

Briquettes Composed of LD Converter Steel Mill Wastes and Blast Furnace Dust to Produce Primary Iron and Liquid Steel Temperature Control

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Several types of waste are generated in the integrated steel industry, in particular from wet or dry LD (Linz-Donawitz) converter dedusting systems and blast furnace cleaning equipment. These wastes contain iron, carbon and, in some cases, zinc, which have been the subject of several studies and technological initiatives in recent decades. In this work, the fine (F) and coarse (C) residues generated in a dry dedusting system of the LD converter were used in the proportion of 50-50% and 70-30%, respectively, and to these proportions were added dust residues from the blast furnace (BF) collector. Previously, the C and F residues were hydrated for 3 and 4 days, respectively, and the mixture was agglomerated with Portland cement ARI (Alta Resistência Inicial) and water to produce self-reducing briquettes, in order to study their behavior in compression, metallization and mainly as an alternative cooling agent in liquid steel to control its final temperature. The results were analyzed considering the energy balance of the briquette-steel bath system and taking into account a thermodynamic sequence for the main reactions and oxygen potentials typical of steelmaking processes. The self-reducing agglomerates proved to cause a high cooling effect in the steel bath compared to iron ore scrap and pellets. Moreover, considering their high metallization degrees, self-reducing briquettes are an effective way to recover the metal (iron) contained in the waste.

1. Introduction

In recent decades, the steel industry has focused its efforts on improving the recovery and quality of by-products (Branca et al., 2020), relying not only on existing technologies (Cappel et al., 2022) but also on the development of innovative sustainable solutions for waste treatment (Shahabuddin et al. 2023).

The steel industry is well known for being an intensive consumer of energy, water and raw materials. Steel mills are also characterized by producing large quantities of gases, effluents, wastes and co-products, whose environmental problems are motivating research and great efforts towards the development of specific treatment, recovery and recycling technologies, in order to increase the generation of co-products (Jalkanen et al., 2005; Biswal, et. al. 2020). In Brazil, steel mills (integrated and semi-integrated) generate about 628 kg of co-products and process residues per ton of steel produced (IABr, n.d.). This highlights the importance of reusing these materials, which are stored or disposed of in landfills, becoming process residues.

In the primary dedusting stage of LD converters, wet or dry systems generate two characteristic wastes: coarse wastes that are typically rich in metallic iron and represent about 30%, and the remaining 70%, fine wastes that concentrate mostly the oxidized phases (Doronin & Svyazhin, 2012; Zhou et al., 2022). The percentage of iron present in this type of powder can vary from 40 to 60%, which is attractive to be used as raw material in upstream processes of the steel mill such as sintering and the blast furnace or basic oxygen furnace (da Rocha et al., 2014). The average rate of total dust generation from the LD converters is about 24 kg/t of steel (Noldin et al.,

2006; Remus et al., 2013). These residues are used in traditional and some emerging processes, mainly as raw material in mixtures for sintering plants, as briquettes to recycle iron content (Takano et al., 2001; Singh et al., 2017) and, in the specific case of the coarse residue, as an alternative cooling material for liquid steel (Noldin et al., 2005; Kumar et al., 2008).

Due to the different particulate generation conditions in wet and dry dedusting systems in LD converters, this research focused on residues (fine and coarse) to make self-reducing briquettes that were compression tested and subsequently metallized. In addition, the steel quenching results obtained in the experiments with self-reducing briquettes were evaluated by defining the main reaction sequences on a thermodynamic basis and calculating the mass and energy balances for the briquette-liquid iron system. Also, a theoretical calculation of the feasibility of using these self-reducing briquettes as a cooling medium to control the temperature of liquid steel in the LD.

2. Materials and methods

2.1 Raw material and characterization

The raw material used for the production of briquettes were LD steel mill wastes and blast furnace dust, both wastes were obtained from Brazilian steel companies as part of a broad cooperation program defined with the Pontifical Catholic University of Rio de Janeiro (PUC-Rio). The chemical and granulometric analyses of both wastes are presented in Tables 1 and 2.

Table 1: Chemical analysis of LD steel mill dust and blast furnace collector dust

LD steel mill dust	Fe _{Total}	Fe _{Metal}	SiO ₂	CaO	MgO	Na ₂ O	K ₂ O	Zn	Al ₂ O ₃	C	S
Fine (%)	58.45	17.55	1.91	11.31	1.91	0.09	0.40	0.07	0.25	0.60	0.07
Coarse (%)	58.13	42.55	3.12	18.34	3.16	0.03	0.18	0.06	0.30	0.64	0.05
BF collector dust (%)	41.49	-	9.07	2.90	0.50	0.18	0.26	0.21	2.64	32.84	0.29

Table 2: Granulometric analysis of LD steel mill dust and blast furnace collector dust

LD steel mill dust	Retained in mesh					
	2 mm	1 mm	0.355 mm	0.125 mm	0.045 mm	Pan
Fine (%)	8.62	3.99	8.27	17.1	21.75	40.28
Coarse (%)	2.65	4.92	19.63	36.25	20.51	16.04
BF collector dust (%)	0.58	0.9	3.88	38.53	40.0	1.11

2.2 Preparation of the briquettes

Since the primary steel mill dust is produced in dry conditions and with the presence of free lime, its prior stabilization by hydration was necessary to avoid early cracks and breakage in the briquettes (Alvarado Quintanilla, 2017). This hydration was carried out for 3 and 4 days for coarse and fine powders, respectively. After stabilization of the steel mill dust, the fines and coarse were mixed in proportions of 50-50 and 70-30, respectively, and an amount of blast furnace collector dust was added expressing the stoichiometric value and with 10% excess. Portland cement ARI at 2 - 6 wt.% with a water/cement ratio of 0.5 was used as binder. The previously moistened mixtures were taken to a hydraulic press to obtain cylindrical briquettes of approximately 8 g (Figure 1-a), which were subjected to a curing time of up to 28 days, and samples were taken for compression tests at 1, 2, 3, 8, 18 and 28 days. For each day of cure, 3 briquettes were used, making a total of 18 according to the mix component conditions specified above.

A tubular electric furnace equipped with a gas line was used for metallization, as shown in Figure 1-b.

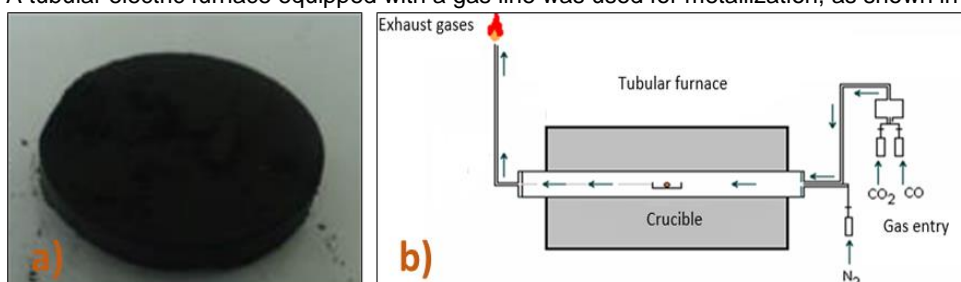


Figure 1: a) Briquette, and b) Tubular electric furnace

The metallization tests were carried out in N₂ atmosphere, at temperatures of 1100 and 1150°C, and sample residence times of 10, 20, 30 and 45 minutes. Subsequently, a kinetic analysis was performed to define the reaction mechanism. In addition, taking into account the importance of the reactivity of the carbonaceous phase of the briquette for metallization (Martins, 2002; Babich et al., 2009), the measurement of this property was performed using ASTM D-5341 (ASTM, 2004) and thermogravimetric analysis (TGA) under CO₂ atmosphere and temperature of 1100°C, for 2 hours.

3. Results and discussion

3.1 Passivation and thermogravimetric analysis of steel mill dust

Figure 2 shows the mass gain over 10 days of hydration. It illustrates the stabilization of the process from the third day for the coarse powder and from the fourth day for the fine powder. The steel mill powder exhibited stable passivation, having good pitting resistance, and passivation depends on many parameters such as the nature of the electrolyte, grain size, grain boundary structure, crystallographic texture or residual stresses (Hug & Keller, 2023).

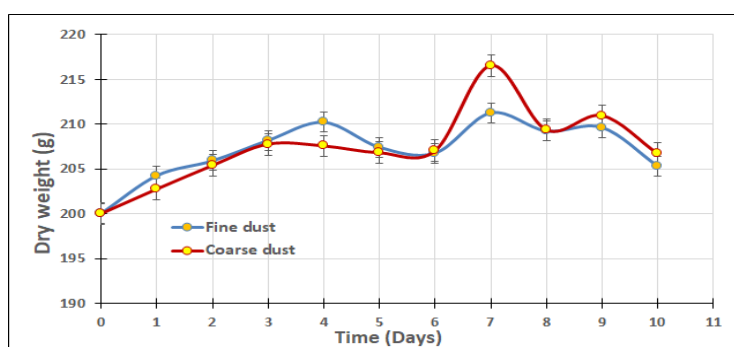


Figure 2: Passivation of steel mill dust: fine and coarse fraction

Figure 3-a shows that the coarse fraction steel mill powders had a mass loss equivalent to 4.02%, in the temperature range from 21 to 882 °C, and the fine fraction (Figure 3-b) had a mass loss equivalent to 6.34% in the temperature range from 21 to 861 °C. These values were compatible with the hydration passivation process, and the mass gain can be attributed to the oxidation reactions of the metallic iron and the water that hydrated the steel mill dust, confirming the passivation of the free lime during the hydration process

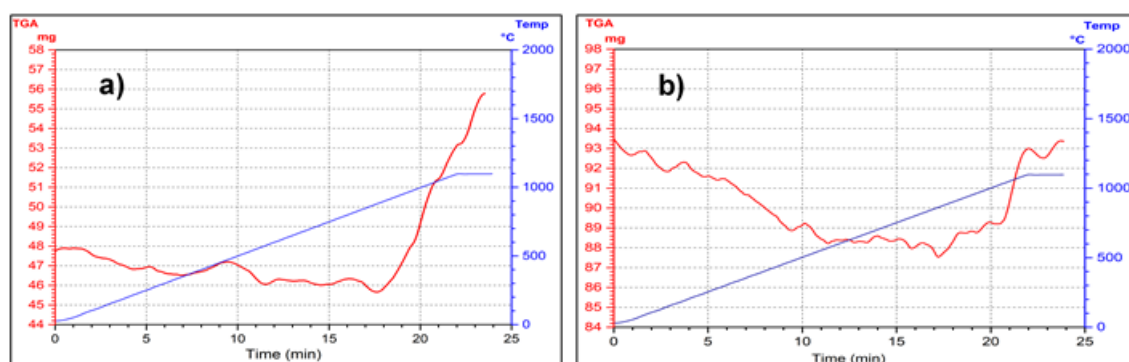


Figure 3: Thermograms of steel mill dust: a) Coarse fraction; b) Fine fraction

The reactivity test via the ASTM D-5341 standard test method showed an average value of 77.1%. On the other hand, the reactivity measured by TGA was a mean value of 53%. The reactivity value was not high because the briquette does not have a large amount of volatile matter, since it is already a product of the devolatilization of mineral coals. In addition, the material should not be very reactive since it must provide carbon to form the reducing gas and must hold the metallic charge in the blast furnace. If it were too reactive, it would be consumed quickly and there would be problems in stabilizing the charge.

3.2. Compressive strength

The results of the compressive strength are shown in Figure 4, indicating small differences between the 50-50 and 70-30 self-reducing briquettes, as well as an increase in the values with longer curing time. Thus, at 28 days of curing, the maximum strength was reached, reaching 207.9 g/cm². According to Blesa et al. (2003), the curing process is one of the final steps of briquetting that produces transformations-interactions-changes between the carbonized materials themselves as well as with the binder, improving their mechanical strength.

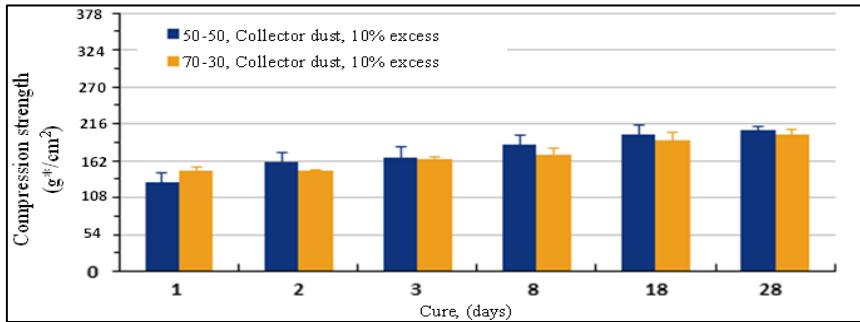


Figure 4: Results of compressive strength with ARI cement

3.3 Metallization

The time-dependent metal conversion curves and continuous fitting curves of the reaction kinetic model were performed for the self-reducing F-C briquettes of 50-50 and 70-30 ratios, in the stoichiometric amounts and with 10% excess. The results showed that the metal conversions increased with temperature (Ye et al., 2023) and the amount of blast furnace collector dust. The self-reducing briquette F-C of 70-30 ratio achieved the highest metal conversion of 95% at 1150 °C with 10% excess blast furnace collector dust (Figure 5). The kinetic model for metallization is represented by Equation 1 (continuous reaction model), which represented the highest value of correlations (mean 0.995). The values obtained for k (min⁻¹) in the experiments studied are shown in Table 3.

$$-\ln(1-x) = kt \quad (1)$$

Where: x , conversion; k , kinetic constant; t , time.

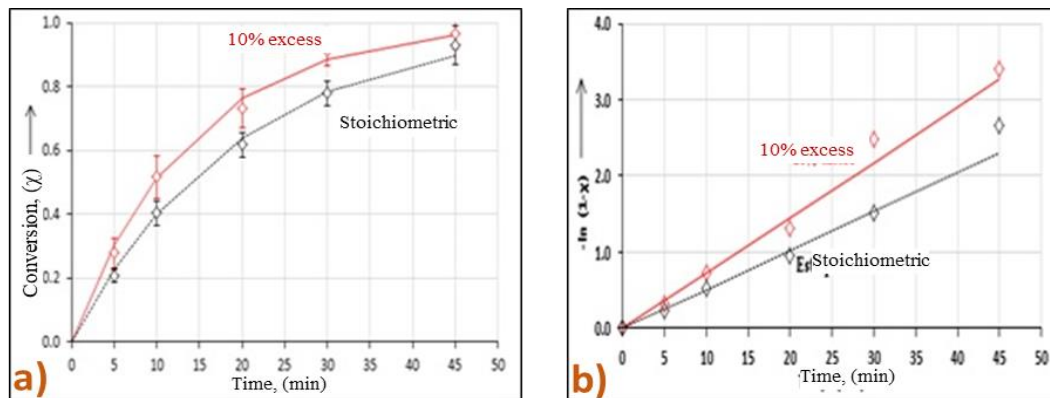


Figure 5: Results of compressive strength with ARI cement

Table 3: Values of kinetics constant, k

Conditions		Briquettes, k (min ⁻¹)	
Fine - Course (%)	Temperature (°C)	stoichiometric	stoichiometric + 10% excess
50-50	1100	0.0323	0.0445
	1150	0.0367	0.0554
70-30	1100	0.0454	0.0613
	1150	0.0512	0.0726

3.4 Energy balance and cooling power

Based on thermodynamic data, the sequence of reactions shown in Figure 6 was proposed for the self-reducing briquettes - liquid steel system. Upon contacting these phases and considering the oxygen potentials of the slag calculated at the temperatures of 1500 and 1600 °C with -321.2 and -308.0 kJ/mol, respectively, and the steel bath at the same temperatures with -349.4 and -353.8 kJ/mol, respectively, it was possible to confirm that at these potential levels all reduction reactions were feasible.

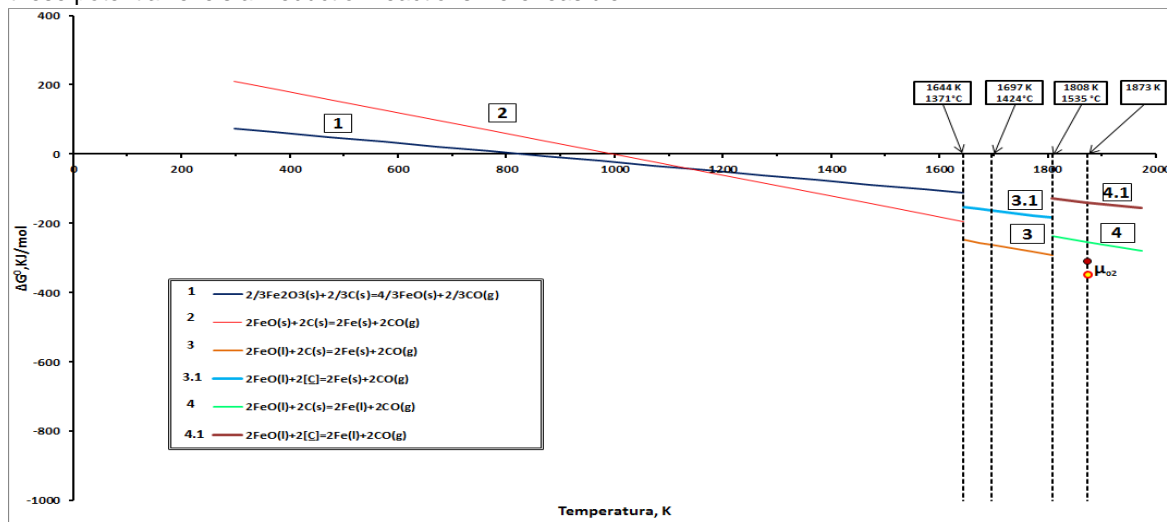


Figure 6: Sequence of reactions in reduction of oxides: self-reducing briquette

For the energy balance at the temperature of 1600 °C the enthalpy of the components (Fe, FeO, Fe₂O₃, CaO, Ca₂SiO and C) concerning the self-reducing F-C briquettes of 50-50 and 70-30 were considered, reaching values of 796.33 and 698.68 kcal/kg, respectively. Comparing the cooling power of scrap (340 kcal/kg, according to literature), the ratio of cooling effect briquette/scrap at 50-50 with 10% excess was 2.05 times higher than scrap, and at 70-30 with 10% excess, the cooling effect was 2.34 times higher than scrap.

Furthermore, according to previous experiments conducted by the metallurgical group of PUC-Rio in an instrumented pilot furnace (Bentes, 1998), it was possible to confirm the strong cooling capacity of the self-reducing briquette, as shown in Figure 7.

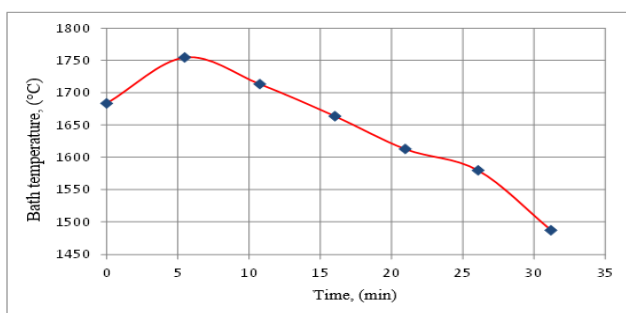


Figure 7: Cooling effect of self-reducing briquette in liquid steel (Bentes, 1998)

4. Conclusions

Passivation pretreatment for volumetric stabilization of steel mill powders was essential to avoid cracking problems of 50-50 and 70-30 self-reducing F-C briquettes that achieved the same compressive strength at 28 days. ASTM (D-5341) and TGA tests showed a highly reactive BF collector powder, strongly influenced by fine granulation. In metallization tests, the highest conversion of about 95% was obtained for the 70-30 F-C self-reducing briquette at 1150 °C, with 10% excess BF collector powder. The continuous reaction mechanism $-\ln(1-x) = kt$ presented a high correlation with the experimental data, higher than 99%. From the thermodynamic sequence of the energy balance and oxygen potentials it was possible to confirm the feasibility of the metallization of the briquettes and their steel cooling power. The estimation rates of the "cooling effect" of the self-reducing briquettes were shown to be significantly higher than those of the scrap metal.

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