abm week 2018 4ª edição

KINECT ANALYSES OF THE REDUCTION OF A FILTER DUST BRIQUETTE*

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Abstract

This work investigates the kinetic mechanisms of the briquettes reduction made of filter dust generated at a stainless steel steelworks facility. At first, chemical and morphological characteristics were investigated. The chemical analysis showed that the material is rich in alloy elements like Cr, Ni, Mo. The morphological analysis revealed that the material is made of oxides and spinels. FactSage simulations were made to show the best briquettes composition and the best reduction conditions. To conduct the experiment three different compositions of briquettes were prepared. Those were filter dust plus 16%, 18% and 20% carbon. After the preparation, twelve reduction tests and three melting tests under the temperature of 1500°C were conducted. The steel used was CK45 and the crucible was made of MgO. The reduction tests showed that after 15 minutes the briquettes deteriorate; the reaction time increase with the deterioration of the material. In the melting test was found that the best results happened with the use of 20% carbon in the briquettes at a temperature of 1500°C. The recovery was 78,95%Cr, 69,42%W, 62,62%V, it was also possible to find out that the control mechanism of the reaction is mass transport and not the self-reduction.

Keywords: Waste Recovery, Thermodynamical Simulation; Reaction Mechanism; Briquettes.

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1 INTRODUCTION

With the increase in the production of stainless steel in the world, large amounts of waste are generated, which are rich in Cr, Ni, and other metals considered for the steel production [1].
Long et al. [2] state that many possible ways to treat those wastes, such as pyrometallurgical, hydrometallurgical, stabilization, and biometallurgical processes. However, among these methods pyrometallurgical processes are traditionally used for this treatment.
Commonly the steelworks byproducts, such as sludge, dust and mill scale are recovered through melting process methods. To do such recovery, the common reducing agent used is carbon [3].
Nolasco [1] and Takano et al. [4] studied the recovery of Chromium, and Nickel from waste with use of Carbon and Silicon base reducing agents in melting tests. In those tests, they were both successful in reaching recovery levels of about 90% of Cr and almost 100% of Ni. They also concluded that the temperature should be as high as possible (in this specific case, something about 1600°C), and the best recovery was achieved for quantities of reducing agents above the stechiometric level.
The equations 1, 2, and 3 show how the reduction of some metals (Cr, Si, Mn,Ti), with the use of carbon as reduction agent, can occur [5].

$$(M_yO_x) \leftrightarrow y\underline{M} + x\underline{O} \tag{1}$$

$$x[\underline{C} + \underline{O} \leftrightarrow CO(g)] \tag{2}$$

$$(M_yO_x) + x\underline{C} \leftrightarrow y\underline{M} + xCO(g) \tag{3}$$

Moon [6] and Bagatini et al. [7] studied the behavior of a self-reducing briquette. Moon [6], measured the reduction speed of two briquettes containing carbon and iron. One briquette was composed of iron and carbon, and the other of iron, carbon and Kaolin. The reduction happened in a TGA (Thermogravimetric Analysis) and the test temperature was 1000°C. The equation used to analyze the reaction speed was the equation 4 (adapted unimolecular irreversible model). The author concluded that the Bourdouard reaction (equation 5) was the controlling mechanism; he also concluded that the adapted unimolecular equation fits with the experiments results.

$$-\frac{\ln(1-X)}{C_{CO2} - C_{CO2}^{eq}} = k.t \tag{4}$$

$$C(s) + CO_2(g) \leftrightarrow 2CO(g) \tag{5}$$

In equation 4 k is a kinetic constant; X is the oxygen concentration in terms of fraction; C_{CO2} is the initial CO_2 concentration and the $\mathbf{C_{CO2}^{eq}}$is the CO_2 equilibrium concentration.
Nolasco [1] examined the reaction speed as well. His analyses were made following equation (6).

$$\ln\left(1 - \frac{Mi - Mt}{Mi}\right) = -k.t \tag{6}$$

Where Mi is the initial quantity of the metal that will be analyzed, Mt is the quantity of that metal at a t time, k is the kinetic constant (1/min) and t is time (min). The equation 6 shows the speed analyses in terms of metal fraction that was reduced.

According to Bagatini et al. [7], the main reaction rate-controlling step is the heat transfer, the reaction occurs much faster at higher temperatures. For the tests under 1050°C the complete reduction happened in 70 minutes, and for 1400°C the complete reduction happened in 15 minutes.

In the present work, in order to improve the recovery of alloys elements, experiments were conducted to evaluate the recovery of those alloys under different circumstances. The melting tests were conducted under 1500°C using briquettes with three different quantities of carbon (16, 18 and 20%) and CK.45 steel. The reduction tests in the furnace were carried under the same conditions of the melting tests, but without the steel. The tests were conducted to analyze the kinetic behavior and the FactSage thermodynamic calculations.

2 DEVELOPMENT

2.1 Raw material

The material is a filter dust with the composition showed in Table 1. The composition was measured by the company BioMar GmbH through the Spark Optical Emission Spectroscopy.

Table 1. Dust composition with Spark Optical Emission Spectroscopy.

Elements	Cr	Co	Ni	Cu	Al	Si	S	Cl	Ca	Fe
%	7.704	0.181	0.05	0.054	0.676	1.157	0.39	0.143	0.237	54.41

Elements	Na	Mg	P	K	Ti	V	Mn	Mo	Sn	W
%	0.01	0.002	0.09	0.144	0.031	0.564	0.344	0.914	-	0.545

To characterize the material, a X-Ray diffraction (XRD) was also demanded. The equipment used was the XRD from the Instituto Federal do Espírito Santo (IFES), model D8 of the brand Brucker. The Figure 1 shows the result.

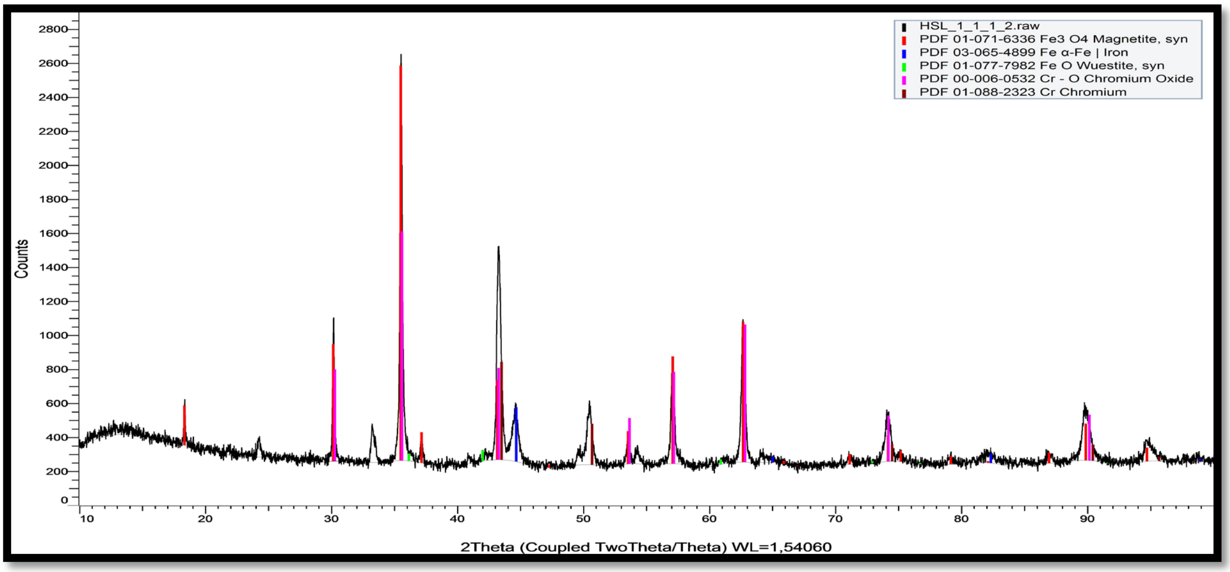

Figure 1. DRX results from the filter dust.

The dust was mixed with graphite. All the mixtures were prepared with the sampler Retsch model PT100 from the UDE laboratory in Duisburg. The Sampler prepared 100 gram material with carbon in each mixture.

The quantity of each material in the mixture was determined through simulations in the software FactSage. Then the mixtures were turned into briquettes, with the use of the hydraulic press from the UDE from the TONI TECHNIK Company.For the tests MgO crucibles were used.

The steel used was CK45. The composition is shown in Table 2.

Table 2. CK45 steel composition.

ELEMENTS	C	Cr	Si	Ni	Mn	P	S	Fe
%	0.45	0.29	0.36	0.11	0.84	0.041	0.033	97.1

2.2 Factsage simulation

The FactSage simulation had the goal to define the best composition to be reduced in the furnace, and to evaluate the differences existing between the tests and simulations.

To run the simulation, the following parameters were followed: the databases FTPS, FToxid, FTsteel were selected; the sub databases SLAGA, FSsteel were selected; and to validate the formation of gases and liquid phases, both needed to be selected. The temperature used was 1500°C and the atmosphere pressure selected was from 1 atm.

2.3 Reduction tests

The first experiments after the FactSage preparation were the reduction tests in the Nabertherm HT 12/17 chamber furnace under 1500°C. The steps followed to carry out these tests were:

- heating the chamber according to the test temperature;
- setting the crucible inside the chamber;
- waiting for the determined time to see the reductions effect and change the sample; for each specific time it was used one sample (5,10,15 and 20 minutes);
- turning down the system.

2.4 Melting experiment

With the simulation results, the melting experiments were conducted. The tests consisted in the reduction. The following steps were used:

- loading of the MgO crucible with steel, in each test was used 600 grams of steel and 80 grams of briquettes;
- opening of the Argon flow in the crucible (atmosphere protection);
- turning on the gas analyzer of the brand MRU AIR fair of model Vario Lux;
- heating of the metal up to the work temperature (1500°C);
- addition of the briquette.
- withdrawal of slag and steel;
- system (induction furnace equipment) shutdown.

The induction furnace was used at UDE (University Duisburg-Essen) Duisburg campus. The furnace is the open induction furnace Hüttinger. The Figure 2 shows the equipment used.

Figure 2. Induction furnace Hüttinger 10kW.

3 RESULTS

3.1 FactSage Simulations

Firstly, to execute the simulations it was necessary to determine the present phases inside the material. Using the XRD and XRF results, and considering some of the elements as oxides, shown in Table 3.

Table 3. Composition used in the FactSage.

Oxides	CrO	Cr	Fe_3O_4	FeO	Fe	CoO	NiO	Cu_2O	Al_2O_3	SiO_2	S_2O	Cl
%	10.12	0.859	41.95	30.694	6.496	0.259	0.07	0.068	1.425	2.762	0.544	0.16

Oxides	CaO	Na_2O	MgO	P_2O_5	K_2O	TiO_2	V_2O_3	MnO	MoO_3	SnO_2	WO_3
%	0.370	0.019	0.004	0.23	0.193	0.06	0.926	0.496	1.53	0	0.767

Through FactSage simulations, it was possible to have an idea of the possible outcome of the experiments, naturally, from the thermodynamic point of view.

3.1.1 Reduction and Melting tests Simulations

The first simulation was made to simulate the Furnace conditions testing the reduction power of the briquette alone. With those simulations, the following results shown in the Table 4 were obtained.

Table 4. Recovery results from the FactSage simulation.

Carbon Quantity in briquete **Element**	**20%C**	**18%C**	**16%C**
C	19.019	18.482	9.571
Cr	99.996	99.995	52.332
V	99.999	99.999	99.999
W	99.999	99.999	99.999

Looking at Table 5 it is possible to see that most of the existing metal elements in the filter dust can be recovered. Cr needs carbon composition above 16% to be adequately recovered. However, to achieve a higher level of recovery, some points needs to be observed, like the carbon levels and phosphorous existent in the waste.

The phosphorous can be fully reverted from the waste in those conditions, and the carbon levels increased with Cr, Ni and other elements that can be reduced by the carbon. As the equilibrium constant shown in equation 7 and in the equation 8, the more metal is recovered, the higher is the carbon quantity absorbed by the metal. The equation 7 is a simplification considering the activity of the oxide 1 and the CO pressure 1.

$$\boldsymbol{K} = \frac{\boldsymbol{P_{CO}^{x} . h_{M}^{y}}}{\boldsymbol{h_{C}^{x} . a_{MyOx}}} \tag{7}$$

$$\boldsymbol{h_{C}^{x} . K} = \boldsymbol{h_{M}^{y}} \tag{8}$$

The Table 5 shows the mass transfer from the briquettes to the other phases, considering the reduction of the briquette alone in the chamber furnace.

Table 5. Variation of phases mass.

Wt% from carbon in the briquetes	**Slag (Solid/Liquid) (%)**	**Metallic phase (%)**	**Gas (%)**	**Percentage of CO in the Gas phase (%)**
16	3.174	62.467	34.359	99.111
18	1.551	63.590	34.859	99.187
20	3.544	62.607	34.249	99.185

The development of the solid/liquid ratio shown on Table 6 points that with only 16% of carbon in the composition, the briquettes are still not completely dissolved in the melt. The reaction reaches an optimum value when the briquettes have 18% of carbon in the composition, but beyond this value, the formation of solid phases starts to grow again. The melting simulations results are shown in the Table 6.

Table 6. Recovery levels from melting test in the FactSage simulation.

Element	**Recovered/Incorporated**		
	16%C	**18%C**	**20%C**
Cr	98.999	99.145	99.652
W	100	99.923	100
V	100	100	93.327
C	15.015	23.643	28.301

According to Table 7, the thermodynamic behavior from the briquette/melt system is approximately the same, despite of changes in the composition of carbon. The difference from those simulations can only be found out through experiments in the laboratory and mainly occur due to reaction kinetics, like control mechanisms (diffusion, reaction, dilution, etc).

Figure 3 shows the results of FactSage calculations.

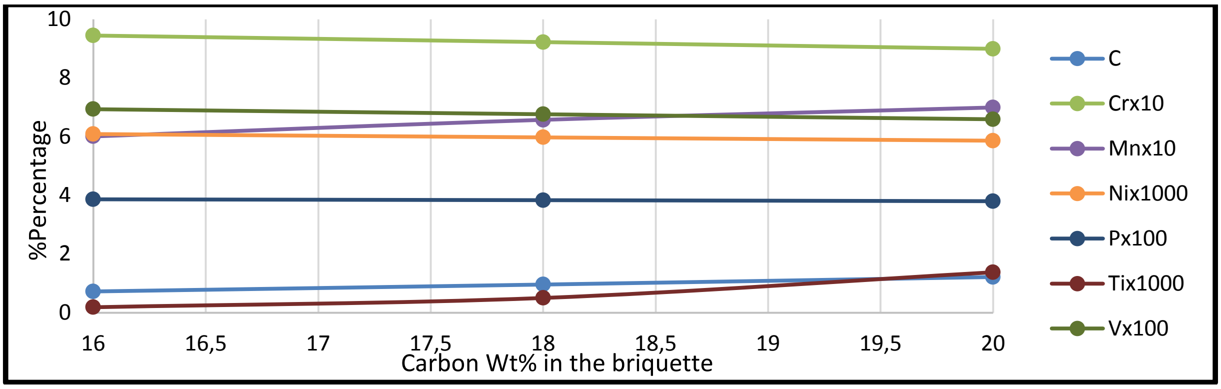

Figure 3. Steel composition variation with the carbon added in the briquette.

The Table 7 show the mass variation of the system.

Table 7. Variation of phases (mass).

Wt% from carbon in the briquetes	Slag (Solid/Liquid) (%)	Metallic phase (%)	Gas (%)	Percentage of CO in the Gas phase (%)
16	0.795	95.608	3.597	99.195
18	0.594	95.854	3.552	99.279
20	0.535	96.038	3.427	99.323

Table 8 shows how the phase proportion changes with the carbon mass variation within the briquettes. Those variations are important to understand how the reduction works, and how the mass is transferred from one phase to another. Almost everything from the dust was reduced.

3.2 Reduction tests

After the tests conduction the Figure 4 diagram was built.

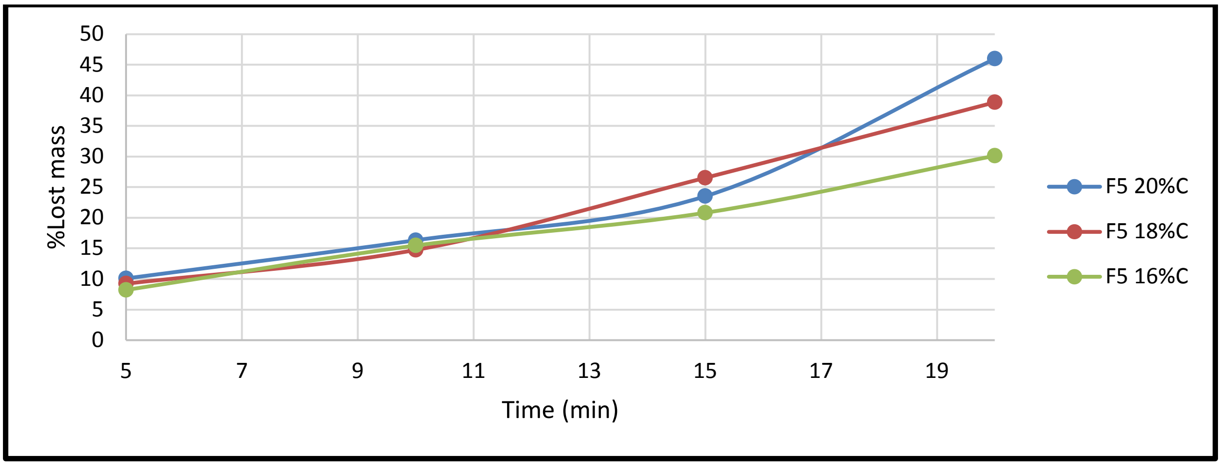

Figure 4. The mass change of the briquettes.

From Figure 4 it can be seen, that the reaction speeds are similar up to 12 min reaction time. For the 16% carbon, we did have a minor mass change and for the 20% carbon, we had the greatest change. Despite those mass changes, the speed reaction was almost the same. However, after 12 min reaction, the material integrity was lost, and because of that the reaction speed of the material with higher carbon content became faster.

The results are shown in detail in Table 8.

Table 8. Percentage of the lost mass after the furnace reduction.

Time (min)	**20%C**	**18%C**	**16%C**
		Mass loss (%)	
5	10.089	9.228	8.205
10	16.326	14.746	15.463
15	23.517	26.527	20.815
20	45.964	38.863	30.128

In Table 6, it is possible to see that the maximal mass loss is achieved 34.9% (from the FactSage calculations). The maximum mass losses in experiments are higher (as shown in Table 9), and that's probably is because the material lost the integrity after 15 minutes in the furnace, as shown in the Figures 5 to 7.

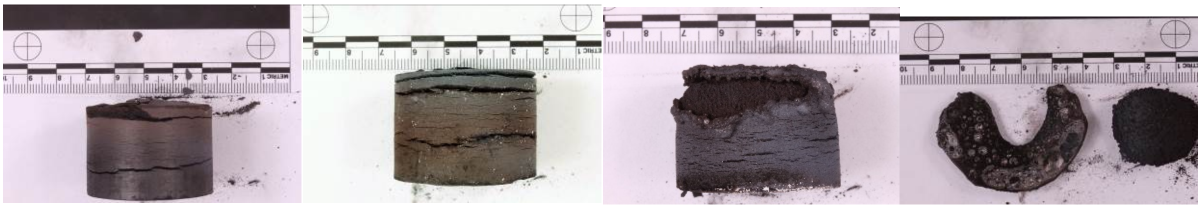

Figure 5. Photos from the briquette with 16%C after the furnace tests with the tests time from 5,1015 and 20 minutes.

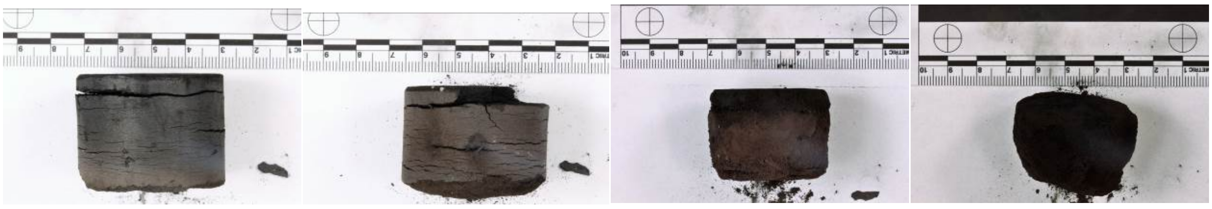

Figure 6. Photos from the briquette with 18%C after the furnace tests with the tests time from 5,10 ,15 and 20 minutes.

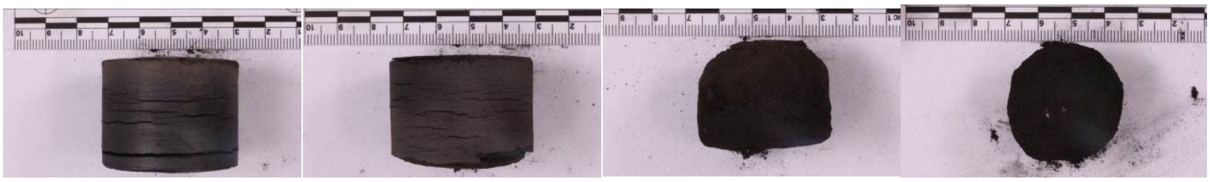

Figure 7. Photos from the briquette with 20%C after the furnace tests with the tests time from 5,10 ,15 and 20 minutes.

The loss of integrity in this matter was a problem because of the difficulty to measure the weight; many small particles were crusted in the crucible which resulted in mass loss. The metal part weighted 46.27 grams and represented 46.27% of the briquette mass. In Figure 8 the rest carbon contents in dependence of carbon content added and reaction time are shown.

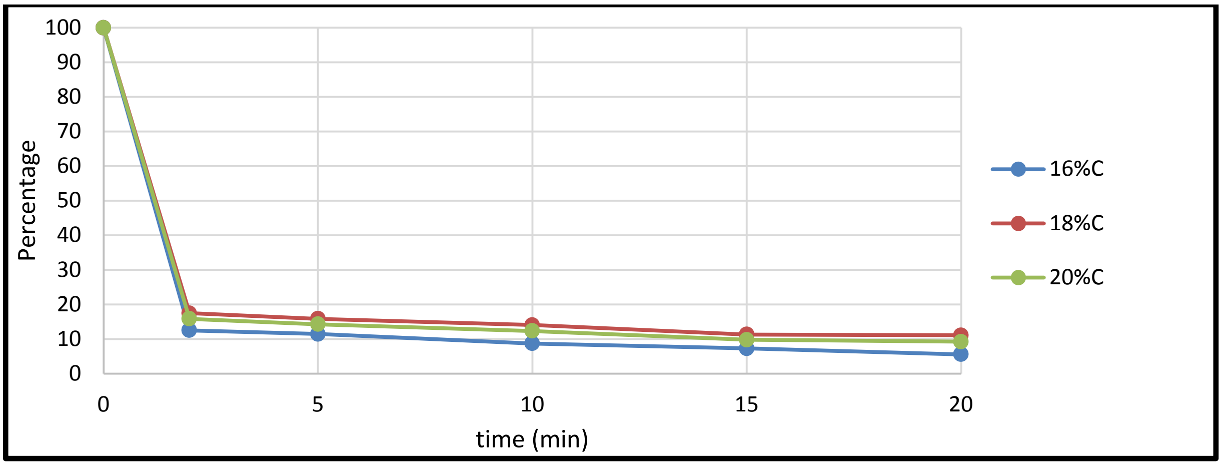

Figure 8. Rest carbon present after the reduction vs the initial carbon composition in the briquettes.

It is possible to see that the reactions with 18 and 20% reached a limit, and less carbon was necessary to the reaction in comparison, and that because of the smaller percentage of waste present in the briquette. It is also possible to confirm that quantities higher 18% of carbon doesn't change much the result. And those level of reduction was possible because in the present situation the carbon/oxygen ratio shows excess for every trial, as presented in Table 9.

Table 9. Carbon oxygen ratio.

Inicial Carbon percentage in the briquettes	20%C	18%C	16%C
C/O	1.478	1.298	1.127

3.3 Melting experiments

In Figure 9 the results of the gas analyses are shown, taken during the melting tests in the Hüttinger induction furnace.

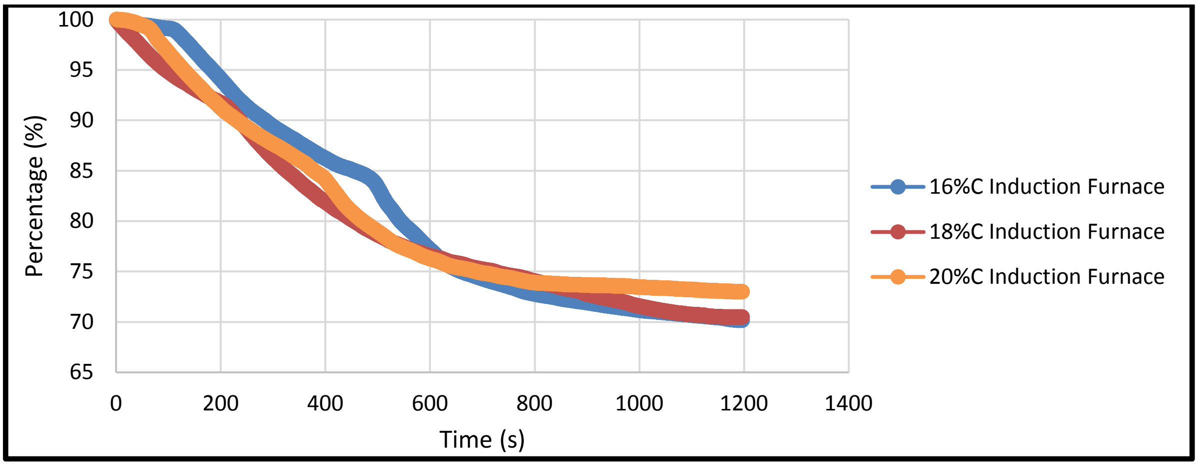

Figure 9. Mass of carbon left in the melt after the beginning of the tests.

In Figure 9, it is possible to see a similar for all the tests. The Figure 10 shows the comparison of the reaction speed results.

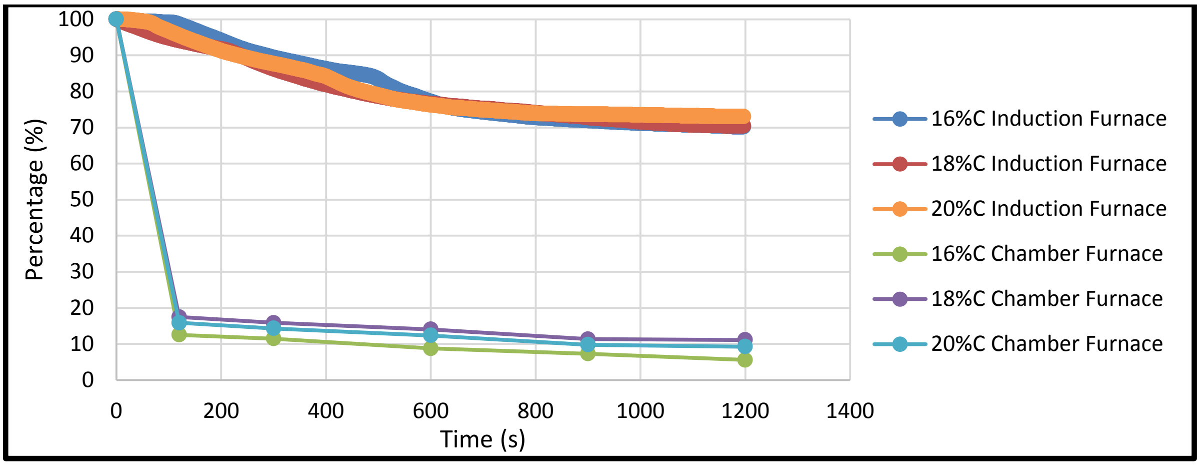

Figure 10. Mass of carbon left in the melt after the beginning of the tests.

The Figure 10 shows the differences between the reductions speed in the chamber furnace test (just the briquette) and in the induction furnace test (briquette plus steel). In the graphics is possible to see that a big difference of the reaction speed in the two experiments is existing, and happens probably because of the change of the reaction control mechanism. In the chamber furnace in tests existed only the self-reduction mechanism, but is possible to see that's not happened to the steel/briquette reduction. Most likely because of the melting of the briquette and dissolution of the carbon, that make the reaction somewhat slower, changing the reaction mechanism.
The figure 11 and 12 shows the graphic using an adaptation of the model from Nolasco [1] to calculate and analyze the reaction speed. The equation (9) shows the adaptation.

$$\ln\left(1 - \frac{Ci - Ct}{Ci}\right) = -k.t \qquad (9)$$

Where C_i is the initial carbon present in the briquette and C_t is the carbon at the time t.

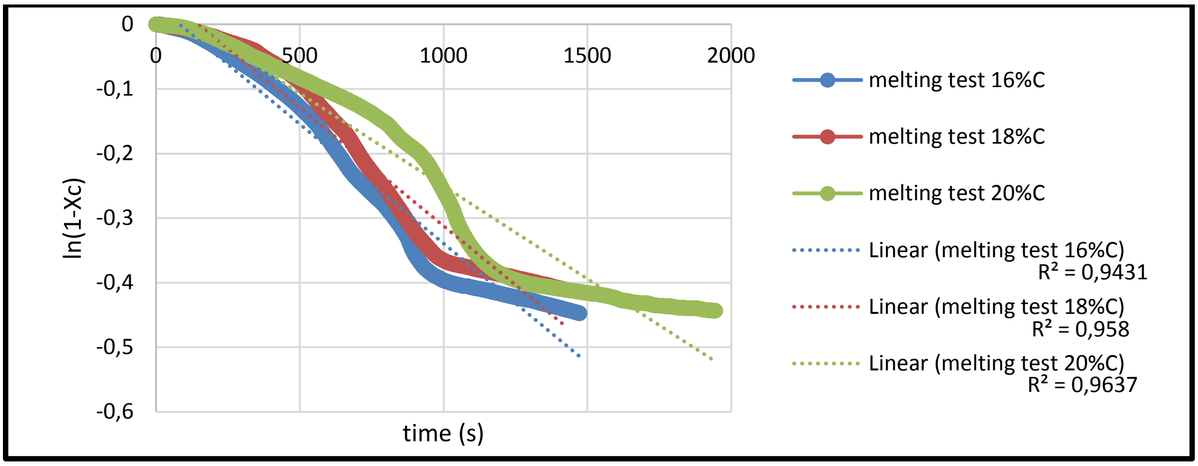

Figure 11. Graphic from the melting test.

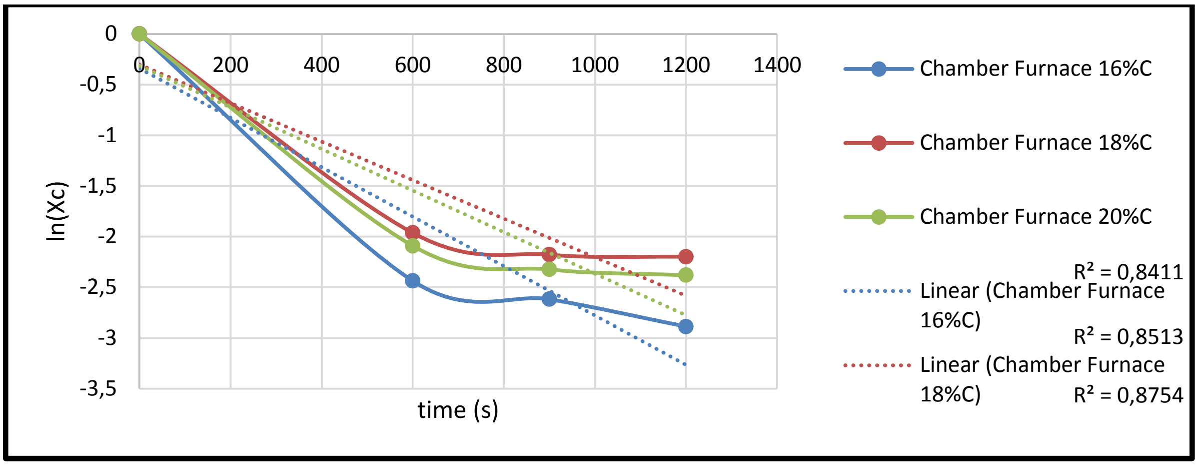

Figure 12. Graphic from the chamber furnace test.

Using the trend line from the figures 11 and 12 it is possible to estimate the kinetic constant (k) from the both reactions. In figure 11 the k is 0,0004 (1/s) for every reaction, for the figure 12 the k is something in average 0,0021 (1/s). Observing the k values, it is possible to conclude that the reaction speed was higher for the chamber furnace reduction test then for the melting test. Another conclusion is the existence for another reaction control mechanism.

The Figure 13 shows the recovery level obtained after the melting test in the induction furnace.

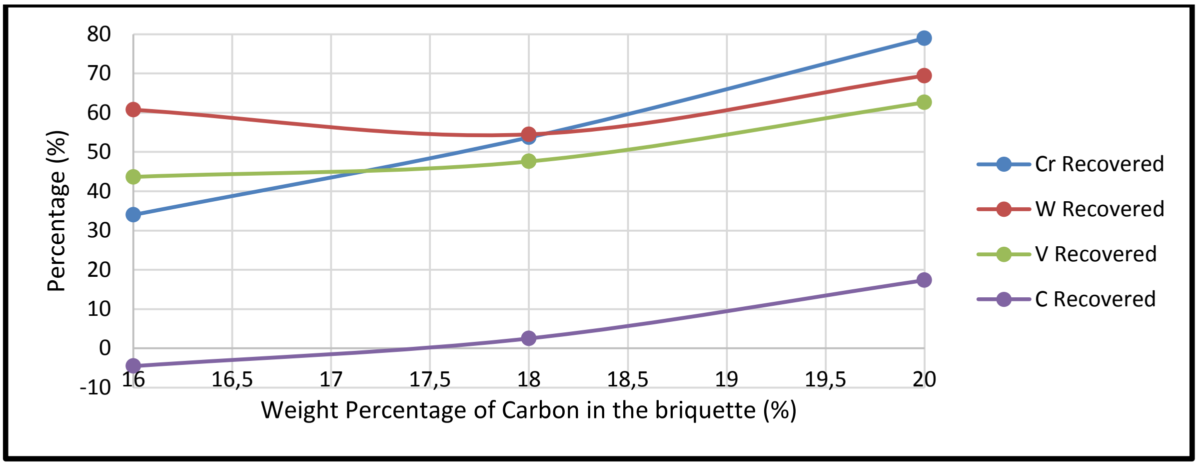

Figure 13. Variation of the composition of the melt after the melting test.

In figure 13 is shown, that despite of the similar kinetic behavior for the induction furnace tests, the final recovery levels were different. The difference is a result of the excess of the carbon existent in the briquettes in comparison with the oxide content.

As is shown in Figure 13, that the recovery of Cr could reach 78.95%, V 69.42% and W 62.62%. The results did not reach the FactSage theoretical values. The probably reason is the not enough time given to the reaction.

The figure 14 shown the comparison of the experimental and the theoretical recovery of Cr, Ni, W, and V in grams.

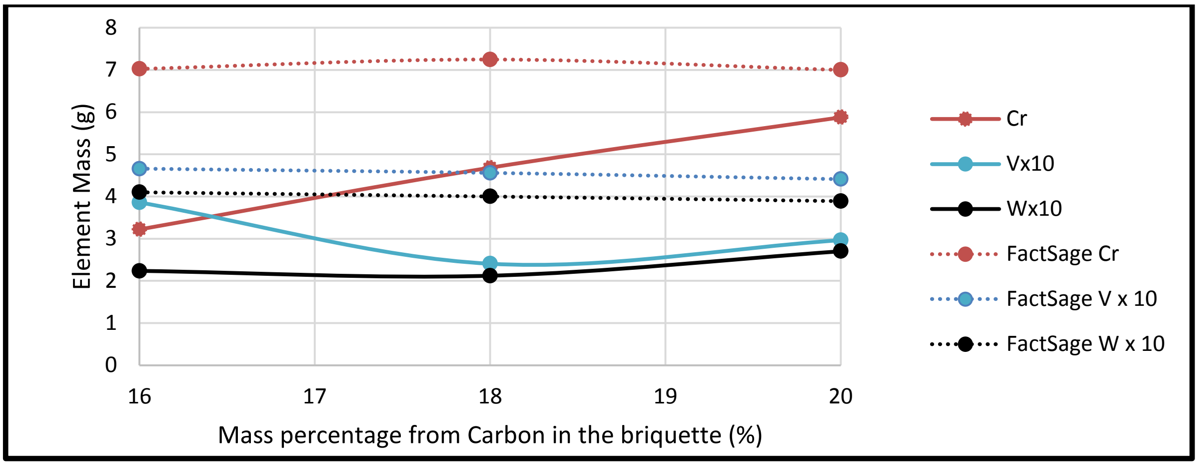

Figure 14. Comparison of the experimental results with the theoretical.

In Figure 14 it is shown, that the theoretical values estimated by the FactSage couldn't reached. A possible reason could be the reaction time that wasn't enough to enable the whole reaction. Taking in account that the possible reaction mechanism is the mass transport. It was also possible to see that the increase of the carbon levels had a negative effect in the vanadium recovery in the simulation and in the inductions tests. That happened because of the existence of more solid phases, which hindered the reaction. The same behavior was observed in the FactSage Cr and W curves.

3 CONCLUSION

With the experiments, it was possible to conclude:

- the reduction occurs easier to the briquettes alone in the reduction furnace;
- mass transport is the mechanisms that control the recovery in the melt;
- the FactSage theoretical values could not be reached probably due kinetics reasons;
- in the melting tests, the tendency that the higher the carbon the faster the reactions reach the equilibria;
- the kinetic model, for this situation, is not sensible to the composition changes in the briquette.

Acknowledgments

The author would like to thank the ITM (Institut für Technologien der Metalle), German Ministry for Education and Research (BMBF), IFES (Instituto Federal do Espirito Santo) and CAPES for the support.

REFERENCES

1 Nolasco, PJS. Reciclagem de Poeiras e Lamas Provenientes da Fabricação de Aço inoxidável. São Paulo: Escola Politécnica, USP, 2004.
2 Long, H; Meng, Q; Wang, P; Chun, T; Yao, Y. Preparation of Chromium-iron Metal Powder from Chromium Slag by Reduction Roasting and Magnetic Separation. Journal of in and steel research; 2015; 22: 771-776
3 Huaiwei, Z; Xin, H, An overview for the utilization of wastes from stainless steel industries. Resources, Conservation and Recycling. 2011, 55: 745-754

4 Takano, C; Cavalamnte, FL; Dos Santos, DM; Mourão, M. Recovery of Cr, Ni and Fe from dust generated in stainless steelmaking. Mineral Processing and Extractive Metallurgy; 2005; 114: 201-206

5 NAKASUGA, T; NAKASHIMA, K; MORI, K. Recovery Rate of Chromium from Stainless Stag by Iron Melts. ISIJ. 2004. 4: 665-672.

6 MOON, J; SAHAJWALLA, V. Kinect Model for the Uniform Conversion of Self Reducing Iron Oxide and Carbon Briquettes. ISIJ. 2003. 43: 1136-1142.

7 BAGATINI, M, C; ZYMLA, V; OSÓRIO, E; VILELA, A, C, F. Scale Recycling Through Self-Reducing Briquettes to use in EAF. ISIJ. 2017.57: 2081-2090.