Zn and Fe Recovery from Electric Arc Furnace Dusts


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Steel production generates dust containing Zn and Fe that can be recovered under certain conditions. The main objectives of the study were to evaluate the recovery of these elements when added in briquette form to liquid pig iron at a temperature of 1500°C and to chemically and morphologically characterize the Electric Arc Furnace Dust (EAFD). In the dust characterization stage, the following techniques were used: granulometric and chemical analyses, Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), and X-ray Diffraction (XRD). After characterization, the dust was agglomerated in order to form a briquette, then, placed in liquid pig iron. To perform the tests, a vertical laboratory-scale furnace was used that maintained an inert gas flow (argon) within the furnace during the experiments. All melting tests were performed in this device. Alumina crucibles were used. The zinc was reduced, volatilized and collected by a flux placed on top of the furnace. It was possible to achieve FeO reduction values higher than 98%. The new dust collected during the tests contained iron and 68% of zinc on the average. [doi:10.2320/matertrans.M2013385]

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1. Introduction

Basically, there are two main routes in steel production. Nowadays, the first and most applied one is the use of Basic Oxygen Furnace (BOF), which, back in 2008, corresponded to approximately 67.1% of steel production. The second one uses the Electric Arc Furnace (EAF), which was responsible for 30.6% of the steel produced in the same year.1)

Independent of the furnace or process used, steel production generates a great amount of steel dust, which is expelled from the furnace through its exhaust gases, especially in processes that use steel scraps as raw material.2)

There are many aspects to be considered in the recycling of such steel dust, including economic, political and administrative ones. However, the greatest difficulty for the application of possible actions for the recycling of this kind of dust is the absence of processes that are compatible with the dimensions and characteristics of the final consumer.

As such, an alternative for the dust recycling would be to reapply it as raw material for steel processing. To achieve this, the iron would have to be separated from the dust; the total Fe content in the dust could be as high as 52%.

This alternative also has the advantage that zinc is present in the dust, which could be reduced, volatilized and collected by the dust removal system, enriching the dust with zinc concentrations appropriate for the developed zinc recuperation processes.

Several studies3–5) were conducted on the reuse of electric arc furnace dust. Félix and Aurora6) added the EAFD in their own electric arc furnace, in the form of briquettes with the coke required to reduce all the oxides existing in the dust. According to the authors6), there was an increase of 3–8% over time and there was no significant variation in power consumption. The new dust generated has about 50% Zn, allowing it to be processed for other purposes; in addition, the authors also report that the estimated prices for applying briquetting process is around 63 Euro/t.

The objective of this study was to investigate the EAF dust’s iron and zinc oxide reduction in the form of briquettes by a silicon and carbon bath. To achieve this, the dust was turned into briquettes that were then added to liquid pig iron baths of different compositions.

Pickles7,8) states that the iron oxides found in the dust were either Fe2O3 or franklinite (ZnO·Fe2O3). From 20 to 50% of the zinc found in the dust combines with iron to form franklinite and the rest of it is in the form of zinc oxide (ZnO).

Zinc ferrite (ZnO·Fe2O3) quickly decomposes into ZnO and Fe2O3 at 1227°C. After decomposition, Fe2O3 reduces in two stages. In the first stage, Fe2O3 is quickly reduced to FeO by the following reaction:

\[
(\text{Fe}_2\text{O}_3) + \text{Fe}_0 \rightarrow (\text{FeO}) \quad (1)
\]

The oxides between parentheses indicate the element dissolved in the slag. In the second stage, FeO is reduced with silicon and carbon in molten iron, as per the following equations:

\[
(\text{FeO}) + \text{C} \rightarrow \text{Fe}_0 + \text{CO}_{(g)} \quad (2)
\]

\[
\Delta G^0 = 89245.2 \text{ J/mol} \quad (3)
\]

The free energy of Reaction (2) is expressed as:

\[
\Delta G = \Delta G^0 + RT \cdot \ln \left( \frac{P_{\text{CO}} \cdot a_{\text{Fe}}}{a_{\text{FeO}} \cdot h_{\text{C}}} \right) \quad (4)
\]

where:

- \(P_{\text{CO}}\) – partial CO pressure equal to 1 atm;
- \(h_{\text{C}}\) – carbon Henrian activity in the alloy;
- \(a_{\text{Fe}}\) – iron Raoultian activity in the alloy; and
- \(a_{\text{FeO}}\) – iron oxide Raoultian activity in the slag.

Iron oxide (FeO) is reduced by the silicon dissolved in the bath, and it is explained by the following reaction:

\[
2(\text{FeO}) + \text{Si} \rightarrow 2\text{Fe}_0 + (\text{SiO}_2) \quad (5)
\]

\[
\Delta G^0 = -328894.02 + 111.18 \text{ J/mol} \quad (6)
\]

The free energy of Reaction (5) is as follows:
\[ \Delta G = \Delta G^0 + RT \ln \left( \frac{\alpha_{SiO_2} \times a_{Si}^2}{\alpha_{FeO} \times h_{Si}} \right) \]  

(7)

where:
- \( \alpha_{SiO_2} \) – silicon dioxide Raoultian activity in the slag;
- \( h_{Si} \) – silicon Henrian activity in the alloy;
- \( a_{Fe} \) – iron Raoultian activity in the alloy and,
- \( a_{FeO} \) – iron oxide Raoultian activity in the slag.

2. Materials and Methods

FeO and ZnO reduction by silicon and carbon dissolved in liquid pig iron were studied. Initially, the EAFD was chemically and physically characterized. Then, it was agglomerated into the form of briquettes and placed in liquid pig iron. Samples of the metal were periodically removed for silicon and carbon analysis.

2.1 EAFD dust collection

About 50 kg of EAFD were supplied by ArcelorMittal Cariacica. The dust was collected by a dust removal system adapted on the upper part of the furnace. The material was then directed into the gas-cleaning system. After this procedure, the EAFD was collected by bag filters and placed in silos where it was stored until it was taken to a special landfill for hazardous waste.

2.2 Physical, chemical and morphological characterization

After sampling, the next step was chemical, physical, and morphological characterization of the dust using various techniques, i.e.:
1. Granulometric Analysis;
2. Chemical Analysis;
3. Diffractometric Analysis; and
4. Microscopic Analysis.

2.3 Load preparations

Tests were performed to investigate how the silicon content in liquid pig iron influences the FeO dust reduction and ZnO recovery.

The calculation of the amount of the added dust considered the complete reduction of the oxides (Fe₂O₃, ZnO, K₂O, PbO, MnO, and Na₂O) through the silicon existing in different concentrations in the liquid metal. The dust was inserted in a steel mold and taken to the hydraulic press, in which a pressure of 14 t was applied for 5 s. The briquette was removed from the mold and weighed. The experiments performed are listed in Table 1. In all tests, it was possible to collect particles of material generated during the experiments, with the exception of Test 7, mainly due to the small quantity of dust added.

2.4 Tests for effects of briquette addition to liquid pig iron

The following experimental device was prepared. It consists of a vertical furnace coupled to a gas-cleaning system. Figure 1 demonstrates the applied methodology.

This study used a bench-scale melting equipment, during this process, to keep a flow rate of inert gas above the bath at 4NL/min, before inserting the crucible in the reaction chamber, in order to prevent hot metal oxidation. This procedure was performed for the entire duration of the experiments in order to maintain an inert atmosphere within the furnace avoiding the oxidation of the bath. The alumina crucible was loaded with solid pig iron. After reaching the working temperature (the experiments were performed at 1500°C) visually observing the melting of the bath, the system was kept in this condition for 30 min. No bath oxidation was observed during the heating stage in any of the experiments. After this stage, briquette was added.

The time of reaction was measured immediately after the oxide loading. Metal samples were obtained at 1, 3, 5, 7, 10, and 15 min, by vacuum samplers.

3. Results and Discussion

3.1 Chemical and physical analyses

Table 2 shows the EAFD chemical composition which was determined using a semiquantitative analysis with no patterns with the analysis of chemical elements from fluorine to uranium. The test was performed in a Panalytical Axios-Advanced X-ray fluorescence spectrometer. The loss on ignition (LOI) was performed at 1050°C for 1 h at the Metallurgical Engineering Department of the University of
São Paulo (USP). The Fe\textsuperscript{2+} and Fe\textsuperscript{3+} contents were obtained in accordance with the Brazilian Standard NBR 8741 and the Fe\textsuperscript{0} percentage was obtained by the Volumetric Method using potassium permanganate. The major elements in the analysis were verified as: Fe, Zn, Pb, Ca, Mn and Mg.

Figure 2 shows the granulometric distribution of the residue studied, whereby the percentage of the particles is presented in function of the granulometric levels.

Through the results provided by the laser granulometric analyzer, it was possible to observe that EAFD is a very fine material, around 85\% of which have a particle diameter of less than 10 µm.

### 3.2 EAFD Morphological characterization

It is observed in the demarcated area of Fig. 3 a predominantly spherical morphology. Also observed by Mantovani et al. (2002),\textsuperscript{9} Badger and Kneller (1997),\textsuperscript{10} this spherical morphology confirms that the dust formation mechanism is that of slag and metal ejection by CO bubble bursting on the surface of the bath.

Furthermore, Guézennec et al.\textsuperscript{11} state that the prevailing mechanisms for dust precursor emission appear to be volatilization (27\% of the dust) and bursting of CO bubbles (60\% of the dust).

### 3.3 Thermodynamic calculations

To evaluate which reactions are predominant, one must have data on slag and metal activity in the trials, in order to calculate the ΔG of the reactions. The FeO and SiO\textsubscript{2} activities were estimated through THERMOCALC TCW v.5 software and the activity of the carbon and silicon of the bath was calculated as follows:

\begin{align*}
   h_C &= f_C \% C \quad (8) \\
   \log f_C &= e_C^C \% C + e_{Si}^Si \% Si + e_S^S \% S + e_P^P \% P \quad (9) \\
   e_C^C &= 0.14; e_{Si}^Si = 0.08; e_S^S = 0.046; e_P^P = 0.051 \\
   h_{Si} &= f_{Si} \% Si \quad (10) \\
   \log f_{Si} &= e_{Si}^{Si} \% Si + e_C^C \% C + e_S^S \% S + e_P^P \% P \quad (11) \\
   e_{Si}^{Si} &= 0.11, e_C^C = 0.18, e_S^S = 0.056; e_{Si}^{Si} = 0.11
\end{align*}

Where:
- \( h_C, h_{Si} \) – carbon and silicon Henrian activity in the alloy;
- \( e_C^C, e_{Si}^Si, e_S^S, e_P^P \) – elements’ mass percent in the alloy;
- \( e_C^C, e_{Si}^Si, e_S^S, e_P^P \) – elements’ interaction parameters present in the alloy with silicon.

The results of FeO and SiO\textsubscript{2} activity generated by the THERMOCALC TCW v.5 software can be seen in Table 3.

With the \( h_C, h_{Si}, a_{SiO_2}, a_{FeO} \) data, it is possible to calculate the ΔG. The iron activity was taken to be equal to its molar fraction \( a_{Fe} = N_{Fe} / N \) and \( P_{CO} \) was taken to be equal to 1 atm.

Table 4 shows the ΔG values for the above mentioned reactions in trials 1–8 in early and final stages, once they contain the data on slag and metal activity required for these calculations.

### 3.4 Test results of briquette addition in hot metal

Figure 4 shows the silicon and carbon content variation as function of time during trials 1, 2 and 3 for an initial silicon content equal to 1.5\%.
Figure 5 shows the variation of Si and C content as function of time for tests 4, 5, and 6, with the initial Si content equal to 1.0%.

The results showed that the Si of hot metal was rapidly reduced in the first five minutes. This behavior was also verified in the other tests. FeO reduction occurs according to the following reaction:

$$2(\text{FeO}) + \text{Si} \rightarrow 2\text{Fe}_{(l)} + (\text{SiO}_2)$$  \hspace{1cm} (5)

or

$$\text{(FeO)} + \text{C} \rightarrow \text{Fe}_{(l)} + \text{CO}_{(g)}$$  \hspace{1cm} (2)

These results are in accordance with the ones found by Oliveira and Tenório (1996)\(^{12}\) who investigated the reduction of slag containing FeO–MnO and \% of SiO\(_2\) concentration in FeC and Si alloy, and stated that a greater part of the FeO is reduced in the first five minutes.

After five minutes, it was possible to observe a small Si reversion within the bath, after which began to diminish again. This could be occurring because of the equation: After five minutes, it was possible to observe a small reversal of Si within the bath, after which it began to decrease again. This may be due to the equation:

$$\text{(SiO}_2\text{)} + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$$  \hspace{1cm} (12)

Table 3 Final activity of SiO\(_2\) and FeO from the slags from the experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Activity (a_{\text{SiO}_2})</th>
<th>Activity (a_{\text{FeO}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0.83</td>
<td>0.05</td>
</tr>
<tr>
<td>(2)</td>
<td>0.81</td>
<td>0.03</td>
</tr>
<tr>
<td>(3)</td>
<td>0.81</td>
<td>0.03</td>
</tr>
<tr>
<td>(4)</td>
<td>0.80</td>
<td>0.03</td>
</tr>
<tr>
<td>(5)</td>
<td>0.79</td>
<td>0.07</td>
</tr>
<tr>
<td>(6)</td>
<td>0.85</td>
<td>0.01</td>
</tr>
<tr>
<td>(7)</td>
<td>0.59</td>
<td>0.005</td>
</tr>
<tr>
<td>(8)</td>
<td>0.40</td>
<td>0.02</td>
</tr>
</tbody>
</table>

On the other hand, this increased Si activity makes the reaction represented by eq. (5) occur, consuming the Si whereupon it starts to decrease again in the bath. This fact can be observed by the free energy in the reactions presented in Table 3. To determine the predominant reactions, it is necessary to have data on the slag and the metal activities during the test trials in order to calculate the \(\Delta G\) of the reactions. It was possible to collect the activity data using Table 4 Variation in free energy involved in the reactions studied (KJ/mol).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Time</th>
<th>((\text{FeO}) + \text{C} = \text{Fe}<em>{(l)} + \text{CO}</em>{(g)})</th>
<th>(2(\text{FeO}) + \text{Si} = 2\text{Fe}_{(l)} + (\text{SiO}_2))</th>
<th>((\text{SiO}_2) + 2\text{C} = \text{Si} + 2\text{CO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Initial</td>
<td>−96.1901</td>
<td>−189.894</td>
<td>−37.8121</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>1.176266</td>
<td>−39.5954</td>
<td>−84.3437</td>
</tr>
<tr>
<td>(2)</td>
<td>Initial</td>
<td>−96.278</td>
<td>−190.308</td>
<td>−37.5735</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>−13.3826</td>
<td>−53.7482</td>
<td>−85.7251</td>
</tr>
<tr>
<td>(3)</td>
<td>Initial</td>
<td>−96.2068</td>
<td>−189.555</td>
<td>−38.1889</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>1.230684</td>
<td>−42.1949</td>
<td>−83.5023</td>
</tr>
<tr>
<td>(4)</td>
<td>Initial</td>
<td>−96.6464</td>
<td>−183.544</td>
<td>45.07485</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>0.39767</td>
<td>−40.4954</td>
<td>−86.8762</td>
</tr>
<tr>
<td>(5)</td>
<td>Initial</td>
<td>−96.6296</td>
<td>−182.338</td>
<td>−46.2511</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>−23.0439</td>
<td>−60.0691</td>
<td>−89.2162</td>
</tr>
<tr>
<td>(6)</td>
<td>Initial</td>
<td>−96.7636</td>
<td>−183.795</td>
<td>−45.0581</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>31.8136</td>
<td>−8.39712</td>
<td>−88.5213</td>
</tr>
<tr>
<td>(7)</td>
<td>Initial</td>
<td>−95.851</td>
<td>−166.343</td>
<td>−60.6844</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>55.2677</td>
<td>33.7266</td>
<td>−104.169</td>
</tr>
<tr>
<td>(8)</td>
<td>Initial</td>
<td>−94.5408</td>
<td>−165.41</td>
<td>−58.9975</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>19.91699</td>
<td>8.949668</td>
<td>−109.229</td>
</tr>
</tbody>
</table>
computational thermodynamic software (THERMOCALC TCW v.5).

In other words, the greater the Si percentage at the end of the tests, the greater the Si activity; and thus, the reaction represented by eq. (5) is favored.

Note that for tests 2 and 5, the reduction by carbon was greater than in the other tests. This was due to the dust mass added (20% above the stoichiometry) which means that the FeO activity is high in the slag allowing the reaction with the Carbon to occur, diminishing the carbon content, according to eq. (2).

Figure 6 shows the curve for the silicon and carbon content variation versus time for the tests 7 and 8, with an initial silicon content of 0.35%.

Tests 7 and 8 demonstrated that the carbon reduction was more accentuated than in the other tests. In other words, for the low silicon content in the liquid pig iron, carbon has a greater reduction potential. However, as analyzed in Table 3, this FeO reduction by the dissolved carbon (eq. (2)) does not occur. This is because the FeO activity at the 15 minute instance is low and with this there are not thermodynamic conditions for this reaction to occur.

3.5 EAFD analysis

3.5.1 Chemical analysis

The semi-quantitative analysis results of the EAFD samples for tests 1, 2, 3, 4, 5, 6 and 7 are presented in Table 5.

<table>
<thead>
<tr>
<th>Tests</th>
<th>%Mg</th>
<th>%Al</th>
<th>%Cd</th>
<th>%Si</th>
<th>%Ca</th>
<th>%Pb</th>
<th>%Fe</th>
<th>%K</th>
<th>%Zn</th>
<th>%C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.95</td>
<td>2.74</td>
<td>—</td>
<td>1.99</td>
<td>7.59</td>
<td>10.48</td>
<td>1.97</td>
<td>71.78</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>—</td>
<td>3.87</td>
<td>0.8</td>
<td>1.54</td>
<td>0.43</td>
<td>5.27</td>
<td>12.37</td>
<td>1.48</td>
<td>71.64</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>—</td>
<td>2.05</td>
<td>—</td>
<td>2.64</td>
<td>—</td>
<td>4.85</td>
<td>9.08</td>
<td>1.2</td>
<td>79.17</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>0.97</td>
<td>5.31</td>
<td>1.02</td>
<td>3.03</td>
<td>1.24</td>
<td>7.41</td>
<td>13.07</td>
<td>2.17</td>
<td>62.68</td>
<td>3.1</td>
</tr>
<tr>
<td>5</td>
<td>0.43</td>
<td>1.08</td>
<td>—</td>
<td>1.38</td>
<td>0.17</td>
<td>4.79</td>
<td>8.3</td>
<td>2.11</td>
<td>79.47</td>
<td>2.27</td>
</tr>
<tr>
<td>6</td>
<td>—</td>
<td>1.65</td>
<td>—</td>
<td>2.22</td>
<td>0.22</td>
<td>3.59</td>
<td>10.47</td>
<td>1.14</td>
<td>77.70</td>
<td>3.0</td>
</tr>
<tr>
<td>7</td>
<td>1.54</td>
<td>1.16</td>
<td>—</td>
<td>3.13</td>
<td>53.13</td>
<td>1.36</td>
<td>35.55</td>
<td>4.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mantovani et al. (2002) propose the recycling of EAFD using the addition of pellets to the liquid pig bath from which all dust was collected. The chemical analysis revealed the total presence of zinc (55.80%) and Fe (3.12%).

Colbert and Irons injected EAFD in steel and pig iron and observed that the Fe content in the dust increased when it was injected in the pig iron by 20% and in the steel by 10%. There was also an increase in the dust’s iron content in the liquid pig iron when carbon was added together with the dust. According to Colbert and Irons, the reason for this result is that carbon generates CO, which, in turn, increases slag agitation and transports Fe into the dust.

4. Conclusions

According to the results obtained from the tests for the effects of EAFD addition to liquid pig iron, it can be concluded that:
(1) EAFD chemical analysis presented FeO (36% total iron) and zinc (10.8%) as the elements that show the greatest percentages.

(2) EAFD characterization showed that 90% of the particles were smaller than 10 µm, that the predominant morphology was spherical, and that there was a presence of agglomerates.

(3) Silicon is transferred from metal phase to the slag in the first five minutes after briquette addition.

(4) FeO was reduced by carbon in a lesser and slower extent than it was when silicon was used.

(5) The low FeO and ZnO contents in the slag indicate that all these oxides can be recovered by the process presented herein.

(6) It was possible to recover 98% of the Fe present in EAFD.

(7) The dust collected after the tests showed a high level of zinc (68% on the average).

REFERENCES