

Self-reducing pellets composed of wastes from steelmaking production for their recycling

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Abstract

This paper presents a study about the recycling of a mixture of EAF filter dust and mill scale; and slag, in the form of self-reducing pellets. At first, chemical and morphological characteristics of the material were investigated. Pelletizing was carried out manually, with the use of graphite 100% fixed carbon and molasses as binder with moisture. The results of reduction tests under the temperature of 1200 °C for the wastes could be analyzed according to the use of different contents of reducing agent, time and mass loss. It was found that 20% of the carbonaceous material was the best configuration for a maximum mass loss, for both wastes. Furthermore, the pellets composed of stainless steel slag, added to the metallic bath presented a chromium recovery of around 95%, indicating its potential reuse.

Keywords: Steelmaking wastes; Pellets; Self-reduction; Recycling.

1 Introduction

Continuous casting and rolling mill wastes, like scale, are residues rich in iron. The waste agglomeration in self-reducing briquettes or pellets is a way of recycling them, since it is a big challenge for all steel works and mini-mills to reintroduce agglomerates made of filter dust or slag into the process [1].

Scale represents about 2% of steel produced [2-4]. It is formed during continuous casting, when steel is submitted to thermal gradients in oxidant atmospheres, which promotes the growth of iron oxide layers at the surface of the steel. The recycling of this waste for steelmaking was already reported. Some attempts involved using the scale for pure iron powder production [5-7]. In mini-mills, which operate by electric arc furnace and where there are no reduction reactors, the scale recycling is more difficult, so this waste is often sent to landfills. However, self-reducing technology has already been reported as a possible means for recycling the mill scale of mini-mill plants [1-8].

Several studies related to the recovery of scale and other wastes have been conducted all over the globe. DK Recycling and Roheisen GmbH process about 400 thousand tpy of different dusts and sludge [9]. Martin et al. [10] have studied the reduction of mill scale to sponge iron using carbon as the reducing gas. The environmental impact of this reduction reaction has been recorded as compared to those

reactions using carbon as a reducing agent [11]. High purity sponge iron powder is currently manufactured from high purity iron ore after the basics steps of magnetic separation, milling and primary reduction.

For steelmaking waste dusts containing zinc, the recovery processes involve physical, pyro and combined methods. Zinc recovery technology uses the low boiling point of zinc for the reduction of zinc oxide at high temperatures, with the gasification of zinc for phases separation. This method is divided into direct reduction and reduction-melting, which are both suitable for treating high zinc iron dust. The Waelz rotary kiln method and the rotary heart furnace method are the most widely used fire methods.

During stainless steel production in an electric arc furnace, the dust generated amounts to around 1% of the charge weight. This dust contains chromium, zinc and other heavy metal oxides; therefore, its final disposal in special landfill sites is also expensive and non sustainable. On the other hand, the content of chromium oxide and iron oxides can be recovered by reduction with carbon or FeSi [12].

Today, the recycling of a large amount of slag generated during the decarburization period of the steelmaking process has been carried out extensively from both the economic and environmental points of view. However, there has been increasing demand for investigation on the characteristics

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of the slags and improvement of such recycling processes. It is necessary to reduce efficiently chromium content in recycling processes, which is one of expensive elements to remove from slags and is also a regulated harmful element in waste materials [13].

Iron-chromium alloy is produced in the reduction process, where the chromium ore, together with carbon and fluxes is loaded in a furnace for smelting and reduction. Recently, new stainless steel production technologies have been appearing and some include the recycling of residues with high chromium content that could substitute part of the chromium to be added during stainless steel manufacturing [14].

With consideration to smelting, foaming-slag practice is being used successfully in many carbon steelmaking plants for the improvement of thermal efficiency and adequate productivity of the reactor [15]. Although many stainless steel companies have tried to adopt this practice, its adoption has hereto been difficult.

This is generally due to the high-chromium-oxide content and low iron-oxide of the stainless steel slags. In addition, it should be considered that the rate of CrO₃ reduction by carbon is much slower than that of FeO_x [16].

Therefore, a self-reduction of metallic oxides/carbon agglomerates was studied having in mind a further quantification of the reduction trials for the mixture of filter dust and mill scale and the possibility of use of the slag recovered as a chromium alloy in the steel production. The present paper reports the initial part of a project about recycling these kinds of different steelmaking wastes as self-reducing pellets. Thus, some physical and chemical properties of the residues are investigated, as well as the pelletizing and other processes, including waste reduction and smelting behavior. Also, microscopic examination of some samples was carried out in order to have a better understanding of the reduction phenomenon.

2 Experimental

The materials used in the tests were collected in a German mini-mill and are composed of a mixture of

Filter Dust and Mill Scale (FD+MS) as well as slag from Stainless Steel (S-SS). Chemical characterization was conducted by Spark Optical Emission Spectroscopy, with method TQ-Powders-mp2 (for the slag). Carbon content was measured with burning method.

Tables 1 and 2 demonstrate the composition of each material, received in the laboratory with the following chemical analysis, considering the sample weight free of carbon, that was measured using another technique.

Elements Fe (36.00) and Zn (12.00) represent the majority of the waste. According to literature [17], zinc concentration in dusts originating from EAF-steelmaking may vary between 11 and 27%. The carbon content of the mixture is 0.68%.

For the slag, magnetic separation was conducted via magnetic separation table and afterwards approximately 50% of the residue was divided into the sample to be used for the pelletizing process.

In addition to the elements traditionally found in a slag, such as Al, Ca, Si and Mg, chromium is also one of the main elements present in the composition. A slag with similar composition was also found by Nakasuga et al. [13].

The carbon content of the analyzed slag is 0.12%. Results of the magnetic separation also showed an increase in chromium (from 13.60 to 16.77%) and in iron (from 1.89% to 3.62%), while the other elements remained in similar amounts, suggesting that recovery or reduction of chromium could be cited as being important for the production of FeCr alloys, for example.

Crushing was done in a disc mill Retsch RS 300 XL with six minutes of operation for slag, mixture and carbon. The particle size analysis was carried out and the sieves used were 500, 250, 125 and 63 μm .

Figure 1 shows the granulometric distribution of the materials.

According to Figure 1, the granulometric distribution of the materials were around 50% below 0.125 mm.

The wastes used in this procedure were dried, at 130 °C for 24 hours, before grinding and then sampled with a Retsch model PT100 at the Institut für Technologien der Metalle

Table 1. Elemental composition of the mixture of Filter Dust and Mill Scale

Elemental	Fe	Zn	Ca	Mn	Si	Mg
composition	36.00	12.00	8.09	3.30	3.20	2.89
of the mixture	Al	Cr	Pb	Ti	V	O*
(% wt)	1.80	0.91	0.19	0.12	0.08	30.74

*Oxygen was calculated by difference.

Table 2. Elemental composition of the stainless-steel slag (magnetic fraction)

Elemental	Cr	Ca	Al	Si	Mn	Fe
composition	16.77	9.81	5.81	5.17	4.29	3.62
of the slag	Mg	Ti	V	S	Zn	O*
(% wt)	2.56	0.30	0.13	0.04	0.05	51.32

*Oxygen was calculated by difference.

(ITM), according to a procedure carried out previously in another research laboratory.

The materials were pelletized manually, with moisture and other additives. Carbon 100% and molasses, along with water, were added to the mixture. In total 350 g of the material, 100 g of carbon (20%) and 50 g of molasses composed the mixture of higher carbon content. The water added was 50 ml. The other two compositions were of 15 and 10% carbon, and proportional in mass with the first composition. Pelletizings for FD+MS and S-SS (magnetic) materials were performed.

After being produced, the pellets were dried at room temperature for one hour and remained in the oven for 45 more minutes at 70 °C, in accordance with a procedure described in literature [18], before being conducted to the reduction and melting tests.

2.1 Reduction Tests

In the first tests the self-reducing pellets (10, 15 and 20% of carbon) were conducted to a Nabertherm HT 12/17 resistance furnace. Alumina open crucibles (under oxidant atmosphere) with an inner and outer diameter of 50 and 75 mm, respectively, were used for the heating. The crucible's height was 115 mm. In each experiment one pellet was added in the opened crucible and heated at a temperature of 1200 °C, under not inert (air) atmosphere, for different time intervals (two repetitions were done for each experiment):

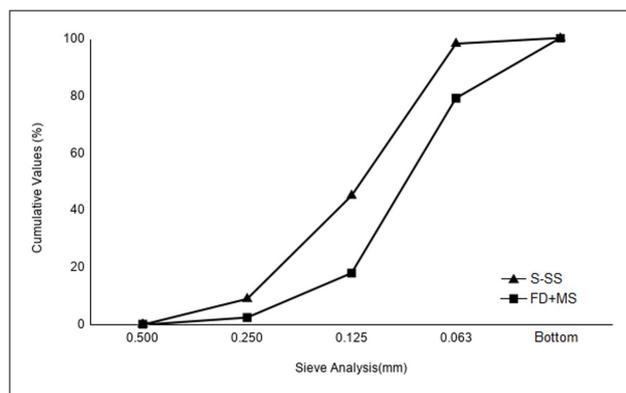


Figure 1. Particle size analysis of the materials after crushing.

Table 3. Stoichiometric carbon percentage and its quantity used in the reduction tests

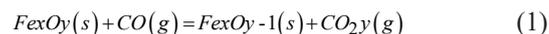
Stoichiometric carbon (%)	%C used in the tests	$C_{\text{fix}}/Fe_{\text{total}}$
9.90	10.00	0.28
9.90	15.00	0.48
9.90	20.00	0.55

Table 4. FeSi75 composition

Elements	Si	Al	Ca	Mn	Cr	P	S	C
%	75.0	2.0	1.0	0.4	0.3	0.035	0.02	0.01

- 3, 6, 9, 12, 15, 30, 45, 60 and 90 minutes (for *Filter Dust + Mill Scale*);

Considering the following reaction (Equation 1) as representing the reduction of iron oxide (in its form FeO) by graphite, like in a scale reduction study [2], it could be stated the stoichiometric carbon for the reduction is 9.90%, in mass. This calculation took into consideration the reduction of iron and zinc oxides (FeO and ZnO).



The reduction assays were carried out with around 66 and 100% of carbon in excess to the stoichiometric quantity. Table 3 shows the stoichiometric calculated percentage of carbon and the percentage used in the reduction trials.

And

- 15, 30, 45, 60, 90 and 120 minutes (for *Stainless Steel Slag*).

The stoichiometric carbon was the same for all tests.

The sample was introduced in the furnace, already at 1200 °C and after achieving the temperature again, the timer was started. Cooling of the pellet occurred inside the crucible.

All samples were dried for 2 hours at 130 °C, before being submitted to the furnace environment, according to a procedure taken in literature [19].

For carbon content analysis, ELTRA CS 800 equipment was used.

2.2 Melting trials

The furnace used was an open induction furnace Hüttinger 10 kV, with 300 kHz of frequency and capacity of 3 kg. The pellets were inserted in the crucible, simulating the furnace loading through the first burden in a melt shop, disconsidering the hot heel.

The system was heated to 1600 °C and after reaching this temperature it remained for 10 minutes for homogenization until being tapped in a specific mold. Adding of FeSi75 alloy (Table 4) occurred in this time and it was done from the top to check the reduction efficiency [12].

Afterwards, the ingot was cut in three pieces, grinded on each surface and analyzed in an Energy Dispersive X-Ray fluorescence spectrometer Shimadzu EDX-8000. Carbon was detected by Spark Emission Spectroscopy.

Two experiments were done in this step (only the Stainless Steel Slag). The first experiment used pellets with 20% of carbon (approximately 50 g) for each batch, in a total of 3 repetitions, plus unalloyed steel CK45 (around 650 g)

(Table 5). In the second experiment, FeSi75 alloy (~25 g) was added during the experiment.

Figure 2 shows the set-up for the tests.

The coil (1) is indicated above. A crucible (2) was placed in the assembly to contain charging materials for heating and smelting. In the metallic bath (3) were added the pellets and unalloyed steel. The slag formed is represented on the upper side of the bath (4), while the thermocouple (5) was fixed in the middle of a refractory. Before the charge melting and during the time of the experiment where there was no sampling or other operations the crucible was closed by the refractory cover (6).

3 Results and discussion

Pellets were produced with the raw material and a moisture of 10%, by mass.

The average diameter of the agglomerates was 10 mm, a size also found in literature [19].

3.1 Reduction Tests

3.1.1 FD+MS

Figure 3 shows the results for the Filter Dust + Mill Scale mixture tests, for the different compositions of 10, 15 and 20% of carbon, at the temperature of 1200 °C.

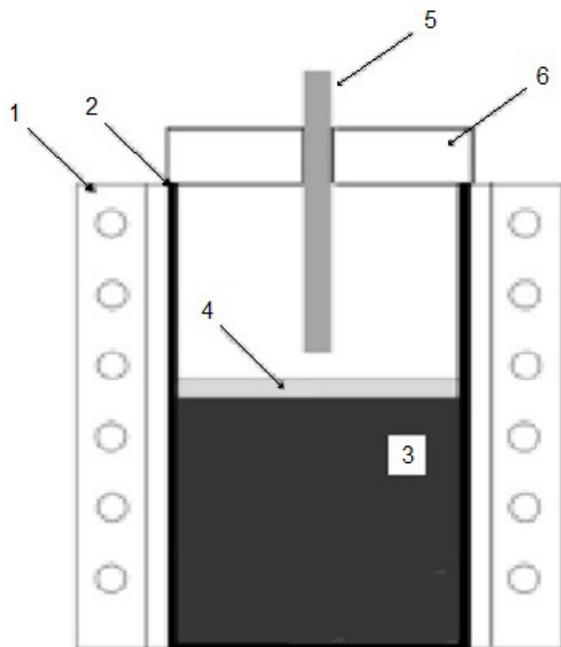


Figure 2. Melting scheme.

Table 5. CK45 steel composition

Elements	C	Cr	Ni	Mn	P	S	Si	Fe
%	0.45	0.29	0.11	0.84	0.041	0.033	0.36	97.10

The graph curves in Figure 3 show similar behavior to that of a thermobalance experiment [20]. Analyzing each curve, it is possible to see a maximum mass loss for the one with 20% of carbon, while the standard for that with 15% of the carbonaceous material stands between the lines of 10 and 20%. It can be seen until 30 minutes all the lines have similar behavior, except for the curve of 15% C. They all have a sharp mass loss until this time and after that tend to a plateau. The mass loss related to this step could be associated to carbon consumption, reducible oxygen and zinc volatilization. After 60 minutes of experiment, the curve, for the 20% of carbon configuration, reaches its maximum, suggesting no more reduction would take place, representing 40% of mass loss, while for the others the mass loss was lower.

Moreover, if zinc volatilizes completely, then $0.12 \cdot (70\%) = 8.4\%$ represents its parcel, while assuming that carbon burns 20% of the total amount of 40% (for the pellet with 20% of carbon), leaves $(40 - 20 - 8.4) = 11.6\%$ for reducible oxygen, since there is no molasses in the system.

The reduction plays role with the formation of CO and the effects caused by carbon oxidation were not taken into consideration. Another remarkable point is that there is a kinetic advantage for the pellet with higher concentration of carbon (above the stoichiometric carbon), comparing to the others, an important factor for recycling inside reactors, since time is one of the main parameters in steel production.

3.1.2 S-SS

Figure 4 shows the results for the slag from stainless steel, in reduction tests, for the different compositions of 10, 15 and 20% of carbon, at the temperature of 1200 °C.

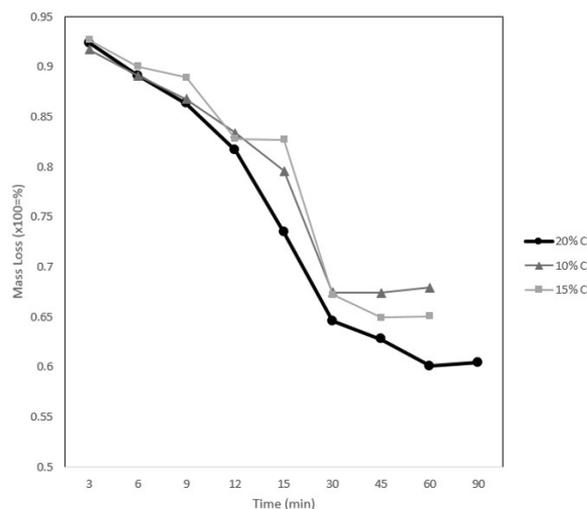


Figure 3. Reduction assays for the pellets composed of FD+MS.

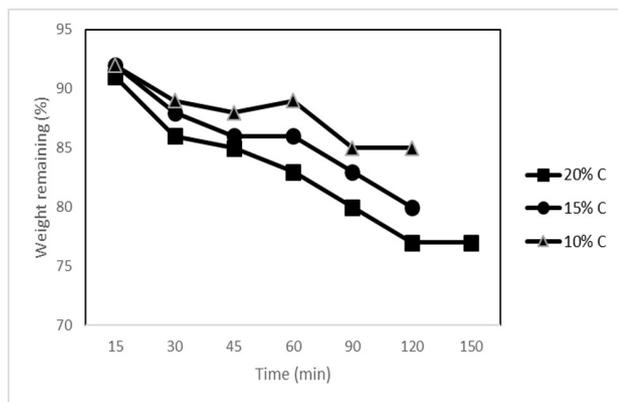


Figure 4. Reduction assays for the pellets composed of S-SS.

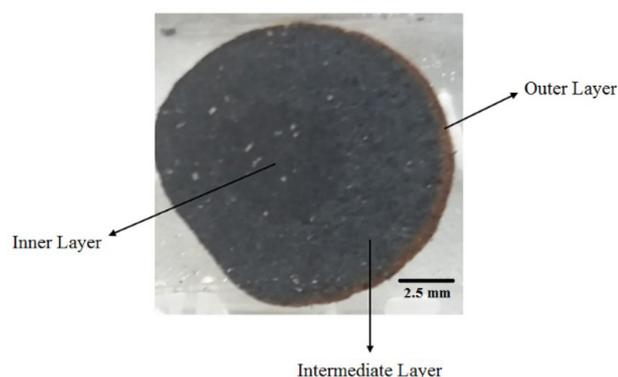


Figure 5. OM for the sample reduced top chemically with 20% of carbon.

Different intervals of time used in the test are shown in the abscissa, while in the vertical axis the weight remaining in the pellet is displayed by mass percentage. A stronger mass loss in the first 30 minutes can be observed, while for the time of 120 to 150 minutes (for 20% of carbon) mass loss remained constant. This constant trend indicates the value of total reduction of the sample (maximum mass loss) of 23%. A pre-test for 1300 °C was also conducted to check if reduction would play a more important role if the experiment were carried out at higher temperatures, but it was not verified. Therefore, reduction at 1200 °C could be related to the reduction of metallic oxides containing reducible oxygen (mostly from probably complex iron oxide) and oxidation/gasification of fixed carbon [20], according to the following reaction (Equation 2):



3.1.3 Optical microscopy (OM) shows the profile for a pellet with 20% of carbon composed of S-SS, after reaction (Figure 5).

Figure 5 shows the different layers formed in the pellet from its top to center.

Which of the reduction products at any given instant during the reduction lie on the surface of the oxide and are in contact with the gas phase depends not only on the corresponding equilibria but is also determined by the rates of removal of oxygen on the one hand and by the diffusion processes in the oxides on the other [21].

The pellet with 20% of carbon was better investigated after the reduction process and the result follows in Figure 6,

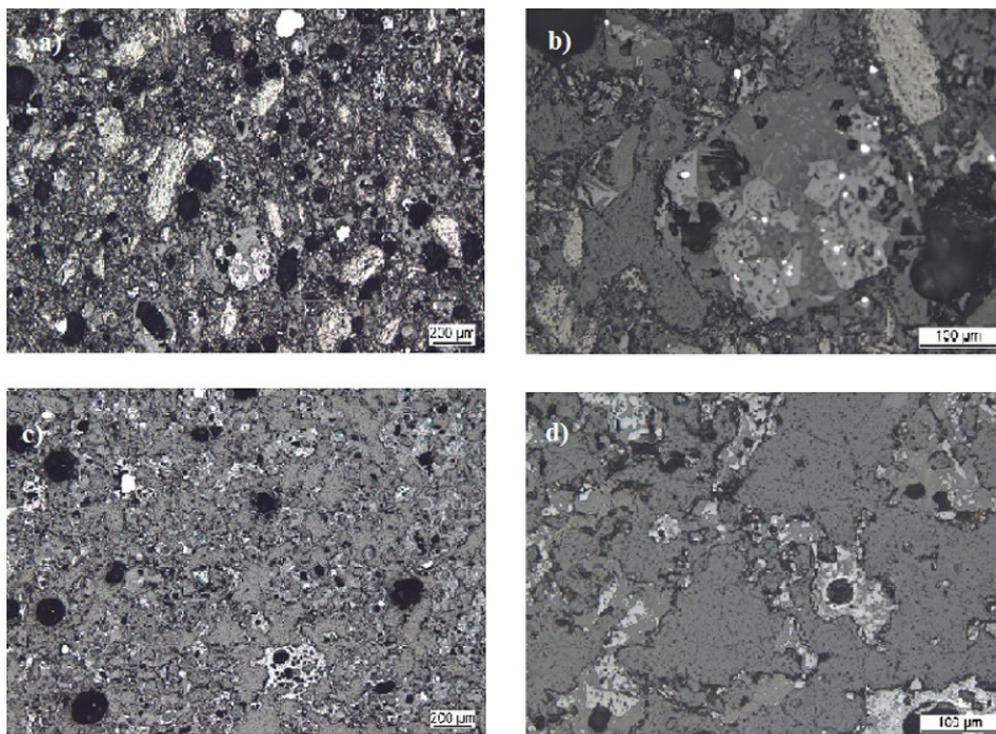


Figure 6. Pellet with 20% of carbon, after being reduced in an experiment under 1200 °C a) b) after 15 minutes and c) d) after 120 minutes.

Table 6. EDX analysis of the molten sample without the use of FeSi75 alloy

Elemental	Cr	Ca	Al	Si	Mg
composition	1.15	1.43	0.07	0.53	0.02
of the sample	Mn	Fe	Ti	Cl	Zn
(% wt)	0.26	94.52	ND	0.00	0.00

Table 7. EDX analysis of the molten sample with the use of FeSi75 alloy

Elemental	Cr	Ca	Al	Si	Mg
composition	1.13	1.64	ND	2.95	0.00
of the sample	Mn	Fe	Ti	Cl	Zn
(% wt)	0.35	94.01	ND	0.00	0.01

where the extremes of time, in the analyzes, were observed, in the center of the agglomerate.

The larger and brighter particles shown in Figure 6a) are carbon particles. The small and highly reflective particles in Figure 6b) are metal particles. After 120 min of reduction time, Figure 6c) and d), no important amounts of reduced metals are detectable, since only complex iron is reduced (6b) which could be oxidized after (6d)

3.2 Melting trials

The results for the melting experiment are shown in Table 6 and 7, demonstrating the chromium yield in the molten material formed, after being analyzed by Energy dispersive X-Ray fluorescence spectrometer (EDX).

The reduction of chromium oxide dissolved in a slag with C(s), depending on temperature, leads to the formation of a carbide, $Cr_3O_2(s)$ or the formation of metallic Cr phases [22].

After the analysis, the average presence of chromium as 1.15% by mass of the ingot can be seen. If for the total mass there was 8.2g (calculated as chromium diluted in all sample mass) of this element, its yield was of around 97%, in weight.

A more conventional way to control chromium content in the slag is through silicon introduction (alloy or scrap form) during the furnace charge. It is expected that silicon oxidizes before chromium (according to the Ellingham diagram) [23].

With the use of the reductant, chromium content was 1.13%, similar to the melt without the presence of the alloy. Again, after the analysis, the ingot's yield of this element was of 95%, a little less than the other one and with higher content of Si, because of the high presence of this element in the alloy (75%). The reduction was not higher in the second experiment probably because of the way the FeSi75 alloy was inserted in the mixture or even because of the homogenization time or slag formation, due to concentration of material added.

The content of elements like Mn (0.84%, for the initial steel), decreased in the sample analyzed by EDX, probably because the new slag obtained captured this element from the metallic bath. The experimental arrangement did not

allowed a new analysis of the slag, becoming harder its comprehension.

4 Conclusions

Some conclusions could be taken into consideration regarding to the production of self-reducing pellets and their use for recycling steelmaking wastes, including a mixture of filter dust and mill scale, along with slag from stainless steel. With respect to the reduction tests, the maximum mass loss occurred for pellets with 20% of carbon and had a value 40%. It also could be stated that this loss was related to FeO reduction combined with carbon oxidation, through Boudouard reaction and, zinc volatilization. For the slag, the maximum mass loss was of 23%, for a pellet with 20% of carbon in two hours of experiment, under the same temperature used for the other waste, 1200 °C. The remaining carbon measured for this pellet indicated that not all the carbon had reacted with oxygen. It could also be noticed, as expected, in the microscopic analysis that no important amounts of reduced metals were detectable.

Regarding the melting trials, according to the spectrometer analysis, chromium recovery for both experiments, with and without the use of the FeSi75 alloy, was close to 95%.

Due to the high recovery rate, it can be seen that the reduction reactions takes place, probably because of the higher temperature (1600 °C), but it could also be possible because of the contact between liquid iron what is locally and temporary enriched and saturated with carbon in the nearer surrounding of the oxide particles. It is shown that agglomeration of wastes generated during steel production, in the pellet form, is an efficient way to recover iron and alloy elements, such as chromium, before their disposal in landfills.

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