CARACTERIZAÇÃO DAS MISTURAS DE CARVÕES E DO COQUE COM ADIÇÃO DE PNEU INSERVÍVEL *

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Resumo
O coque é um produto intermediário numa usina integrada, produzido a partir de misturas de carvões metalúrgicos, formuladas para atender tanto as condições operacionais do processo de coqueificação como os requisitos de qualidade do processo de produção de gusa. No atual cenário acirrado de competitividade, umas das linhas para redução do custo da mistura de carvões é o desenvolvimento de matérias-primas alternativas nacionais que minimizem o custo do coque, e consequentemente, do gusa.A utilização de pneus inservíveis na mistura de carvões sugere uma rota de destinação ecologicamente correta a fim de mitigar o impacto causado pelo acúmulo de pneus no meio ambiente, além de uma alternativa para redução de custos de produção do coque metalúrgico. Os resultados mostraram que o melhor coque foi produzido pela adição 3% de pneu médio (20 a 30 mm) com malha de aço, o que levou a uma estrutura reforçada do coque, e, portanto, de alta resistência.
Palavras-chave:Coque; Mistura de Carvão; Pneu inservível; Qualidade do coque.

CHARACTERIZATION OF COAL BLENDS AND COKE WITH WASTE TIRE ADDICTION

Abstract
The Coke is an intermediate product in an integrated plant, produced from metallurgical coals blends, formulated to meet both the operating coke process conditions and the quality requirements of the hot metal production process. In the current fierce competitive scenario, one of the lines to reduce the coal blend cost is the development of domestic alternative raw materials to minimize the coke cost and hence the hot metal. The use of unserviceable tires in the coal blend suggests an ecologically correct destination route to mitigate the impact caused by the tires accumulation in the environment, as well as an alternative to reduce metallurgical coke production costs.The results showed that the best coke was produced by addition of waste tire 3% of the medium tire (20 to 30 mm) with the steel mesh which led to a coke with reinforced structure, therefore, of high strength.
Keywords: Coke; Coal blend; Waste Tire; Coke quality.

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1 INTRODUCTION

With the increase of competitiveness in the steel industry, companies aim at reducing their production costs. The use of alternative and cheaper materials replacing the usual raw materials is a viable strategy. Brazilian coke production is part of a scenario of excess of steel production capacity in the world and a significant decline in the profit margins of steel products. In addition, most conventional coking plants are at the end of their useful life, which makes the use of coals and alternative materials with non-coking capacity even more challenging. The possibility of using waste tires to make the blend of coals cheaper, keeping the metallurgical coke quality as required by the blast furnace was evaluated in this study. The disposal of waste tires in the environment leads to serious problems, such as damage to nature and the proliferation of disease-transmitting mosquitoes[1], supporting the need of an ecological way to recycle them. Coke ovens can be used for that purpose because the gases produced are collected, treated and reused. Another motivation to use tires as alternative raw material was their great percentage of carbon. Fernández[2] concluded that the addition of tire's rubber (< 3 mm) decreased the Drum Index (DI) 150-15[3]of the coke. Different grain sizes and levels were tested in pilot scale to analyze which way to use waste tire in coal blends is the best. Figure 1 summarizestheobjectivesofthestudy:

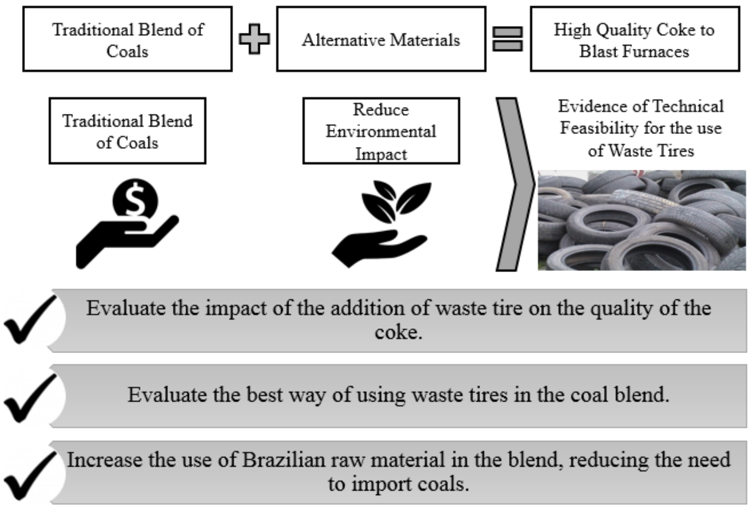

Figure 1. Summary of study objectives.

2 EXPERIMENTAL PROCEDURE

The tests and analysis standardization are shown in Table 1. A basic blend (BB) of coals was supplied by a Brazilian Steel Company. The physic-chemical parameters of this BB were done as well as the Immediate Analysis, Rheology and Petrography as can be seen in Table 2:

Table 1. Tests and analysis standards

TESTS AND ANALYSIS	CONTENTS	STANDARD
Immediate Analysis	Ash Volatile Matter (VM) Total Sulfur Humidity	ASTM-D-3174 ASTM-D-3175 ASTM-D-2492 ASTM-D-3173
Chemical composition of the ashes	Fe_2O_3, SiO_2, Al_2O_3, MnO, CaO, MgO, P_2O_5, ZnO, Na_2O, K_2O, TiO_2	Atomic Atomic Absorption
Plastometry	Fluidity	ASTM-2639
CSR-CRI	Reactivity and Strengh after Reaction with CO_2	ASTM-D-5341
DI	Mechanical Cold Strength	JIS 2185
Granulometry	Percentage withdrawal in the Tyler series of sieves	Gerdau
Strenght and Compression	Maximum load at break	DEGEO/UFOP
SEM and EDS	Steel Mesh/Coke Interface Analysis	Nanolab/UFOP

Table 2. Characterization of the Basic Blend of Coals

Immediate Analysis (%)	VM 23.46 70.44 Ash 7.57 S(%) 0.81	**Rheology**	Fluidity Log (ddpm) 2.5 Softening Temperature (°C)309 Maximum Fluidity Temp. (°C) 360 Solidification Temperature (°C) 382
Chemical Composition of the Ashes (%)	Na_2O 0.36 K_2O 1.26 AL_2O_3 25.65 CaO 1.42 MgO 0.75 Fe_2O_3 6.23 SiO_2 58.46 TiO_2 1.36 Basic Index 0.12	**Petrography (%)**	Reflctance 1.14 Vitrinite 60.20 Sporinite 0.30 Cutinite 0.10 Resinite 0.70 Semi-fusinite 10.20 Macrinite 0.30 Fusinite 0.50 Inertdentrinite 4.60

The waste tires were provided by a Brazilian Recycler in three different grain sizes: Small Tire (ST) with particles of up to 5 mm, Medium Tire (MT) containing particles between 20 and 30 mm and Large Tire (LT) with the diameter of particles between 50 and 100 mm. The ST is constituted only by the rubber of the tires and the others are composed by steel mesh and rubber. An Immediate Analysis was also made in the tire rubber, as shown in Table 3:

Table 3. Immediate Analysis of the rubber of tires (%)

Ash	VM	C_{FIX}	Sulfur
4.0	48.5	47.5	2.2

The basic composition of the tires is shown in Table 4:

Table 4. Basic tire composition (%)[4].

C	Fe	Zn	S	H	Others
70	15	1.2	1.3	7	5.5

The blends were prepared using coal with a particle size 85% less than 2.83 mm, to avoid ultrafines particles generation which can decrease the charge density at the coke oven and, consequently, the mechanical strength of the coke[5]. To these blends were added each type of tire (ST, MD and LT) in four percentages: 1, 3, 5 and 10%. These final mixtures were homogenized by the conical cells method. A sample of BB was coked and used for comparison. Heats were performed in a 200 kg capacity Pilot Electric Furnace, the temperature was about 1000° C and the time, 20 hours. The coke produced was extinguished in water. All heats were performed twice and the considered results were the average. Samples of 80 kg were collected to perform the characterization tests.Immediate Analysis was performed at the obtained coke as well as the chemical composition of the ash. Then the specific coke analyzes as CSR, CRI [6]and DI 150-15 were carried out. Five sub-samples of each coke class were selected (grain size between 19-21 mm) to observe the obtained coke by Scanning Electron Microscopy (SEM) coupled with the punctual chemical composition by Energy Dispersive Spectroscopy (EDS). Those samples were metallized with gold to increase their conductivity. The observations of the morphology and interfaces tire/coke were executed to evaluate and justify the obtained results.Compression tests were also performed to measure the maximum force applied to the coke to initiate the breaking process. A universal testing machine *Alfred J. Amsler& Co* with a capacity of 5000 kgf was used to perform that test.The summary of this Experimental Procedure is shown in Figure 2:

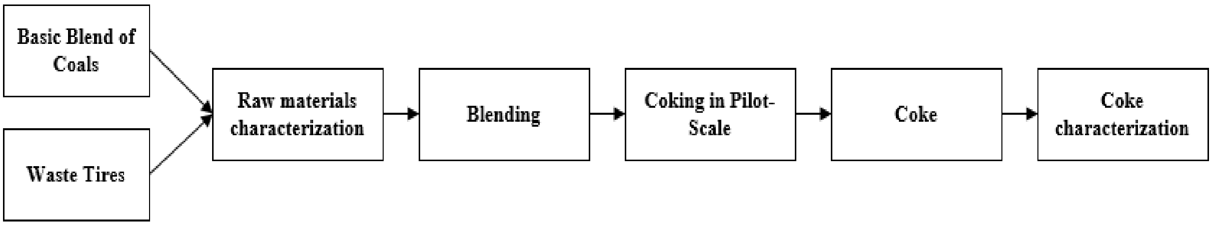

Figure 2. Summary of the Experimental Procedure.

3 RESULTS AND DISCUSSION

3.1 Visual Inspection of Coke

The coke produced with ST, which contains just the rubber of the tire, was very similar to the coke produced just with the basic blend of coals. But the cokes fabricated with the blend of MT and LT with coal exhibited in their structures the tire cords, as can be seen in Figure 3:

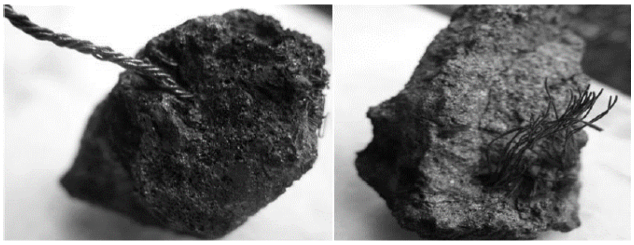

Figure 3. Coke with the tire cords.

It was also found that these cokes had a high mechanical strength. It happens because the steel mesh acts as a structural agent of the coke, just like it happens at the reinforced concrete. Figure 4 shows the possible interactions between the steel structure and the carbonaceous matrix at the “reinforced coke”.

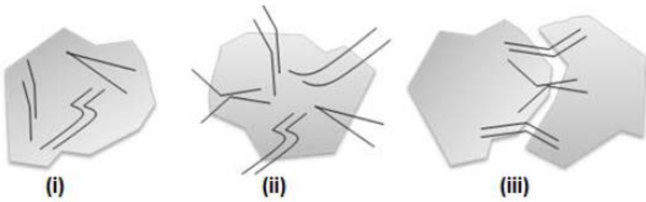

Figure 4. Possible interactions between the steel structure and coke matrix. (i) Steel mesh located inside the coke particles, (ii) cokes with steel mesh outcrop and (iii) cokes interconnected by steel mesh.

3.2 Ash, Sulfur and Fluidity

Figure 5 shows the ash contents in the coke produced with different percentages of waste tire added to the blend, in three grains sizes.

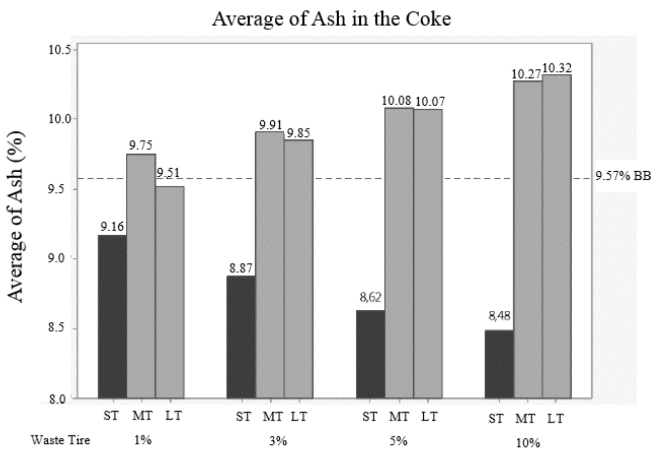

Figure 5. Average of ash in the coke with different percentages of waste tire in three grains sizes.

As expected the coke produced with ST had less ash than the BB and the cokes with MT and LT, in all percentages. It happens because the tire rubber contains just 4.0 % of ash in their composition. This amount is less than the content in BB (6.97%) and in the MT and LT (because they have about 15% of the weight in steel mesh). The consequence of this fact at the blast furnace is the increase of the fuel consumption by reason of the need to smelt this extra ash and the lower percentage of fix carbon in the coke.

Figure 6 demonstrates the sulfur percentage behavior in all type of obtained cokes. Samples obtained with ST had more content of sulfur than BB. This can be explained by the ST composition, just vulcanized rubber, with a high content of sulfur (2.2%). The same propensity occurs in the cokes with MT and LT, but in a smaller scale, because the steel mesh contains metal oxides as ZnO that reacts with Sulfur during de coking process forming inorganic sulphides as Zn_2S and Fe_2S. This sulphides are decomposed in H_2S and released from the coke structure. But, as the present amount of Sulfur is very large there is still more of this element when compared to the BB in addition of 3, 5 and 10% of MT and LT[7]. Increase of Sulfur in coke demands actions to increase the desulphurization at the blast furnace and/or increase in the consumption of desulphurizing agents at the steel plant, so the costs of the production chain must be studied[8].

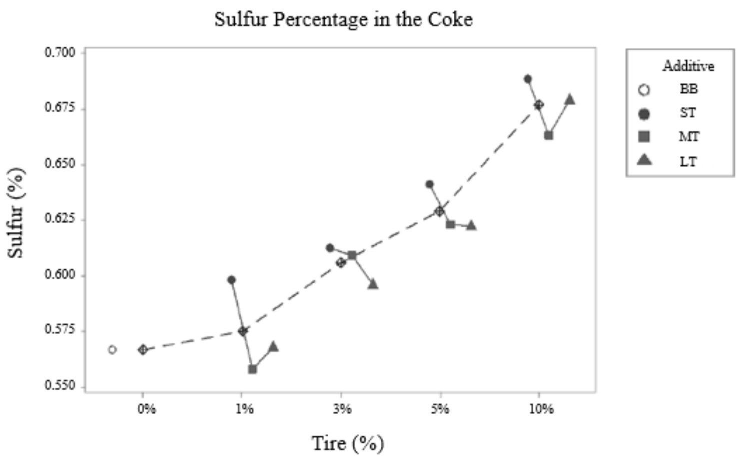

Figure 6. Sulfur percentage in the coke with all type of additions.

Figure 7 shows Fluidity behavior with the increase of the ST percentage added:

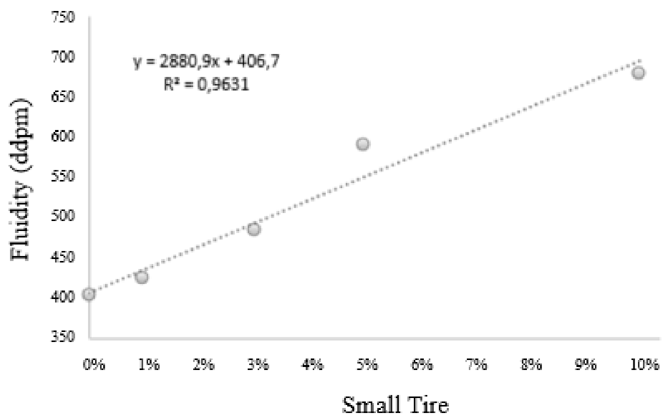

Figure 7. Fluidity behavior with different percentages of ST.

It can be observed that fluidity increases about 30 ddpm for every 1% of small tire added. This result is in agreement with that demonstrated by Liu [9]. He demonstrated that the addition of rubber of tires increases the gas release, rising the fluidity of the blend of coals. This result implies a greater probability of contact between the coal particles, but the large volume of volatile matter can generate an excess of pores in the coke produced and may reverse the effect of increased fluidity.

3.3 CRI, CSR and DI

In general, it is observed an increase of the CRI with the addition of tire, however the rates vary according to the type of additive, as it can be observed in Figure 8. The ST had a greater increase rate, that indicates the catalytic effect of the rubber in the reaction with CO_2.

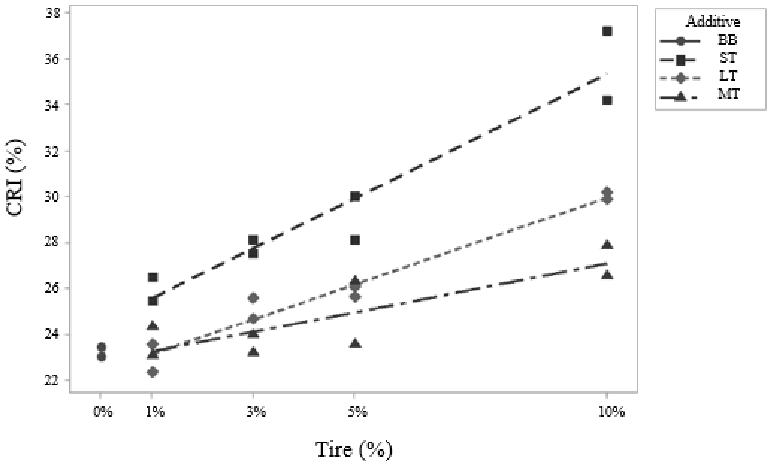

Figure 8. Variation of the coke CRI with percentages and tire types.

Figure 9 demonstrates the proposed model to explain the different behavior of coke reactivity with different types of added tire.

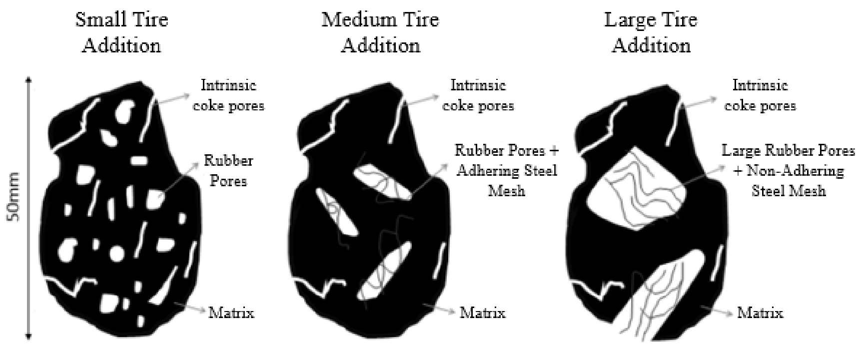

Figure 9. Model of coke reactivity behavior with different types of tire.

The use of ST involves the addition of finely dispersed rubber in the blend. During coking, rubber releases from 40 to 45% of volatile matter, increasing coke porosity and its reactivity. The addition of LT causes the appearance of few pores, but they are large and the steel mesh has low adhesion in the carbonaceous matrix, generating fissures that facilitate the penetration of CO_2, also increasing the reactivity of the coke. Nevertheless, the addition of MT generates a coke with a more compact structure, due to the equilibrium between the pore generation and the good interaction between the steel mesh and the matrix. Figure 10 illustrates the variation of CSR of the cokes obtained with the different types of blends. The results are according to the levels of reactivity obtained. Addition of ST and LT decreased CSR at all percentages of addition. For the incorporation of up to 3% of MT, the results are similar to those of BB, demonstrating the structural role of the steel mesh.

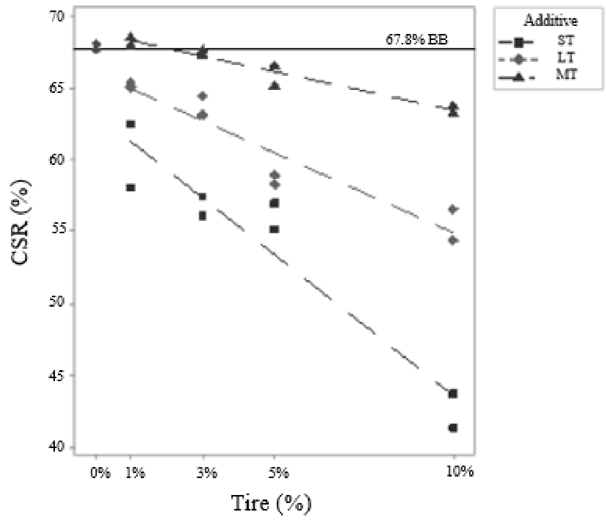

Figure 10. Variation of the coke CSR with percentages and tire types.

Figure 11 demonstrates the effect of tire addition in all percentages and grain sizes in the DI 150-15:

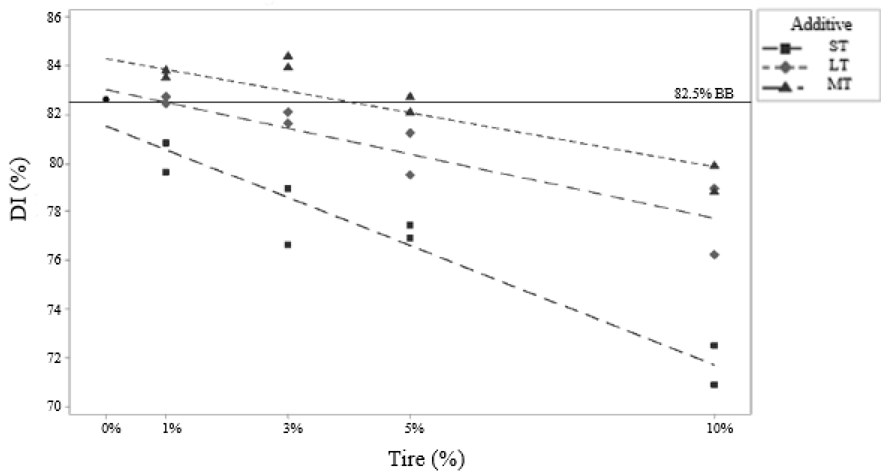

Figure 11. Variation of the coke DI 150-15 with percentages and tire types.

All the samples showed a tendency to decrease DI 150-15 with the increase of the percentage of tire added. However, for PM, maximum elevation of DI 150-15 is observed with addition of 3%. Corroborating, once again, the structural effect of the steel mesh.

3.4 MEV and EDS

The micrographic tests were carried out with the purpose of validating the structural importance of the steel mesh. The study of the steel mesh/carbonaceous matrix interface is essential to justify the increase of the mechanical strength of the coke. Figure 12 shows the different surfaces of the coke samples produced with BB and with the addition of 3% of the tire in each grain size (ST, MT and LT).

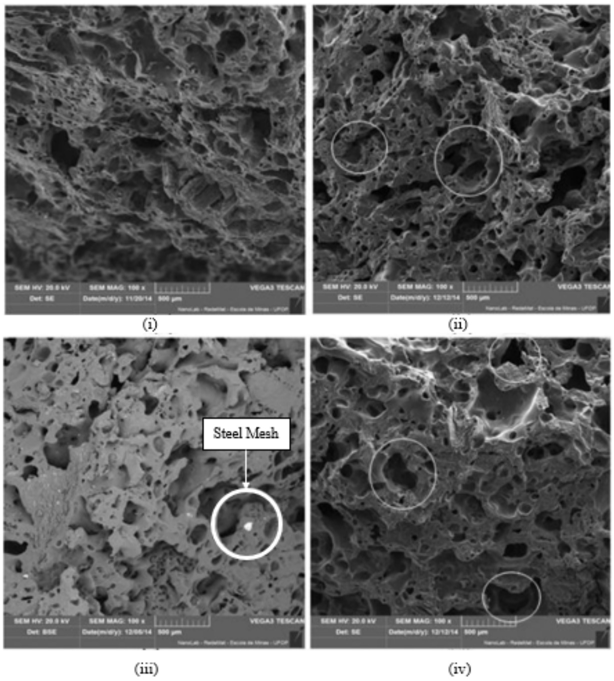

Figure 12. Micrographs (Magnification = 100x) of the cokes produced with: (i) BB, (ii) BB+ST, (iii) BB+MT and (iv) BB+LT.

The surfaces of the cokes in (i) and (ii) are similar, but qualitatively the porosity increases with ST addition, which corroborates the obtained reactivity result. In (iii) it can be seen the outcropping of the tire cords and the reduction of the porosity in relation to (ii), proving the positive effect of the addition of MT on the mechanical strength of the coke. In (iv) it is not possible to observe the outcrops of the steel mesh, however, the increase of the porosity in relation to the coke produced with MT is evident, indicating that the rubber in coarse granulometry is not completely absorbed by the carbonaceous matrix of the coke. In Figure 13 the micrographs show the outcrop of the steel mesh with addition of 3% MT at different magnifications. The tire cord scales that can be seen in (iii) are due to metal corrosion due to atmospheric exposure.

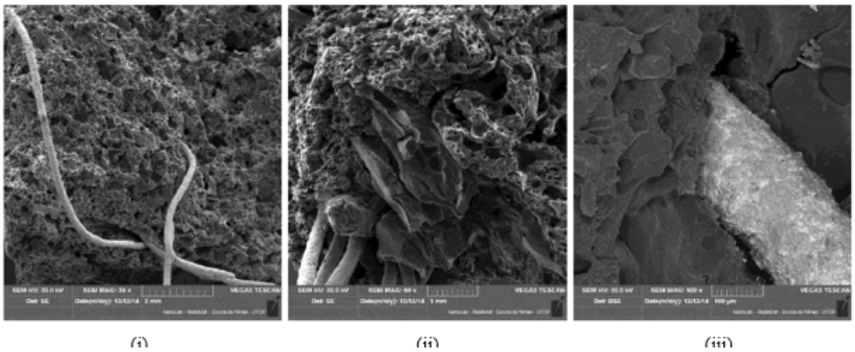

Figure 13. Tire cord on the surface of the coke produced with 3% MT with different magnifications (i) 35x, (ii) 50x and (iii) 500x.

Figure 14 presents a more detailed study of the coke surface produced with 3% MT. In (iii) the end of the steel mesh is observed. However, there were no microcracks or porosity at the steel mesh/carbonaceous matrix interface, which indicates good interaction between the components. As expected, no evidences of molten steel were seen, since the coking temperature is lower than the melting temperature of the steel, eliminating the possibility of metallic deposition inside the coke oven.

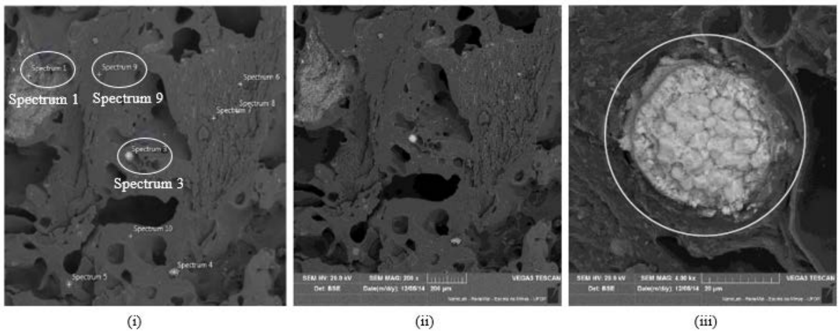

Figure 14. Micrography of the coke produced with 3% of MT. (i) Specified sites to EDS analysis, (ii) magnification of 200x of the Spectrum 3 and (iii) magnification of 4000x of the Spectrum 3**.**

The punctual chemical composition of the Spectrums 1, 3 and 9 presented in Figure 14 was made by EDS and the results can be seen in Figures 15, 16 and 17.

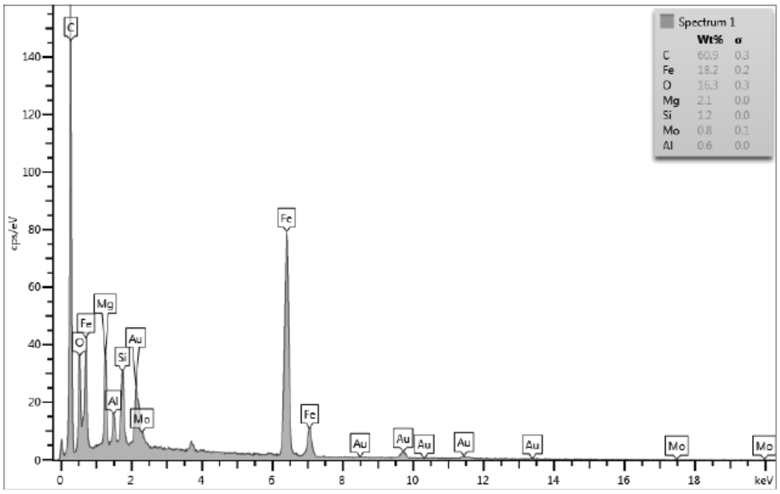

Figure 15. EDS Analysis of Spectrum 1 (Sample Coke + 3% MT).

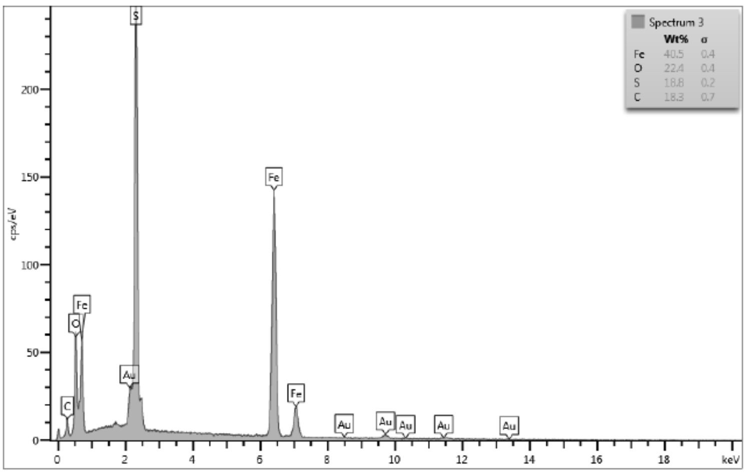

Figure 16. EDS Analysis of Spectrum 3 (Sample Coke + 3% MT).

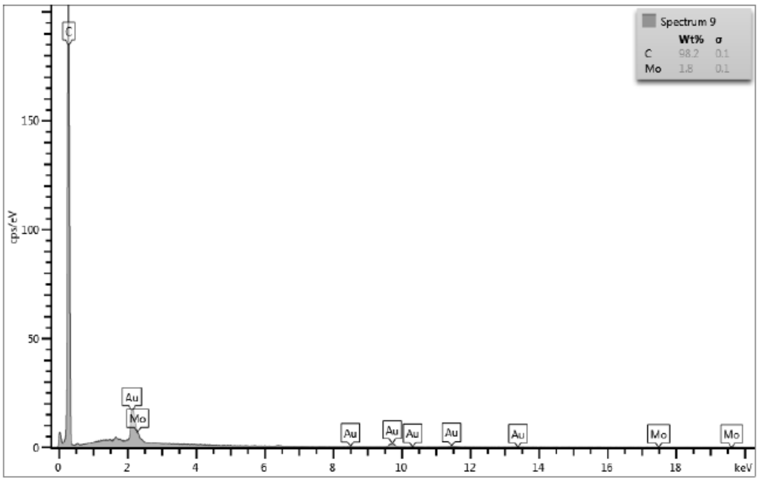

Figure 17. EDS Analysis of Spectrum 9 (Sample Coke + 3% MT).

The presence of a high percentage of carbon can be verified in Spectrum 1 because this is a region of the coke matrix. The presence of other elements can be explained by the detachment of corrosion products from the steel mesh and also by the chemical composition of the rubber of the tire, which contains stabilizers and vulcanization accelerators. Spectrum 3 has a large steel mesh outcrop and, as a consequence, has a high content of iron as well as rubber sulfur. Spectrum 9, however, represents a typical carbonaceous matrix of coke and is composed primarily of carbon.

3.5 Compressive strength

Figure 18 shows the values obtained in the compression test of the cokes with tire addition. The compressive strength of the cokes added with 1% and 3% of MT, were similar to results obtained to the BB. The cokes produced with FT and LT had a compressive strength well below the BB, confirming the results of DI and also the proposed model to explain the interaction of the metal mesh and the carbonaceous matrix.

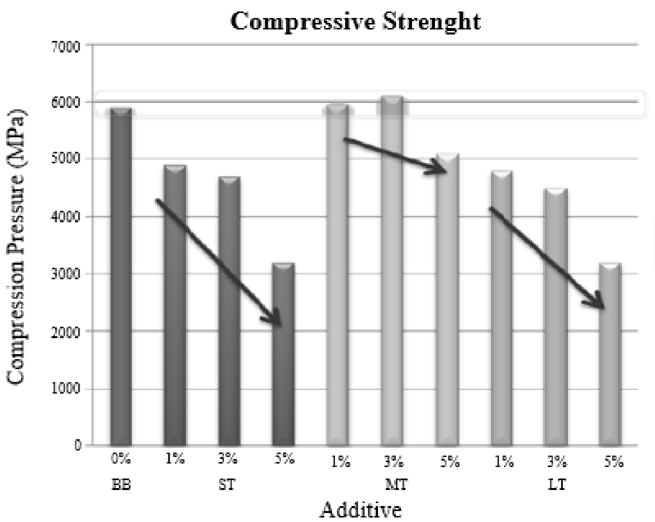

Figure 18. Compressive test results for produced coke.

4 CONCLUSION

The use of waste tires in the coal mixture to produce metallurgical coke is an alternative to reduce the cost of coke and contributes to the reduction of environmental damages caused by the inadequate disposal of this material. The Steel mesh added to the mixture through the MT and the LT performs fundamental structural role in the coke, generating the "Reinforced Coke".
The addition of MT balances the pore generation with the interaction capacity of the steel mesh with the carbonaceous matrix, generating a more compact structure and reducing coke gasification.
It can be concluded that the best way to use waste tire in the coal blend for coking is to add up to 3% of the medium tire (20 to 30 mm) with the steel mesh. This addition can be some deleterious effects, as the increase of sulfur and ashes. Nevertheless, the coal blend got cheaper and the coke maintained the characteristics specified by the blast furnace, allowing its industrial use.

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REFERENCE

1 V.E.S. Alves, G.M. Vasconcelos, R.N. Moreira, M.J. Alves Filho and T.S. Barreto, "Environmental ImpactCausedbyIncorrectDiscardof Tires", ENIAC Pesquisa, Vol. 4, No. 2, Jul-Dec 2015, pp. 162-175.
2 A.M. Fernández, C. Barriocanal, S. Gupta and D. French, "Effect of Blending Carbon-Bearing Waste with Coal on Mineralogy and Reactivity of Cokes", Energy & Fuels, Sep 2013.
3 JIS K 2151, Coke Testing Methods, Japanese Standards Association, 2004.
4 A.J. Andrietta, "Pneus e meio ambiente: um grande problema requer uma grande solução", Oct 2002.
5 M.B. Ulhôa, "Aplicação de Petrografia de carvão na Siderurgia", ABM Oct 1991, Volta Redonda, RJ, Brazil.
6 ASTM D5341/5341M-14, Standard Test Method for Measuring Coke Reactivity Index (CRI) and Coke Strength After Reaction (CSR), ASTM International.
7 R.D.S. SOUZA, "Caracterização de coque metalúrgico produzido com adição de pneu inservíveis nas misturas de carvão mineral", Master Dissertation in MaterialsEngineering, Universidade Federal de Ouro Preto, Brazil, 2016.
8 G.L.R. Silva, "Utilização de moinha de biorredutor e pneu inservível na produção de coque metalúrgico", DoctoralThesis in MaterialsEngineering, Universidade Federal de Ouro Preto, Brazil, 2016.
9 X. LIU, H. LIAO, Z. ZHANG and D. DENG, "Study on Improving Quality of Coke Co-coked with Addition of Waste Tire", Iron e Steel, 2006..