, 2006, Bagatini et al., 2011), the reduction kinetics of self-reducing agglomerates, mainly in low temperatures, is controlled by the Boudouard reaction. It could be observed in Figure 6 for temperatures from 900 to 1000 °C, when this reaction starts. In this range of temperature, with the use of petroleum coke, the Boudouard reaction occurs, according to Bagatini et al., 2011. After this, the reduction of the iron and zinc oxides takes place, including the volatilization of Zn. It could be concluded that if there is enough carbon and sufficient energy, the overall reduction reaction of iron oxides will not be affected by the presence of zinc oxide.

Furthermore, from the point of view of practical application, the study carried out can be used as a methodology to determine the optimal carbon content in formulations of this kind of experiment. Therefore, according to Figure 6, economy in usage of reductant or reaction kinetics can be taken into account, for the case where weight losses are close, for example in mixtures of 10 and 15% PET. In this case there is the option to use percentages below 15% of reductant agent. Greater contents of PET lead to higher consumption of raw material, but this percentage has a more favorable kinetic value, which could be advantageous, for instance, in EAF operations with a focus on the reintroduction of pellets.

4. Conclusions

Taking into consideration the self-reducing mixtures behavior in thermogravimetric tests, it could be concluded that:

As expected, elements of economic interests, such as iron and zinc, represent 22.80 and 34.23%, respectively of the EAFD sampled. These elements are present in chemical species ZnFe\(_2\)O\(_4\) (36.9%), ZnO (30.2%) and Fe\(_3\)O\(_4\) (7.9%). From this content, the EAFD reducible oxygen was estimated as 17.9%.
Throughout carbothermic tests via thermogravimetry, it was stated that the optimal content of petroleum coke (fixed carbon = 89.4%; ashes = 0.6%) used in the mixtures varies from 10 to 15%, in weight. It was verified that the oxide reduction occurs from 900°C, which is linked to the effective beginning of the petroleum coke gasification reaction.

Considering the way of determining the optimal content of reductant and the temperature used, it could be stated that the utility potential of this assay is satisfactory in the industrial field as a support for the production of self-reducing pellets that could be used in meltpans for steel production.

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**References**


NYRIENDA, R. I. The processing of steelmaking flue dust: a review. *Minerals*...
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