1. Introduction

One of the most important problems in the secondary steel mill industry throughout the world is the disposition of dusts produced from electric arc furnaces (EAF). In a typical electric arc furnace operation, approximately 1 to 2% of the charge is converted to dust, which is collected in the baghouse. Dusts generated during carbon steelmaking tend to be richer in zinc and lead, while EAF dusts from stainless steelmaking are relatively low in lead and zinc, but richer in the alloying elements such as Cr and Ni.

EAF dust has been classified by various government regulatory agencies as a hazardous waste. Due to its classification as hazardous waste, the EAF dust cannot be disposed of in an ordinary landfill site. The disposal or treatment of the dust is expensive and has been 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 becoming scarcer and more distant from the generation point, increasing pressure is being placed on steelmakers to adopt some method for the treatment of the EAF dust.

There are currently many different EAF dust treatment methods. These can be categorized into the following classes: (1) high temperature metal recovery (HTMR) processes; (2) hydrometallurgical processes and; (3) vitrification or chemical stabilization treatments.

At the present time, there is no process, which is completely satisfactory for the treatment of the EAF dust. A suitable process should satisfy the following requirements: (1) have low capital and operating costs; (2) generate a minimum of residue which must be non-hazardous by present and future standards; (3) be able to treat a wide variety of dust compositions with minimum preparation; (4) be capable of treating small amounts of dusts (approximately 20,000 tons per year) in order to avoid the costs and liabilities of transporting the dusts; and (5) be able to recover the iron, zinc and alloying values.

The purpose of this work was to study the cold and hot behaviors, that is, cold compressive strength, decrepitation, swelling, compressive strength after heating and efficiency of zinc removal of self-reducing pellets containing coal fines and EAF dust. Pellets with 3 and 5 wt% Portland cement, 12 wt% CaCO₃ and without additive were produced. The effect of binder addition on the cold compressive strength was studied during 28 days. For the study of the high temperature behavior, pellets were submitted to thermal cycles with different heating intensities. The best results of cold compressive strength were obtained with 5 and 3 wt% Portland cement due to hydration of components that are contained in this binder. Pellets with Portland cement (3 and 5 wt%), after drying, did not present decrepitation, showing a correlation between the decrepitation, moisture content and mechanical strength of the pellet. Abnormal swelling was observed in pellets submitted to the thermal cycle with lower heating intensity. Such abnormal swelling was due to the growth of whiskers, and as consequence, it was recorded a maximum swelling (higher than 30%). With the gasification of carbon promoted by the release of H₂O(g) and CO₂(g) from the Portland cement and CaCO₃, it was possible to obtain a higher zinc removal as compared to the value obtained with pellets without additives, mainly at 1124°C.

KEY WORDS: dust; waste; recycling; iron ore-coal composite; cement bonded pellet.

2. Experimental

Initially, the raw materials were characterized chemically and physically. Subsequently, the raw materials (EAF dust, coal fines and additives) were mixed and pelletized. The self-reducing pellets were cure in air atmosphere (28 days or more) for gaining strength to handle. Next, self-reducing
pellets were analyzed with relation to decrepitation, swelling, compressive strength after heating and efficiency of zinc removal.

2.1. EAF Dusts

Two samples of EAF dust were characterized by chemical analysis, optical microscopy, scanning electron microscopy with X-ray energy dispersive analysis (EDS), X-ray diffraction, particle size distribution and specific surface area (BET). Tables 1 and 2 show the chemical composition and the particle size distribution of the EAF dusts, respectively. The specific surface area (BET) of the EAF-1 and EAF-2 samples were 4.32 ± 0.21 and 0.59 ± 0.04 m²/g, respectively.

2.2. Reducing Agent

Anthracite coal fines presenting 70.5 wt% fixed carbon, 15.4 wt% ash, and 14 wt% volatile matter were used. The chemical analysis of the ashes of coal fines is shown in Table 3. Particle size less than 146 μm was 90% and the measured specific surface area (BET) was 98.4 ± 3.4 m²/g.

2.3. Additives

Additives used were commercial Portland cement (90% less than 36 μm) and CaCO₃ (analytical reagent grade) in order to study the effects on the cold compressive strength and efficiency of zinc removal. Table 4 shows the chemical composition of Portland cement.

2.4. Pellets

Self-reducing pellets were produced in a laboratory-size disc pelletizer (0.52 m diameter disc) with and without additive. Table 5 shows the compositions of the self-reducing pellets.

2.5. Cold Compressive Strength

Cold compressive strength was evaluated up to 28 days of curing (batches 1 to 3). The tests were repeated 5 times.

2.6. High Temperature Properties

Pellets with 12 mm diameter (batches 1 to 6) were selected in order to determine the high temperature properties (swelling and zinc removal tests). These high temperature properties were observed and tested in a special thermogravimetric apparatus shown in Fig. 1. It consists of a furnace that is able to move up and down, an electronic balance and an alumina tube. In the upper part of the tube there is a water jacket. Based on the measured of the temperature profile of the furnace, a scale of positions of the furnace and their respective temperatures can be obtained. The sample was placed in a Ni–Cr strip basket, which was supported by a Ni–Cr wire connected to the electronic balance. Further, the furnace was moved up to the position for a given temperature and a specified time.

The swelling and zinc removal tests were conducted in argon atmosphere with flowrate of 1 000 Ncc/min, and with linear velocity of 65.8 cm/min. The argon is introduced from the botton of the alumina tube, and it escapes by the small orifice at the cover where the Ni–Cr wire is passing.

2.6.1. Decrepitation Test

Before decrepitation tests, pellets were submitted or not to drying. In these tests pellets from room temperature were placed directly to 700°C, keeping 3 min at this temperature. The tests were repeated 5 times.

2.6.2. Swelling Test

Table 6 shows the thermal cycles used for evaluation of the pellets (decrepitation, swelling and zinc removal tests). The thermal cycle 1 presents a higher heat intensity at second level of temperature than the thermal cycle 2. The rea-
Table 6. Thermal cycles used in the swelling, compressive strength after heating and zinc removal tests.

<table>
<thead>
<tr>
<th>Thermal cycles</th>
<th>685°C Cumulative time (minutes)</th>
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<tbody>
<tr>
<td>1</td>
<td>3</td>
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<td>6</td>
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<td>9</td>
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<td>3</td>
<td>3</td>
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<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

son is to evaluate the swelling as a function of this difference. The meaning of Table 6, for example, for thermal cycle 1 is: the sample was taken from room temperature directly to 685°C (after lifting the furnace), keeping it during 3 min. Further, the furnace was moved up to region of 1 195°C, keeping 1 min, and so on, with total cumulative time of 9 min. For the above thermal cycle, for each given temperature, after keeping the sample during the cumulative time, the volume expansion was measured. The following expression was used to measure the swelling index:

\[ V_f/V_i = (D_f/D_i)^3 \] .......................... (1)

where \( V_f/V_i \) = apparent volumetric variation, \( D_i \) and \( D_f \) = initial and final diameter (mm) after heating. The swelling tests were repeated 3 times. The same samples were used for compressive test after heating.

2.6.3. Zinc Removal Test

In this case, the objective was to study the effect of Portland cement and CaCO\(_3\) addition on the efficiency of zinc removal from self-reducing pellets containing EAF dust. Thus, chemical analyses (atomic absorption spectroscopy) were made to determine the residual content of zinc.

2.6.4. Microscopic Examination

For microscopic examination of the reacted pellet and EAF dust were used scanning electron microscopy and optical microscopy. The reacted pellets were broken and coated with either gold or carbon.

3. Results and Discussion

Table 1 shows the chemical composition of the EAF dusts used in this work. The sample EAF-2 is a primary dust, and EAF-1 is the dust generated after recycling the primary dust to the electric arc furnace together with scrap. The composition of the EAF dust is extremely site-specific because of differences in scrap feed composition or due to recycling of the dust to the electric arc furnace. According to the several researches, the dominating mechanism of dust formation in EAF and BOF is the ejection of the slag and metal particles by bursting of bubbles at the bath surface. This is in agreement with the spherical morphology of the particles shown in Fig. 2. The mineralogy of the EAF dust is varied and complex. The most common phases are solid solution of the iron spinels which are enclosed within a matrix of calcium-iron-silicate glass (Fig. 3). Frequently, these particles are polymineralic and exhibit a variety of internal crystalline configuration, that are specially characterized by skeletal textures which form from the rapid cooling of the particles.

3.1. Cold Compressive Strength

Figure 4 shows the effects of the Portland cement addition on the cold compressive strength. Better results were obtained with 5 and 3 wt% Portland cement due to hydration of components such as aluminates, ferrites and calcium silicates which are present in the Portland cement.

After curing period, pellets with 5 wt% attained around 60 N/pellet. This strength is acceptable in terms of laboratory scale. Normally, at industrial pelletizing scale, the strength for the same pellet should be almost double. Therefore, it should be enough for special process, as INMETCO. However, strength of around 300 N/pellet is desirable for charging at special shaft furnace, as in the Tecnored process.
3.2. Decrepitation

Decrepitation can be defined as the disintegration of self-reducing pellets, usually with an audible pop, that occurs when they are heated. The extent of pellet disintegration may vary from merely splitting off to a few fragments to almost total disintegration. Decrepitation is caused by gaseous generation, and is dependent on heating intensity, the porosity of the pellets, and the mechanical strength. The sources of gaseous phases in a self-reducing pellet are many: (1) moisture content of cured pellets; (2) water chemically combined from EAF dust; (3) water chemically combined from binder; (4) volatile matter of reducing agent; and (5) gaseous phases generated during the reduction process. When the rate of gaseous phase generation inside the pellet is higher than it can release at a tolerable pressure, the pellet may split or even explode.

As it can be seen in Table 7, pellets without drying are totally susceptible to the decrepitation phenomenon. That is, all the pellets did present decrepitation immediately after they are placed at 700°C (3 to 4 sec). These results show that moisture content is one of the important variables. However, Table 8 shows that pellets with 3 and 5 wt% Portland cement and submitted to drying did not present decrepitation. The results show that the decrease in the moisture content of the pellets and the increase in the compressive strength (after drying), decrease the decrepitation phenomenon. Pellets with Portland cement (3 and 5 wt%) presented lower decrepitation, showing a correlation among the decrepitation index, moisture content and mechanical strength of the pellet.

3.3. Swelling and Compressive Strength after Heating

The main strength mechanism of a cold bonded cement pellet is the hydration reaction of components present in the cement. At temperature higher than 600°C these hydrated components starts to decompose, and as consequence, the pellet loss strength. In addition, in the range 950–1100°C the strength is critical, that is, the pellet can also present a decrease in the mechanical strength due to the swelling.

Swelling of iron oxide during gaseous reduction is not a new phenomenon, but more attention has been paid to it in the recent years as an increasing proportion of self-reducing pellets have been used in rotary hearth furnace aiming to produce DRI, and also in the Tecnored process aiming to obtain hot metal, for instance.

The magnitude of the apparent volume increase that accompanies reduction varies, and is related to the nature and composition of the iron-bearing material with some other factors. Self-reducing pellets are prone to present swelling with negative consequences in furnace operation. Swelling up to 20% has generally been accepted as “normal” whereas the high values are called “abnormal swelling” or even “catastrophic swelling”. Swelling of self-reducing pellets has two major consequences; loss of strength and degradation or disintegration of the pellets during the reduction. Previous researchers have not yet agreed upon the causes of swelling of self-reducing pellets (iron-rich materials) during the reduction process. The main causes of catastrophic swelling proposed in the literature are as follows:
- The disruptive stresses set-up during the transformation Fe₂O₃→Fe₃O₄;
- Formation of iron whiskers during “FeO” →Fe reduction step;
- Iron-bearing material nature (iron ore or EAF dust) and the presence of substances such as Na₂O, K₂O, CaO, etc.;
- Temperature of reduction and reducing gas composition.

Figure 5 shows the apparent volume variation in the pellets of the batches 1 to 3 (thermal cycle 1). As it can be seen, all the pellets did not present catastrophic swelling. In addition, Fig. 6 shows that the compressive strength presented lower decrepitation, showing a correlation among the decrepitation index, moisture content and mechanical strength of the pellet.

Table 7. Results of decrepitation tests performed at 700°C. Pellets without drying.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Curing time (days)</th>
<th>Cold compressive strength (N/Pellet)</th>
<th>H₂O (%)</th>
<th>Decrepitation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42</td>
<td>82.4 ± 7.2</td>
<td>3.1</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>128.4 ± 8.1</td>
<td>3.3</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>38</td>
<td>142.6 ± 9.7</td>
<td>3.3</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 8. Results of decrepitation tests performed at 700°C. Pellets submitted to drying.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Curing time (days)</th>
<th>Cold compressive strength (N/Pellet)</th>
<th>H₂O (%)</th>
<th>Decrepitation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
<td>88.5 ± 7.2</td>
<td>0.1</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>43</td>
<td>128.4 ± 9.3</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>41</td>
<td>140.2 ± 11.8</td>
<td>0.1</td>
<td>0</td>
</tr>
</tbody>
</table>
further decrease of the compressive strength in the range 685–1 059°C (Fig. 9). Such a result was due to the growth of whiskers inside the pellet, as it can be seen in Fig. 10. However, from higher temperatures than 1 059°C there is an
increase in the compressive strength due to the sintering process.

In a previous work, it was shown the physical aspect of a self-reducing pellet (EAF) that presented abnormal swelling (Fig. 11). As it can be seen, the pellet presents cracks due to the abnormal swelling.

The SEM-EDS analysis from the region 1 (Fig. 10) is shown in Fig. 12. As it can be seen, the region 1 (substrate) analyzed contains several kinds of elements such as Fe, Mn, Ca, Si, Na, and Zn. According to several researchers the effect of Ca\(^{2+}\), Na\(^{+}\), and K\(^{+}\) ions in promoting whiskers growth is very powerful, that is, they can enhance the storage of a large amount of iron and provide surface defects for nucleation.

Therefore, nucleation of iron whiskers can be assumed to take place as a result of local supersaturation of ferrous ions and electrons, and is followed by a reduction in the surface concentration of these species when iron first appears, so that no nuclei form. The number of active nuclei, however, it can be expected to have a very important influence upon the morphology of the reaction product. Thus, when iron whiskers are observed, it can be deduced that growth has occurred from relatively few nuclei, whereas when a coherent layer (region 2 in Fig. 10) appears where many nuclei must have been involved. It can be concluded from the results discussed so far, that the reduction history of a pellet and presence of contaminates (Ca and Na) are of decisive importance in determining its swelling behavior.

The structure of wustite (nonstoichiometric composition), which largely controls the surface area and hence the potential number of nuclei available for “FeO”–Fe reduction step, it seems to be sensitive to temperature changes.

Therefore, it was necessary to promote a quick heat transfer to the core of the pellet, that is, to employ a temperature higher than 1059°C (thermal cycle 2), as it was done in the thermal cycle 1 (1195°C), to avoid the abnormal swelling.

3.4. Zinc Removal

According to Grebe and Lehmkuhler the removal of zinc and lead occurs parallel to the reduction of the iron oxides. At 90% iron metallization, zinc is 90% expelled, and lead 95%. The same authors show that this behavior also can be assumed for self-reducing pellets with higher zinc and lead contents.

The reduction of a self-reducing pellet containing EAF dust involves the following reactions: (1) direct reduction reaction (solid/solid) between oxides and carbon; and (2) a sequence of gas/solid reactions. As the solid/solid reaction is very slow comparatively to the gas/solid reaction, then the global process occurs via gaseous intermediates such as CO\(_2\)(g), CO\(_2\)(g), H\(_2\)(g) and H\(_2\)O(g).

During reduction of self-reducing pellets containing EAF dust and coal, evolution of volatile matter takes place from the coal. This volatile matter has some effect on iron reduction, but it is not considered important for zinc oxide reduction, since temperature higher than 907°C is required.

The representative reduction reactions are given by:

\[
\text{ZnO}_{(s)} + \text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{Zn}_{(g)} + \text{CO}_{2g} + \text{H}_2\text{O}_{(g)} \quad (2)
\]

\[
\text{ZnFe}_2\text{O}_4_{(s)} + \text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{Zn}_{(g)} + \text{Fe}_{(s)} + 4\text{CO}_{2g} + \text{H}_2\text{O}_{(g)} \quad (3)
\]

It is known that at temperatures below 1100°C the Boudouard reaction controls the overall process of reduction. Therefore, the gasification of carbon by CO\(_2\)(g) and H\(_2\)O\(_g\) plays significant role on zinc removal at temperatures below 1100°C.

\[
\text{C}_{(s)} + \text{CO}_{2(g)} \rightarrow 2\text{CO}_{(g)} \quad (4)
\]

\[
\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{CO}_{(g)} + \text{H}_2\text{g} \quad (5)
\]
Figure 13 shows that at 1 124°C (thermal cycle 3), the results confirm the importance of carbon gasification reactions due to generation of \( \text{H}_2\text{O(g)} \) and \( \text{CO}_2\text{g)} \) from hydrates (cement) and calcium carbonate.

Hydrated components of cement→\( \text{H}_2\text{O(g)} \)+oxides... (6)

\[
\text{CaCO}_3(\text{s}) \rightarrow \text{CaO(\text{s})} + \text{CO}_2\text{g)} \quad \ldots (7)
\]

The decomposition of hydrates, formed during curing of cold bonded pellets, starts around 600–800°C, and the decomposition of the calcium carbonate around 900–950°C. Therefore, when the sample was taken from 685°C to 1 124°C the above decomposition reactions took place, and their gaseous products induced the reactions (4) and (5), contributing for the zinc removal.

At 1 176°C some decomposition of the hydrates and calcium carbonate can still be taking place. This behavior is credited to the temperature gradient from the surface to the core of the pellet, due to short time left at 1 124°C (thermal cycle 3).

The results also show that it is feasible to remove 99% of zinc from EAF dust by using self-reducing pellets heated around 1 200°C.

4. Conclusions

From the work performed the following conclusions may be drawn:

(1) The best results of cold compressive strength were obtained with 5 and 3 wt% Portland cement due to hydration of components that are contained in this binder.

(2) The decrease of moisture content of the pellets and the increase in the compressive strength (after drying), decreased the decrepitation phenomenon. That is, pellets with Portland cement (3 and 5 wt%) did not present decrepitation, showing a correlation between the decrepitation, moisture content and mechanical strength of the pellet.

(3) The swelling tests showed that self-reducing pellets submitted to the thermal cycle 1 (higher heating intensity) did not present abnormal swelling. On the other hand, pellets submitted to the thermal cycle 2 (lower heating intensity) did present abnormal swelling due to the growth of whiskers. Therefore, it is important to employ a high heating intensity and high temperature to avoid the abnormal swelling caused by the formation of whiskers.

(4) Due to gasification of carbon promoted by the release of \( \text{H}_2\text{O(g)} \) and \( \text{CO}_2\text{g)} \) from the Portland cement and \( \text{CaCO}_3 \) during heating, it was possible to obtain a higher zinc removal as compared to the value obtained with pellets without additives, mainly at 1 124°C.

(5) When self-reducing pellets are submitted to thermal cycles with high heating rates and a maximum temperature around 1 200°C, it is possible to remove 99% of zinc from EAF dust.

Acknowledgments

The authors would like to thank the Brazilian Council for Research (CNPq) and ACOS VILLARES S. A. by the financial support.

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