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ASSESSMENT OF MILL SCALE FORMATION IN STEEL INDUSTRIES USING THERMOGRAVIMETRIC ANALYSIS

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Abstract. *Normally, the steel industry generates a high amount of waste, thus is necessary to realize environmental studies which aim the reduction of them. To reduce the amount waste, reduces cost generates by treatment, once these treatment are expensive for companies. Mill scale is a co-product from the oxidation of the steel surface, when subjected to the thermal gradient or to the simple action of time. This is generated in processes, such as: casting, lamination for profile and rebar, lamination and welding to produce trusses, among others. The mill scale must be stored according to the relevant environmental standards, due to its classification as hazardous waste. (Class I, NBR 10004: 2004) There are few studies conducted on mill scale formation models and how this co-product can to have a value added. In this context, studies using thermal processes controlled, morphological and structural analysis of the steel, before and after the oxidation, as well as mill scale physicochemical characterizations are very important. Thus, in this project was studied the mill scale reduction. For this, a thermo-gravimetric analysis was used to have a process controlled. This methodology allowed the deep investigation of mill scale formation. The results shown, the initial temperature of mill scale formation is 900°C, on condition determined. The mill scale production is about of 4% of material, but this can be reduced until 2%.*
Keywords: mill scale, steel industry, hazardous waste, thermogravimetric analysis.

1. INTRODUCTION

The Brazilian steel industry accounted for 2.1% of world steel production in 2014 and 2015, rising from 9th to 8th place in the ranking led by China, with crude steel production in Brazil of 33.3% million metric tons in 2015. The Brazilian iron and steel industry has an average generation of 700 kg of waste per ton of steel produced, with about 50% of this waste being blast furnace slag and melt shop and the other half involving fines, (Cunha et al., 2006). However, it is important to note that there is a lack of adequate treatment and storage of the residues, which are disposed of in landfills or even in direct contact with the soil. Such an arrangement and the inadequate treatment of industrial waste creates risks of contamination of soil, atmosphere and rivers. In this way, environmental issues are increasingly significant, due to the treatment and the expense attached to them.

In 2015, total co-products and direct wastes were 19.8 million tons, according to data from the Brazilian Steel Institute, so the investment in new materials and also in new applications for waste are increasing. Therefore, materials that would be erroneously discarded become raw material for road paving, soil corrective and cement manufacturing (Pereira, 2011). The reuse of iron derives from its by-products, such as the mill scale, which is characterized by high iron content, 72% (Bivenven et al., 2010 apud Benchibeub et al., 2010). This is generated in large quantities, as the co-product in preliminary stages of mechanical forming processes.

Continuous reheating furnaces have an important function in the rolling area where intermediate products, such as plates or billets, are reheated until they reach around 1250 °C for further processing of lamination which would produce steel reels. Figure 1 shows a schematic of a reheating furnace.

The inside of the reheating furnaces is divided into seven zones for temperature control: upper and lower preheating; upper and lower heating; and flood zone, with two upper and one lower zones. All areas can burn natural gas, coke oven gas and oil by the same burners, generating heat exhaustion gas. The combustion air is preheated by means of recuperative heat exchangers to the lower preheating zone with the total of six side burners with rotary promoters, three on each side of the furnace. Such a reheating and walking-beam furnace, which allows the displacement of the cards into the thermal insulated tubular surveillance system and cooled with industrial water, called skids (Reis, 2013).The reheating time of the plates is about 5 hours and 48 minutes, with the initial temperature being ambient until the final temperature of 1250 ° C.

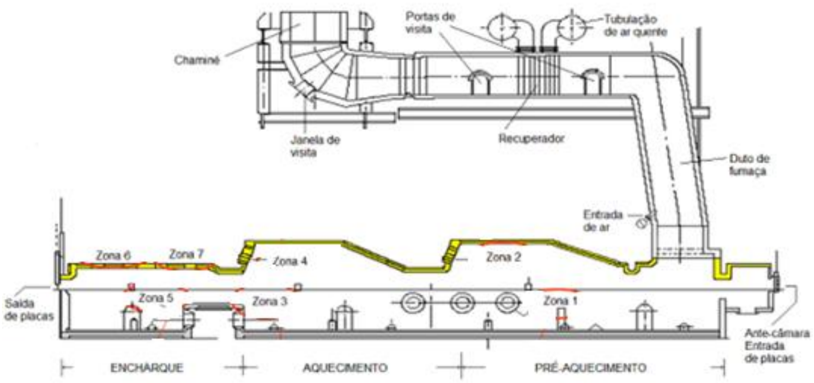


Figure 1. CSN plate reheating furnace (Reis, 2013)

The mill scale composition is a mixture between: wustita (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3), this is formed into heating furnaces following the reactions Eq.(1) , Ef.(2) and Eq(3):

$$O_2 + 2Fe \rightarrow 2FeO \qquad (1)$$

$$FeO + Fe_2O_3 \rightarrow Fe_3O_4 \qquad (2)$$

$$3O_2 + 4Fe \rightarrow 2Fe_2O_3 \qquad (3)$$

This mill scale is considered as waste, for each ton of steel, 20 kg of mill scale are generated (Oliveira, 2004). The waste disposal is carefully carried out in yards following the rigorous environmental Standards. In Brazil, they can be classified as hazardous waste (Class I, NBR 10004: 2004) due to the oils present into mill scale.

Due to the high iron content, mill scale can be reused as a raw material and / or additive in other processes (Al-Otaibi, 2008), but its production generates maintenance costs owing to stopped for cleaning of furnace. In addition, the heat transfer between heat gas and steel plates is reduced consequentely the heating time is increased.

These maintenance costs must be reduced in order to improve the production process, therefore, this is great importance to carry out studies of the reduction mill scale formed .

In this paper, it is sought to determine the quantitify of mill scale formed in different conditions. In order to reproduce the industrial conditions, the steel surface must be cleaned, without any incrustation or oxide.The diffusion rate of heat exhaustion gas within of steel was linked to three parameters, being: 1) oxidative gases concentrations, 2) heating rate which influences the growth rate of mill scale; 3) oxides formed concentration.

2. MATERIALS AND METHODS

2.1 Materials

SAE 1020 Steel was used to study the formation of mill scale, due to its high employability in the steel industry. For this purpose, the samples in several dimensions (Fig. 2) were used and cutted in order to be inserted into the alumina crucible of size 5x5 mm. Next, all samples were cleaned with 1M hydrochloric acid for 16 minutes.

Figure 2. Samples prepared of SAE 1020 Steel

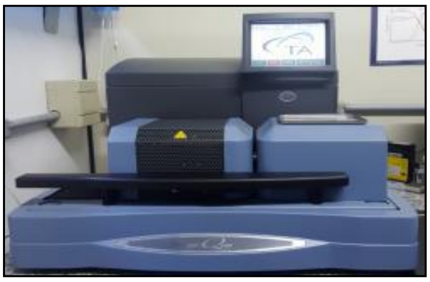
2.2 Methods

In order to simulate the reheating process in which the mill scale is formed, a thermogravimetric oven was used (Fig. 3). A gas mixture was used as a purge gas at a flow rate of 100 ml/min being 96 mL of N_2 and 4 mL of O_2. The temperature range used in the oxidative process was from 30 °C to 1250 °C. The use of the thermogravimetric oven can reproduce the preheating, heating and drenching zones of the reheating processes in the steel industry (Fig. 3).

This paper shows the influence of the heating rate on the mill scale formatition, as well as the temperature influences in the furnace zones and its performance on the reaction / reactivity of the sample.

Thus, several samples with mass equal to 215.7 ± 1.6 mg were exposed to several heating rates, being: 2°C/min, 3.5°C/min, 5 °C/min and 10 °C/min, aiming the behavior of mill scale formation.

It should be noted that the rate of heating (ß) equal to 3.5 °C/min is that used in the steel industry.



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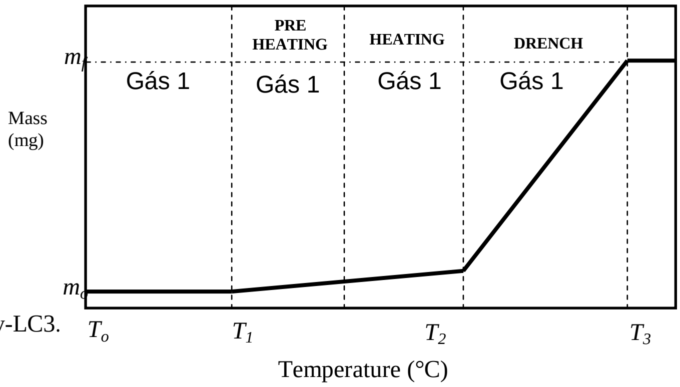

Figure 3. Thermogravimetric oven and diagram of the curves representing the various zones of industrial reheating furnaces

3. RESULTS AND DISCUSSIONS

Table 1 presents the results of the tests performed, ß is the diverse heating rates used, m is mass of the sample, W is the final mass of the sample in percentage and ΔW is the final mass incremented of the sample.

It is observed in the heating rates of 2.0 and 3.5 °C/min, the percentage of mass incremented is similar, with approximately 8.59 ± 0.09%. The increase of 1.5 ºC/min in the initial heating rate of 2.0ºC /min is not able to generate significant changes in the mill scale formation.

However, when higher heating rates were used, it observed a reduction of mill scale formation (Table 1). When compared the T2-2 and T3-2 experimental tests (which had the same increase of the heating rate that, T1-2 and T2-2, i.e. 1.5ºC/min), there was a reduction in the mill scale formation of approximately 31.6%. When compared the T2-2 and T4-2 experimental tests, the reduction in the mill scale formation reached 54.7%.

Table 1. Results of the experimental tests.

Experimental tests	ß	*M*	W	ΔW
	(°C/min)	*(mg)*	(%)	%
T1-2	2,0	214,2	108,65	8,65
T2-2	3,5	214,3	108,53	8,53
T3-2	5,0	216,8	105,83	5,83
T4-2	10,0	217,3	103,86	3,86

It is noticed that the influence of the heating rate with the mass gain is an inversely proportional relation, even if, for smaller rates, the behavior does not present great differences, the linearity is keeped.

In order to observe the thermal events involved in increasing the mass of the oxidative process the TG / DTG curves of the tests are shown in Fig. 4. The thermogravimetric curves shown in Fig. 4 describe four oxidation tests ie T1-2, T2 -2 T3-2 and T4-2 in which the influence of the heating rate was evaluated.

It is observed the reduction that occurs between the test T2-2 and T4-2 of 54.7% of mill scale, similarity occurs between the chemical and thermal events, which is no longer the case with them.

The DTG curve of the T2-2 experimental test, presents two unique events, the DTG peak at a temperature of 751 °C could indicate a crack in the material due to the heating step, in this same figure it is also observed that the most intense oxidative process that only happens the crack of the material, the second peak DTG or maximum peak DTG is at 1100 ° C, reaching at this point the maximum conversion.

The DTG curve of the T4- experimental test shows a single maximum peak at 961 ° C, the maximum peak rounded is an indication that the oxidative process was slower. It is also noted that a small fissure could have occurred at 762 °C, but it was not as intense as observed in the T2-2 test. This would indicate that the small fissure probably caused the oxidative process to occur more slowly, as the diffusion of oxygen into the sample became more difficult.

The DTG curve of the T3-2 experimental test indicates that the material had multiple cracks in temperature between 755 °C - 923 °C, this in contrast to T2-2 provides that the diffusion of oxygen within the sample is faster, hence two peaks DTG maxima were observed at temperatures of 1062 ° C and 1184 °C.

Taking into account the differences in the chemical and thermal events of the samples through the DTG curves, it was necessary to observe the changes in the sample sizes. Therefore, if measurements were made before and after the oxidative process, the measurements taken after the oxidative process were carried out by removing all the mill scale formed in the diverse samples. All results are presented in Table 2.

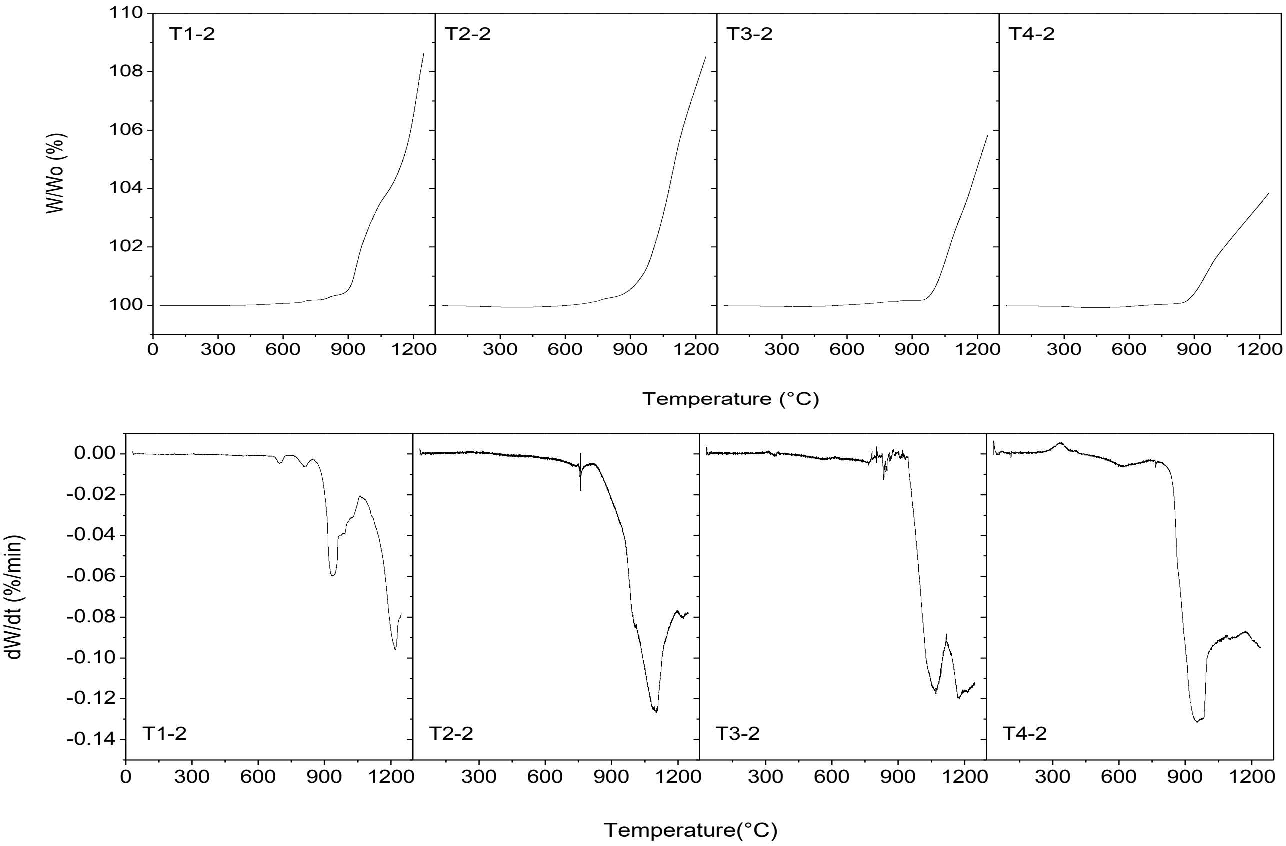

Figure 4. TG /DTG curves of the oxidation tests in the thermogravimetric oven

Figure 5 shows the sample T4-2 after the mill scale, it is noticed that the mill scale forms as a shell around the whole sample, which demonstrates that the oxidative process in the oven occurs continuously and that no region is more favorable to oxidation.

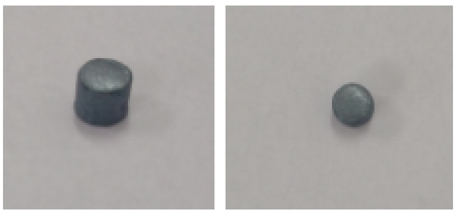

Figure 5. Sample T4-2 with mill scale a) frontal view b) top view

Table 2. Volumes and dimensions of the samples before after the oxidative process.

Experimental tests	Before the process			After the process			Reduction of the sample		
	Diameter (mm)	Length (mm)	Volume (mm^3)	Diameter (mm)	Length (mm)	Volume (mm^3)	Diameter (mm)	Length (mm)	Volume (%)
T1-2	3,44	2,95	27,42	3,38	2,88	25,84	0,06	0,07	5,75
T2-2	3,42	2,95	27,10	3,36	2,8	24,83	0,06	0,15	8,39
T3-2	3,45	2,97	27,76	3,39	2,88	25,99	0,06	0,09	6,37
T4-2	3,55	2,96	29,30	3,52	2,93	28,51	0,03	0,03	2,68

In Table 2, can be observed that a reduction in the volume of the sample of 5.75%, 8.39, 6.37% and 2.68% was obtained for the T1-2, T2-2, T3-3 and T4 -2, respectively, due to the formation of mill scale. The mill scale formed had a thickness of 0.06 mm for the first three experimental tests (T1-2, T2-2 and T3-2), whereas the T4-2 test had a 50% smaller thickness, i.e. 0.03 mm.

It was also observed that the diameter was the least affected in the oxidative process, and the average reduction was 0.05 ± 0.02 mm, while the reduction of the height of the cylindrical sample was 0.09 ± 0.05 mm. The T4-2 test is presented as the best condition found, with a higher initial sample volume and a lower thickness of the molding and consequently lower mass loss.

4. CONCLUSIONS

The experimental tests shown the influences of heating rate on the mill scale formation, consequentely, the chances in the thicknes of steels were observed.

Acording experimental tests, the heating rate is a important parameters in the reaheating furnace. Being that, the mill scale formed (i.e. ΔW) is inversely proportional to the heating rate.

5. ACKNOWLEDGEMENTS

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7. RESPONSIBILITY NOTICE