ASPECTS OF STEEL DESULPHURIZATION AND PRELIMINARY RESULTS USING BRIQUETTES IN THE EAF STEELMAKING HEATS[1]

Bruno Suveges Cerchiari [2]
Poliana Cristina Araújo [2]
Hugo Linhares Mendes [2]
Luiz Matanta Chavana [3]
Paulo Santos Assis [4]
Brahma Deo [5]

Abstract

This report presents a theoretical approach for steel desulphurization in the ladle, just after its production in the Electric Arc Furnace. Basic points for this experience were pointed out, mainly based on cost of the material. Methods and materials used were shown for the evaluation of the desulphurization, so the main results obtained from the experiments as well. The last two heats were made using a standard briquette that is commonly consumed in a big Company, which operates BOF converter. It was concluded: the desulphurization rate obtained by using formulation I and II were in the same interval obtained when the standard briquette was used; the obtained values varied from 20 to 30 %, including the high influence of the briquette rate used; the heat temperature level does not influence greatly the desulphurization rate; the fume generation was the same when the three materials were used as a desulphurization agent; by using the materials I and II, the slag was more homogeneous; some dephosphorization was observed by using the materials I and II, which is higher than when the standard material was used.

Key-words: Steelmaking; Desulphurization; Electric arc furnace.

ASPECTOS RELATIVOS A DESSULFURAÇÃO DE AÇO E RESULTADOS PRELIMINARES USANDO BRIQUETES EM CORRIDAS DE UM FORNO ELÉTRICO A ARCO

Resumo

Este documento apresenta fundamentos da dessulfuração de aço na panela, logo após a sua produção em um FEA. Pontos básicos de experiência no FEA foram mostrados, principalmente a questão de custo. Métodos e materiais usados foram mostrados para avaliação da desfosforação, bem como resultados obtidos dos experimentos. Nas duas últimas corridas briquete padrão, que é consumido em uma grande empresa que opera convertedor LD, foi usado. Concluiu-se: - a taxa de dessulfuração obtida usando os briquetes de formulação I e II foi no mesmo intervalo quando foi usado o briquete padrão; - os valores oscilaram entre 20 e 30 %, incluindo a forte influëncia da quantidade específica; a temperatura de vazamento não influencia de maneira sensível a taxa de dessulfuração; a geração de fumaça foi aproximadamente a mesma, quando do uso dos três agentes de dessulfuração; a escória se apresentou mais homogênea, quando do uso dos briquetes I e II, bem como observou-se desfosforação comparativamente ao briquete padrão.

Palavras-chave: Dessulfuração; Briquetes; Aciaria elétrica.

1 *Technical Contribution to the XXXIX[st] International Steelmaking Seminar of the ABM, May, 12-16[th] 2008, Curitiba – PR – Brazil.*

2 *Grad-Stud at Escola de Minas, Ouro Preto, Minas Gerais, Brazil*
3 *Manager. at Steel Company Semeato, Vespasiano, Minas Gerais, Brazil*
4 *Full professor at Escola de Minas, Prof. at REDEMAT, Brazil; Honorary Professor by Hebei Technology University, China; Researcher at CNPq, Brazil*
5 *Full professor at Indian Institute of Technology, India.*

1 INTRODUCTION

It is known that synthetic materials can be used in iron and steelmaking plants, as in Ferroalloys plants as well. Nowadays, some companies like CST, Usiminas, Cosipa, Gerdau and others use these materials. To develop other kinds of synthetic materials, experiments were made last year to confirm some results obtained in big companies that uses BF and BOF as main route for steelmaking.
Recently, based on environmental constraints and needs for cost reduction, other raw materials have been tried in order to substitute costly materials for desulphurizing agent production. This way, two new formulations have been developed just to see if it could be used to reduce the steel sulphur content.
However, this practical research in a BOF with 200 ton per heat normally takes 10 t or even more to test the material quality. This will be expensive to the supplier. This way Semeato (a Steel company that produces steel for agricultural purpose and steelmaking use) the first research to be done about this. This company has an EAF with a capacity of 10 ton per heat. After discharging steel in a ladle with Argon Stirring, it goes to Casting, foundry and stamping.
This report shows the first experiments done in 2007 showing not only the first results but a theoretical approach.

2 OBJECTIVES

The main purposes of the research were:

- Produce briquettes with three types of different formulations;
- Use of these briquettes for desulphurizing the EAF Steel;
- Evaluate the first results obtained.

3 DEVELOPMENT

3.1 Historical Aspects

Steel can be desulphurized in the pretreatment of pig iron, in the primarily process in steelmaking, and/or in the secondary metallurgy. Many companies have been choosing to use a desulphurizing agent in the process, during the charging of steel ladle taken from BOF or from EAF. This is used because of the dynamic conditions during this process, what might cause higher desulphurization; which decreases the ladle treatment time. In some cases, an increase of 2 % in the steel production can be obtained by using this method.
Both factors will definitely influence the steel cost, so the steel productivity as well. It should be emphasized that the steel quality is improved due to the low sulphur content.
In Brazil, this process was firstly used in the beginning of 21st century, with the first experiments in the Steelmaking #2 of Usiminas. During the last 6 years, this practice has been improved in this Company.
To do the research at Semeato two new agents have been used, as main compound CaO (pure CaO, not hydrated) and contains Al, Na and eventually Fluoride Calcium, if it is permitted.

3.2 FUNDAMENTALS

The desulphurization process using CaO with a base material can be written as:[(1)]

$$(CaO) + [S] = (CaS) + [O]$$

Where:
(i) Component "i" in the slag
[j] Component "j" in the metal

When synthetic material is added in the bath, three conditions must be full filled to promote higher sulphur reduction, as known [2]:

a) High content of CaO, that means, high activity of CaO;
b) Smooth contact between synthetic material and steel;
c) Less oxygen content in the steel, what means, less oxygen Henrian activity in the steel

Besides these three factors, it might be emphasized that the process temperature should be higher according to two points: the thermodynamic point of view (the reaction is endothermic) and the kinetic factors (Arrhenius Law).
Evidently, there are limitations of the above factors, one of them is that the slag must be liquid. Then, when desulphurizing agent is added, the difference between the new slag temperature and its Liquidus temperature should be more than 50 ^{o}C.

4 MATERIALS AND METHODS

Three types of slag were produced, the first one was the standard. The other two were made by substituting some compounds used in the first for other less expensive materials with similar properties.
Table 1 shows the materials used in all of the three formulations. 600 kg of the first two formulations were produced and 200 kg of the third was used for comparison. The latter is used in a big company in Brazil.

Table 1 – Formulations used for the experiments at Semeato (unit: kg)

Formulation (1)	Lime	Al	A	B	C
I	201	19	45	34	
II	200	-	50	49	
III (2)	126	15.4	30.3		27.4

(1)It was added 1,2 kg of Sodium estearate in each formulation; (2)Formulation III: standard used at big plant in Brazil A, B, C: materials used

The chemical composition in the synthetic slag can be seen in the Table 2. It should be highlighted that the formulations I and II were proposed considering both cost and slag quality.

Table 2 – Estimated chemical composition of the synthetic slag used at Semeato during the trials

Formulation/Compound(1)	CaO	A'	B'	Al	Others
I	67.0	15.0	-	6.3	11.3
II	66.7	16.7	-	-	16.3
III	63.1	15.1	13.7	7.7	-

(1) *A', B': compounds obtained.*

The materials were produced in two different dates, initially, 600 kg of the above two formulations (300 kg of each), afterwards 200 kg of the third formulation (standard), just to compare the efficiency and other parameters.
Just to guarantee higher reaction between the material and steel, in the first experiment, 100 kg of the material I was added in the heat stream and in the bottom of the ladle, during the steel tapping.
Figure 1a and 1b show the added materials during the tapping.

(a) (b)

Figure 1 – Photo showing the added material during the tapping (a) and in the bottom of the ladle (b)

The types of steel produced during the experiments were AISI 1020, 1030, 1045, 1080. The tapping heats numbers of the experiments were from 5143 to 5152.

Table 3 shows the final chemical composition of treated steels.

Table 3– Chemical composition of the steel produced during the trials

Steel	C	Mn	P	S	Si	Cr	Cu	Al
1020	0.180	0.611	0.0203	0.0129	0.451	0.183	0.133	0.0375
1030	0.314	0.744	0.0409	0.0116	0.428	0.116	0.112	0.0122
1045	0.531	0.899	0.0223	0.0183	0.403	0.145	0.135	0.0323
1080	0.87	0.91	0.026	0.017	0.028	0.27	0.013	0.023
5160	0.594	0.835	0.0165	0.0145	0.218	0.763	0.146	0.0234

5 RESULTS AND DISCUSSION

Table 4 shows the obtained results in all of the treated heats, where desulphurizing agent (=DA) was added. The amount shown in the table is a specific rate of DA in kg/t Steel.

The specific rate was variable in order to determine its influence on the desulphurization rate (I_S). It must be observed that the I_S varies from 3.6 to 30 %. It was also observed that in some heats dephosphorization occurred, due to the fact that the material was better prepared. This was observed by some operators from Semeato.

Like mentioned in the fundamentals, the main factors besides temperature that affect the desulphurization rate are oxygen content in the steel and desulphurizing agent amount (kg/t Steel).

The steel oxygen was not determined, but it can be calculated based on carbon in the end of the heat. That means, the higher values of carbon, lower oxygen content value is expected. On the other hand, the final oxygen content varies with the slag that is carried out with the steel. The final steel oxygen content from the experiments varied, what made the oxygen values not predictable.

Table 4 – Synthesis of the obtained results using the three above formulations

Formulation	Heat	Steel	Quantity (*)	S_i	S_f	I_S	I_P	Al (%)	T (^oC)
I	5143	1080	10 (1)	0.018	0.016	5.6	3.7	0.023	1700
I	5144	1020	16.9 (2)	0.0185	0.0129	30,0	- 18,0	0.0375	1670
I	5145	1045	18.2 (3)	0.0234	0.0165	29.5	- 8,3	0.0323	1600
II	5146	5160	9.0 (4)	0.0140	0.0135	3.6	5.2	0.0234	1620
II	5147	5160	10 (4)	0.0163	0.0115	29.4	17.2	0.0187	1563
II	5149	1030	11.2 (4)	0.0154	0.0116	24.7	-2.9	0.0122	1715
III	5151	1030	10.0 (4)	0.0154	0.0119	22.7	7.9	0.0262	1686
III	5152 (5)	1045	16.7 (4)	0.0123	0.0094	23.6	2.2	0.0752	1716

(*) in kg per t Steel; (1) added during the tapping; (2) added 50 kg during the tapping and 50 kg in the bottom of ladle (see Photo 2b); (3) 100 kg was added during the tapping (photo 2a); (4) 90 kg were added, 50 kg in the bottom of the ladle and the rest in the tapping; (5) Part of the last heat returned liquid in the furnace, this increased the P pick-up and reduces S content. $I_S = (S_I-S_F).100 / S_I$. *In the case of P,* $I_P = (P_I-P_F).100 / P_I$

The temperature was measured just before the tapping and also after, during argon stirring in the ladle. It must be said that the temperature where desulphurizing occurs, varies according to the thermal condition of the ladle, the quantity of the steel tapped, Ferroalloys additions in the ladle, and the argon stirring time. That is why the temperature shown in the table 4 is only a reference. Figure 2 shows data obtained from the conducted research.

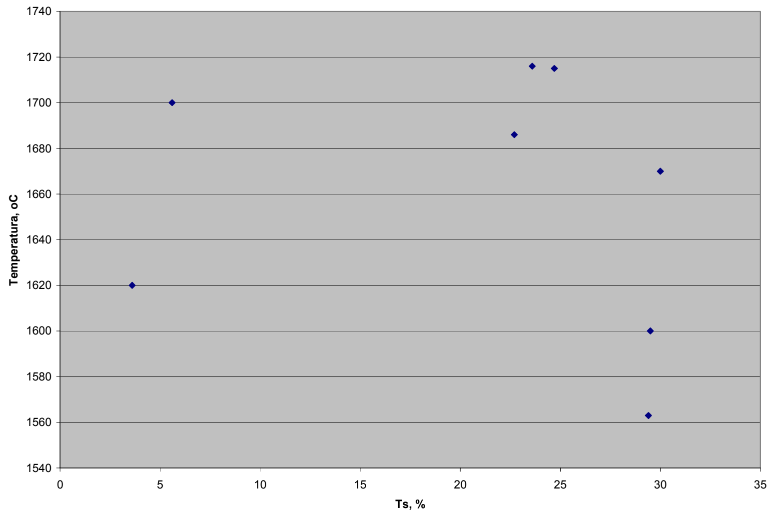

Figure 2 – Effect of temperature on the desulphurization rate

From this figure, it can be seen that a good correlation between the temperature and the desulphurization rate could not be obtained. This is explained due to the fact that the process was not under control (thermal variations without control) and other factors related with thermal loss occurred in the process. It was tried to segregate some data, but the problem lied in the small number of experiments.
It is interesting to note that there is a secret influence because of the discontinuity of operation, during the heats from 5143 to 5146. This corresponds to the stoppage of EAF, what indicates a lower thermal level for all steelmaking process.
A variable that is important to get higher desulphurization rate is the effect of the amount of the desulphurization agent. Figure 3 shows this effect. This picture proves the effect of the stoichemistry on the desulphurization rate.

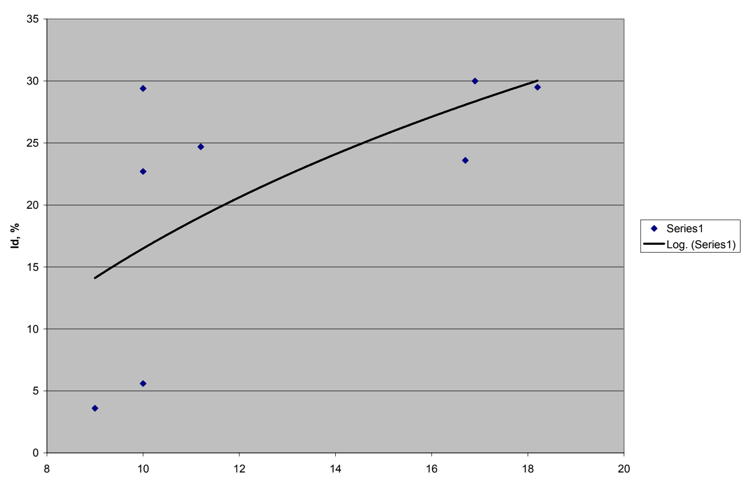

Figure 3 – Effect of specific desulphurization amount on the desulphurization rate

The data were grouped, due to the formulation, obtaining two new pictures shown in the Figure 4, with the same tendency observed in Figure 3.

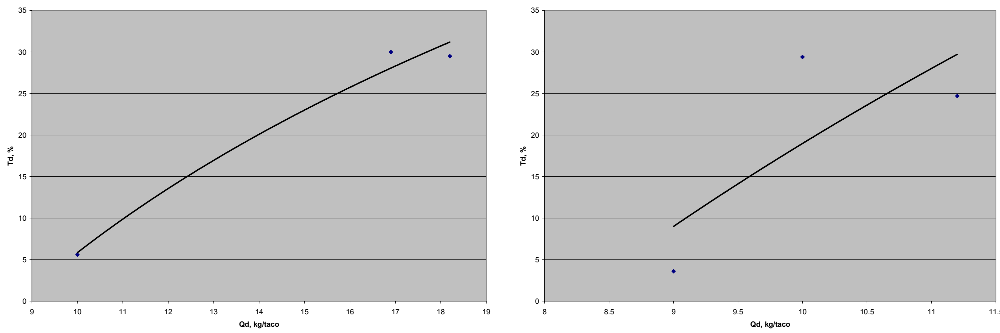

Figure 4 – Effect of desulphurizing agent amount on the desulphurization rate, for two types of formulation (left: formulation I; right: formulation II)

Based on the industrial data, it was found a relationship between the desulfurizing agent amount and the desulfurizing rate. It can be noted that to achieve a desulfurizing rate higher than 20 %, the amount of desulphurizing agent should be between 10 and 14 kg per ton steel, what varies according to the Al presence in the formulation. Higher Al content in the formulation, less desulphurization rate obtained. This could be explained based on a higher oxidation of the steel bath.

It might be observed that there is a relationship between the residual Al in the steel and the oxygen dissolved into the metal. Theoretically, when higher Al is dissolved into the metal, less Oxygen can be determined. For higher residuals of Al, less oxygen into the steel can be expected, what implies higher desulphurization rate. Based on this, a correlation using the two formulations was made, as can be seen in Figure 5.

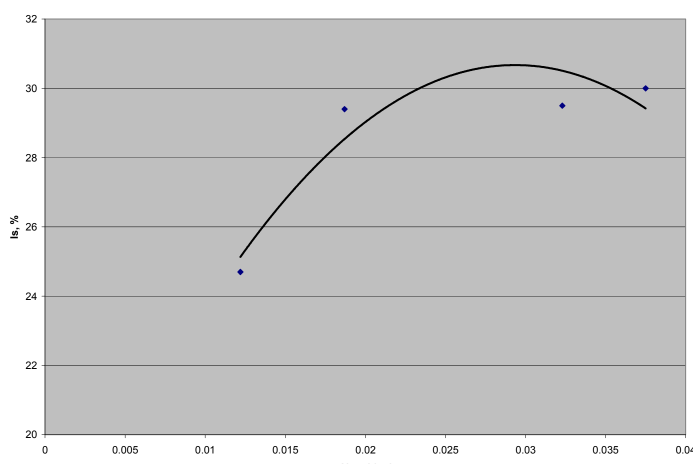

Figure 5 – Effect of residual Al in the desulphurization rate, by using the first two formulations.

The results showed a concordance between the desulphurizing rates obtained by the use of formulations I and II compared with the material used in the big company. It should be said that the results obtained in this steelplant should be higher than the obtained values, due to the fact that the slag for the latter has lower oxidation level in

comparison with the former. It is estimated that the first slag in the EAF has 5 % more FeO than the slag generated in the BOF. On the other hand, the quantity of the tapped slag in the BOF is fewer than in the EAF.
During the test, it was observed a normal amount of gases generated during the tapping by using the three formulations.
It was observed that a better slag is obtained when the formulation I and II were used, with a slag liquidus temperature less than when the standard material was used. Figure 6 shows a typical slag using one of the alternative formulations.

Figure 6 – Slag produced using one of the alternative formulations.

Finally, it should be highlighted that erosion was not observed in the ladle refractory during the experiments. The ladle life was normally maintained from 100 till 120 heats without repair. This was expected because there was no big variation on the conditions for treating the steel during the trials.

6 CONCLUSIONS

The conclusions that came from the experimental work were:
- the desulphurization rate from materials I and II was the same as when the standard material was used;
- the values varied from 20 till 30 %. It was observed a great influence from the amount of desulphurizing agent in the desulphurization rate;
- the temperature level of the steel did not highly influence the desulphurization rate.
- by comparing the two formulations with the standard one, a slightly increase of fumes generation was observed;
- the obtained slag using the desulphurization agent I and II was more homogeneous than the one obtained from the standard formulation.
- when the DA I and II was used, some cases of dephosphorization were observed;
- it was not detected erosion in the refractory when formulations I and II were used.

Acknowledgments

The authors thank the company that produced the briketts for the trials at Semeato. To Usiminas to do some chemical analysis of the slag. To CNPq, FAPEMIG for supporting the teacher's research in this area, so as the help given of FAPEMIG to present the paper in Curitiba. To UFOP and both companies to permit the publication in India.

REFERENCES

1 CASTRO, L.F.A; TAVARES, R.P.; SAMPAIO, R.S. Curso: Termodinâmica Aplicada ao Pré-tratamento de Ferro-gusa. ABM. 2006.

2 SOBRINHO, P.J.N et alli. Development of the synthetic slag Vamflux BP to refining of steel into ladle furnace at Belgo - Arcelor Brasil, Piracicaba Steel Plant. XXXVIII Steelmaking Seminar – International, May 20th to 23rd, 2007