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Evaluation of zinc removal and compressive strength of self-reducing pellets composed of Electric Arc Furnace Dust

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Abstract

The amount of Electric Arc Furnace Dust (EAFD) is continuously increasing in mini-mill steel plants. This dust is considered a hazardous waste because of the presence of elements like lead, cadmium and chromium. Among many different treatment processes for this issue, there is the possibility of returning the EAFD back to the Electric Arc Furnace. This article presents a study of the compressive strength of self-reducing cold bonded pellets as well as their zinc removal, in an agglomerate containing EAFD, petroleum coke (PET) and Portland cement. The effects of the reductant and binder employed were discussed. Moreover, an apparatus was built to prevent zinc gas reoxidation inside an electric vertical laboratory furnace. Thus, the fraction of weight loss complemented the result of a previous study indicating the optimal content of PET source usage between 10 to 15%, in mass. Zinc removal and additional X Ray Diffraction outcomes are shown and discussed, concluding that 80% of zinc removal for this system could indicate the possibility of the EAFD reuse.

Keywords: Electric Arc Furnace Dust (EAFD); pellet; compressive strength; self-reduction; zinc removal.

1. Introduction

One of the most important problems encountered in mini-mill steel plants throughout the world is the disposition of dusts produced by Electric Arc Furnaces (EAF) (Mantovani *et al*., 2002). According to a previous study, the production of Electric Arc Furnace Dust (EAFD) is increasing in Brazil and in the world (Ferreira *et al*., 2018).

The main recyclable solid wastes in the semi-integrated process are from the slag of electric steelmaking, EAFD and mill scale from continuous casting and rolling (Araújo and Schalch, 2014). The Waelz process is the most used pyrometallurgical process for the treating and recovering of zinc from EAFD, when its content is over 15-20%. The sale price is strongly dependant on the zinc content of the product. This dust is enriched in zinc being used in EAF and the higher the zinc content in the dust, the more valuable it becomes. Some Waelz plants sell the crude Waelz oxide directly to zinc smelters or other chemical plants (Rütten, 2006). According to Menad *et al.* (2003), the Waelz process enriches the dust to a content of approximately 61% of zinc, from an initial 32%. The operation of a Waelz furnace consists of a mixture of dust, coal and fluxants. This mixture is pelletized, charged in the furnace and as the furnace rotates, the pellets dry and the zinc oxides are reduced and volatized (Zunkel and Schimitt, 1995). However, in Brazil there is only one plant, located in Minas Gerais, which uses the Waelz process. Therefore, Buzin (2009) and Bagatini (2011), have suggested the recycling of metallic wastes using self-reducing agglomerates as part of the EAF burden.

Several studies have demonstrated that cold bonded composite pellets with an appropriate strength can be charged as burden material in the shaft furnace, rotary kiln and possibly new ironmaking processes in the future (Mantovani *et al.*, 2002; Contrucci and Sperman, 1997). Agra *et al.* (2015) studied the application of different binders taking into account compressive strength, drop shatter test and tumbler test, aiming to reintroduce pellets in the EAF. They concluded that a mixture of rice husk ash and hydrated lime obtained the best results for compressive strength, an important factor in pellet insertion in the basket, right after the use of cement.

These agglomerates are composed of the waste and a carbon source, besides the binder. The intimate contact of the pellet constituents, under heating at high temperatures, causes the reduction of some EAFD oxides (Flores *et al.*, 2013). The reduction process of iron oxides by carbon is stated to proceed, mainly with gaseous intermediates. Only a low significant fraction of the reduction process occurs by a solid-solid reaction (Fruehan, 1977). In practice, the gaseous product of the iron oxide reduction is constituted by the gaseous mixture of CO/CO_2. The proportion of this formed product depends on the temperature that the reduction takes place. The main chemical reactions during the heating of self-reducing mixtures occur via gasification of the carbonaceous materials (Boudouard reaction) (Flores *et al.*, 2013).

Carbothermal reductions are the main reactions in the pyrometallurgical treatment methods. Zinc and lead can be recovered by this method. On the other hand, the byproduct, slag, can be used as construction material (Lee *et al.*, 2001). Many reports on the carbothermal reduction of EAF dust or related topics are available and include the reduction of pure zinc oxide with carbon (Guger and Manning, 1971; Rao and Jalan, 1977; Rao, 1983; Zhang *et al.*, 1989; Chen, 1999).

The present work aims at the study of what would be the results achieved with the pellet production in the laboratory, in order to evaluate mechanical (compressive) strength, ferrous metallic yield and mainly, zinc removal content, which is the focus of this study. The removal would enrich the new dust in zinc, formed inside an EAF. This article is also a complement for the characterization of EAFD and petroleum coke (PET) mixtures conducted in a previous study (Ferreira *et al.*, 2018). Furthermore, the reducing effect of the PET is also discussed. This whole process was carried out specifically to give support to the reuse of the pellets in the EAF.

2. Materials and methods

2.1 Raw materials

The chemical composition of the EAFD can be observed in Table 1.

Elemental Composition of the Dust (% wt)	Zn	Fe	Mn	Ca	Mg	Pb	Na
	34.23	22.80	2.75	2.49	1.76	1.10	1.00
	K	Al	Cu	Ba	Cd	Ni	C
	0.97	0.20	0.15	0.05	0.03	0.01	0.91

Table 1
Chemical composition of the EAFD studied.

PET composition is shown in Table 2.

	Fixed Carbon	Volatile Matter	Ashes
(% wt)	89.4	10.0	0.6

Table 2
PET Approximate analysis.

Comments about compositions are better described in the first article (Ferreira *et al.*, 2018). Additional raw material information, such as EAFD phases diffractogram, Mössbauer spectroscopy, granulometric distribution of EAFD and PET (physical characterization) and morphology structure of the dust are detailed in other works by Ferreira (2016) and Ferreira *et al.* (2018).

2.2 Pellets production

The equipment used in this study had a 600 mm disc. The parameters set were a slope of 52 º and a rotation speed of 30 rpm, according to pretests and a procedure described by Kurt Meyer (1980). After the pellets were produced, the moisture content (15%) was immediately measured and also the moisture after the cure, 8% (in weight). According to Mantovani (2000), the cure time consists of an evaluation after it completes 28 days. This period is when the binder reaches its maximum plateau in a curve of cure time vs. compressive strength. In addition, the main phases that provide the cement mechanical strength are consolidated after this period of around a month; the C-S-H, hydrated calcium silicates that decompose only with temperatures up to 900 ºC (Mantovani, 2000).

2.3 Compressive strength tests

Using an adaptation of ASTM E382-12 (2012) standard, this test consists of simulations for industrial handling, as well as preparation of the basket burden used in melt shops. Therefore, pellets obtained with different cure periods were taken for compressive strength tests in a universal testing machine Shimadzu Autograph AG-X 50 kN, located in the Federal University of Rio Grande do Sul.

The compressive strength of the pellets was determined from the average of twenty repetitions of the strength applied on each sample. Pellets that were used in this procedure had a diameter of approximately 10 mm. The size of the pellet was chosen according to the pellet production efficiency (with the majority of pellets produced inside the range of 9.5 to 12.5 mm).

Pellets that were tested had three different compositions: 5, 10 and 15% cement, for an equal content of PET (10%, in mass), determined in the Ferreira *et al.* (2018) research.

2.4 Self-reducing pellets reduction tests

Reduction tests with pellets were prepared using a composition of 5% cement, according to literature (Ferreira, 2016), varying PET in 5, 10 and 15%, in mass. These contents aimed at a comparison with the results from thermogravimetry (TGA) obtained in a previous study (Ferreira *et al.*, 2018).

Tests to evaluate the reduction of pellets had a variation of time. A temperature of 1000 °C was used, while the times employed in the experiments were of 15, 30 and 60 minutes for weight loss and 30 and 60 minutes for zinc removal. The experiments were repeated twice.

The Formule 1 to calculate zinc removal is shown below:

$$\frac{m_{f\,Zn}\ x\%\ m_{pellet}}{m_{0\,Zn}} \quad (1)$$

Where $m_{f\,Zn}$ corresponds to the final mass of zinc (in percentage) and $m_{0\,Zn}$ to the initial mass. The remaining mass of the pellets after the reduction is also stated in percentage and is represented as m_{pellet}.

Figure 1 illustrates the furnace used and the metallurgical apparatus.

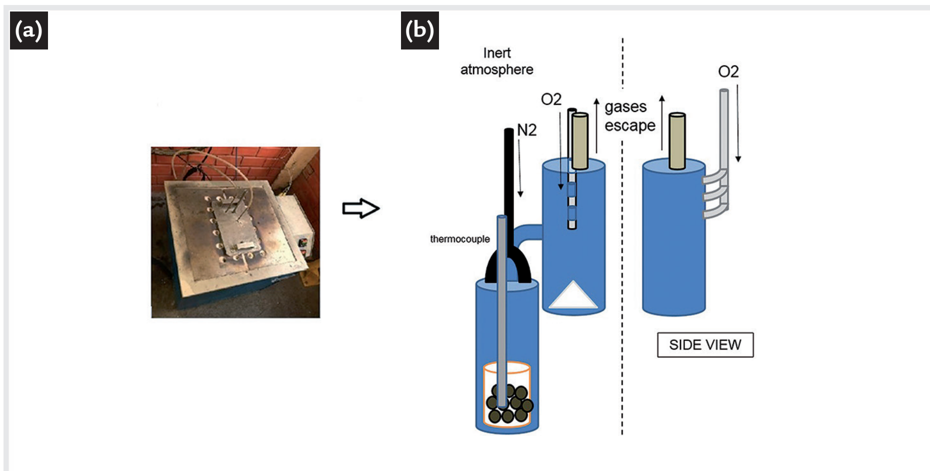

Figure 1
a) Electric vertical furnace used in the experiments (upper view). b) Scheme of the apparatus used in reduction and zinc removal tests (side view).

The furnace used in this study was an electric vertical furnace (Figure 1a) with two cylinders/retorts (Figure 1b) inside it, inserted with a 10 l/min nitrogen flow in order to mitigate oxidation of the zinc gas. The first cylinder, where the pellets were inserted, contained a thermocouple and an entrance for the inert gas, besides a connection to the second cylinder. This second one, on top of the first (Figure 1b), had an entrance for blown air in order to oxidize the gas and capture it in the solid phase. This retort also had an escape tube for the exhaust. On the right side of Figure 1b (separated by the dotted line), there can be seen the upper retort in the side view, with the entrance for blow air.

The evaluation of zinc removal was determined by ICP analysis and additional X Ray Diffraction (XRD).

3. Results and discussion

Regarding the results achieved, shown are the following tests for discussion: compressive strength of the self-reducing pellets; fraction of weight loss and zinc removal - XRD (for the reduction tests); besides the pelletization process.

3.1 Pellets production

Pellets production indicated the range of the most produced (in mass) sizes. In this case, between 9.5 to 12.5 mm (~40%), being used in all tests.

3.2 Compressive strength tests

Figure 2 shows the compressive strength results for three different contents of cement according to increasing cure time, in days. From 21 up to 42 days, there was drawn a tendency line because the results between these cure days were not obtained.

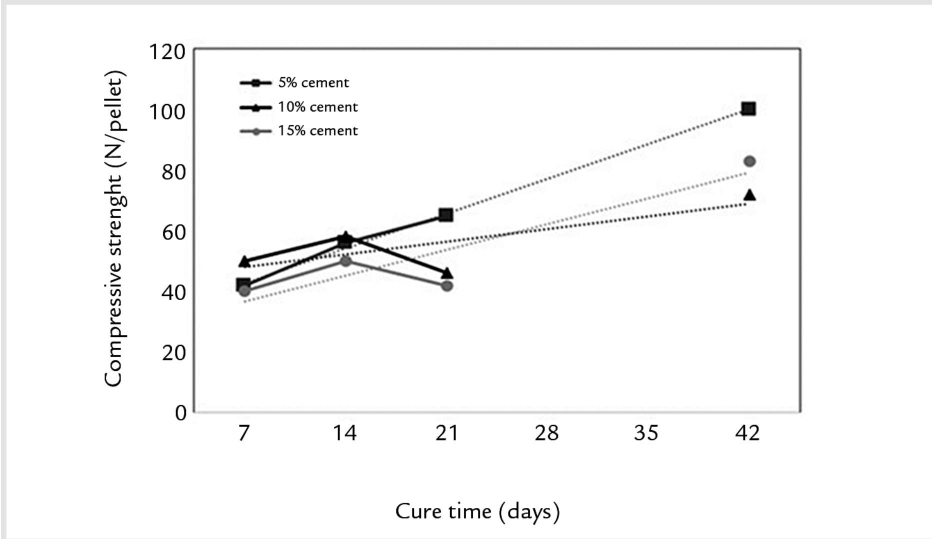

Figure 2
Compressive strength results for three cement contents, according to cure period of days.

Notice that pellets with 42 cure days and 5% of cement were the ones presenting the best result for compressive strength (a value around 100N/pellet). This occurs because, according to literature (Lea, 1971), there is an optimal content for cement in order to reach the best mechanical properties possible. This content is related to the formation of a surface layer between the particles. Cement contents higher than this certain amount, creating more than a layer over the particles, are not going to increase the final strength of the agglomerate.

Another point that can be observed is after a cure of 21 days, the compressive strength of the agglomerates keeps elevating, indicating the importance of time. It is likely due to a more stable hydrated cement phase appearance in the long term (Mantovani, 2000).

The pellets with the higher results in compressive tests were the ones with a lower quantity of cement added to the agglomerate (5%). This is advantageous when taking in consideration the necessity of the binder acquisition, making its usage more economic. According to Mantovani (2000), values for compression strength of 120 N/pellet may be acceptable for industrial trials.

3.3 Self-reducing pellets reduction tests

Fraction of weight loss analysis

The results for fraction of weight loss experiments are shown in Figure 3. The maximum value for fraction of weight loss (100%) involves the reduction of oxides (iron and zinc) and volatilization of the reduced zinc.

Figure 3
Fraction of weight loss for 5, 10 and 15% of PET at 1000 °C.

This initial sharp value, for the three PET compositions is similar. The low weight loss for the pellets in 15 minutes could be related to the low reactivity of the reductant. It could have induced an insufficient CO gas formation inside the pellets, according to another study (Bagatini *et al.*, 2014). After the initial 15 minutes, a sharper weight loss for the samples with 10 and 15% of PET was observed and indicated, after 60 minutes. For the sample with 5% of PET, mainly after 30 minutes, a sharper line was also observed.

The slope for all weight loss results does not tend to a standard. It keeps a declivity, indicating reduction is still playing a role; in other words, complete reduction was still not achieved. Furthermore, the usage of 10 and 15% PET corroborates to the previous study (Ferreira *et al.*, 2018), where mixtures of EAFD and PET were done to simulate an agglomerate in TGA and the results were analogous.

Zinc removal

Figure 4 demonstrates the zinc removal for the three samples, analyzed by ICP data.

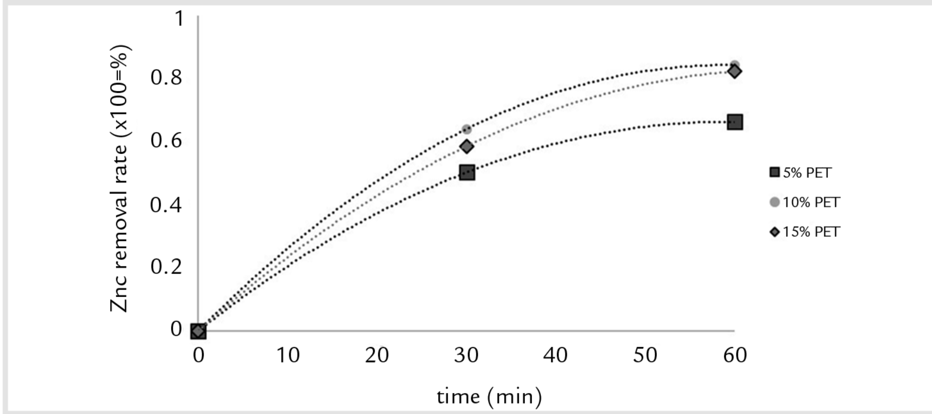

Figure 4
Zinc removal at 1000 °C.

In the present study, carbon reduces zinc oxide as follows (Peng *et al.*, 2004; Pickles, 2009), according to reaction (2):

$$ZnO + CO = Zn + CO_2 \qquad (2)$$

while zinc ferrite could reduce by direct reduction or via Boudouard reaction. Reaction (3), franklinite reduction, is shown below (Wu *et al.*, 2014):

$$3ZnFe_2O_4 + CO = 3ZnO + 2Fe_3O_4 + CO_2 \qquad (3)$$

The maximum removal content (obtained by the use of Formule 1) after an experiment time of one hour can be seen, and the value is over 80%, in weight. Pickles (2007) stated that this is due, basically, to the decomposition of franklinite, as well as the reduction and volatilization of zincite. On the other hand, in the presence of metallic iron, the decomposition of zinc ferrite to zinc vapor and iron oxide becomes highly favorable as the temperature increases, in case different temperatures take place (Pickles, 2007). It suggests higher temperatures would be favorable to total removal of zinc from the pellets.

XRD assays (Figure 5) for three compositions of the pellets (5, 10 and 15% of PET), after one hour in the electric vertical furnace, were used as validation tests for zinc removal.

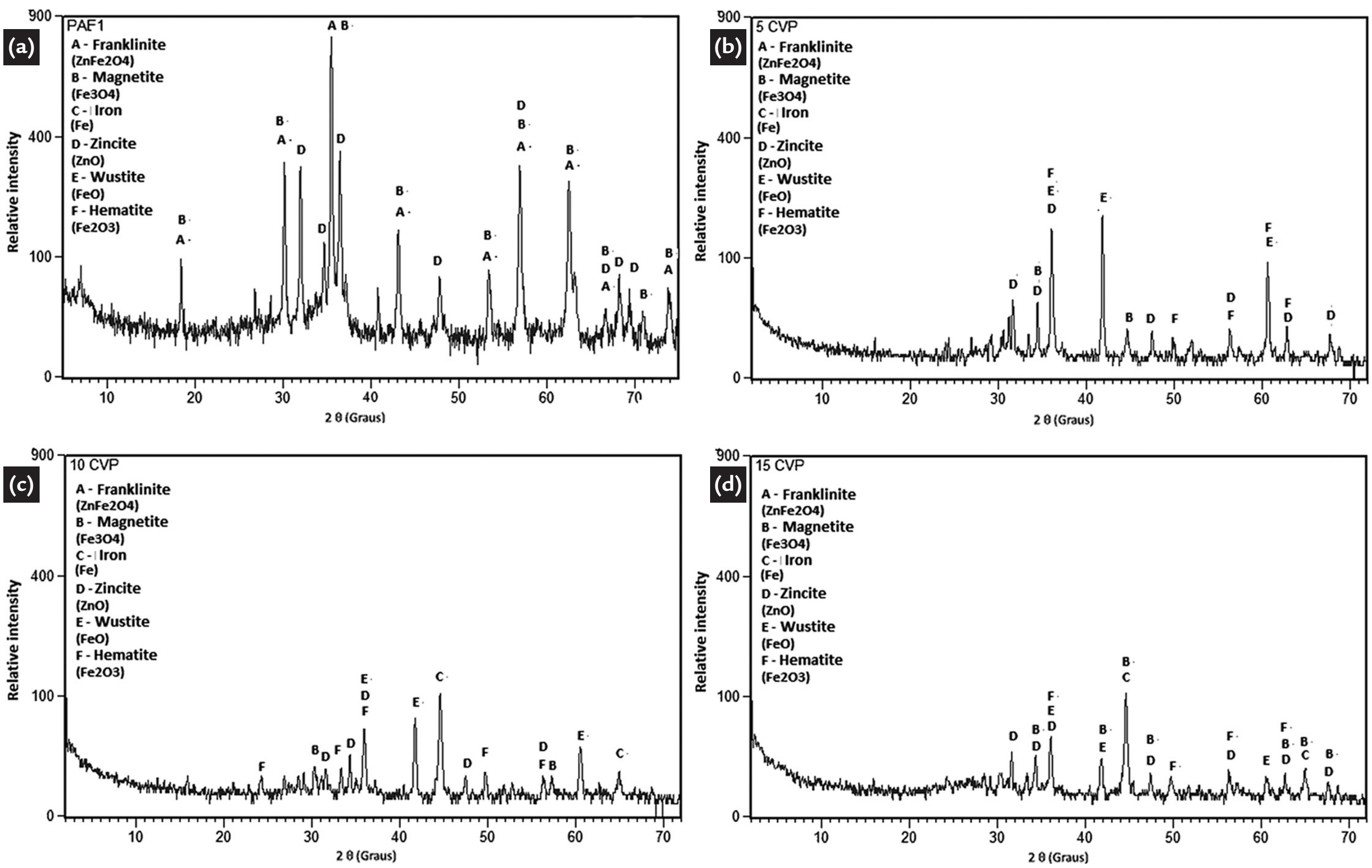

Figure 5
XRD for EAFD (a), pellet 5% PET (b), 10% PET (c) and 15% PET (d).

In the first diffractogram (a), the phases of the dust characterization can be seen where franklinite, zincite and magnetite are shown in the previous study (Ferreira *et al.*, 2018). In the second diffractogram (b), after one hour of experiment with 5% of PET, it is noticed that franklinite cannot be seen anymore, demonstrating its decomposition into zincite and hematite, like stated in Lee *et al.* (2001). In diffractograms (c) and (d), a higher intensity of iron peak is observed compared to the other graphs and lower intensity of zincite, which is a good evidence of zinc removal from the system.

For pellets with 10 and 15% of PET, it was observed a simultaneous increase of iron metallic peaks for a decrease in intensity of zincite peaks and iron phases of higher oxidation.

4. Conclusions

After analysis, it could be concluded:

- Compressive strength result obtained after a 42-day cold bonded cure for pellets with a diameter of 10 mm, with 10% of PET and also a 5% cement content, in mass, was 100 N/pellet;

- For the compositions 10 and 15% of PET (in mass), the fraction of weight loss was close to 100%, for a 60 minutes experiment, at 1000°C;

- The highest zinc removal achieved was approximately 80%, in mass. This was for pellets produced with 10 and 15% of PET, for an experiment of one hour, at the temperature of 1000 ºC;

- Franklinite, present in self-reducing pellets, decomposes in all experiments at a temperature of 1000 °C;

Finally, and having an overall view of this study, mechanical strength, metallic yield and zinc enrichment of the new dust obtained still need to be assessed in melting batches in EAF.

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