

PRODUCTION OF METALLURGICAL COKE USING GREEN PETROLEUM COKE

Paulo Henrique Grossi Dornelas, paulohgrossi@hotmail.com¹

Carlos Eduardo Reis de Carvalho, carlos.carvalho@ifmg.edu.br¹

Alfredo Carlos Bitarães Quintas, quintas1794@gmail.com¹

Tamires Miranda Milagres Portilho, tamires.milagres@hotmail.com¹

Guilherme Liziero Ruggio da Silva, guilherme.silva@gerdau.com.br¹

¹Instituto Federal de Minas Gerais. Afonso Sardinha Street 90, Ouro Branco, Minas Gerais, Brazil

Abstract. *Is a tendency in steel industry the research for new additives which reduce the metallurgical coke cost production, keeping and/or optimizing its quality. In this subject, the green petroleum coke (GPC) has availability and economic viability in the search of cost reduction and it has characteristics which directly influence on metallurgical coke quality. The amount and size particle of the additions of GPC in the coal blend presents great influence in many relevant parameters in the metallurgical coke produced. This study was possible to conclude that the GPC although reduce the blend fluidity in exponential scale, it is an excellent additive when it's used in a smaller particle size (100 % < 2.83 mm).*

Keywords: *green petroleum coke, coal mix, metallurgical coke.*

1. INTRODUCTION

To maintain market competitiveness, the steel industry is looking for alternatives to reduce raw material costs which are essential to the survival of organizations. According to Da Silva (2013) the mineral coal is responsible by 30% of steel price, and develop alternatives raw materials is essential to ensure perpetuity in steel sector.

The coke production challenge is in to project coal blend which produce a low cost coke with high quality. In this subject a possible additive is the Green Petroleum Coke (GPC). The GPC is a petroleum sub product which presents characteristics close to mineral coking coal. In the 1990s the use of GPC on coal blends was already discussed. According to Ruiz (1990) the reduction of reserves of “good coking coals” was already attention focus, besides that, due de need of reduce raw materials costs, alternative materials were already studied for the metallurgical coke production.

Besides of long GPC utilization period, it still is subject to many studies, because its utilization does not bring linear effect in metallurgical coke properties, thence its utilization is limited until some fractions. Alvarez (2012) studied the addition of GPC among different particle sizes and different fractions (3 and 6%). All tests were realized in close conditions for avoid any results dispersion. In this study, the GPC particles were reduced until particle size lower than 0.425mm, the influence between different GPC particles sizes weren't observed. With regard to coal fluidity, the results showed an exponential drop. DI (drum index) and CSR (coke strength after reaction) the results were satisfactory until 6% of GPC in smaller particle size.

Is notorious the importance of research in this area, in view of the crescent petroleum production in Brazil, generating an increase of GPC availability which can be used in steel industry reducing the coke production costs and minimizing environment impact caused by lack of application of this sub product.

In this way, this paper developed alternatives blends using GPC varying fractions and particle size added in order to study the effects caused by GPC utilization in the characteristics mechanicals and chemistries of metallurgical coke produced.

2. MATERIALS AND METHODS

The tests were made with 250kg of regular blend (RB – mineral coal) and green petroleum coke (GPC) in various portions. Were analyzed the mechanical and chemistry properties. Follow below these characteristics.

Table 1. Blend characterization

	Volatile matter	Ash	Sulfur	Fluidity log (ddpm)	Reflectance	Vitrinite
RB	23.46%	6.97%	0.81%	2.60	1.12	62.20
GPC	11.90%	0.35%	0.78%	-	-	0

Table 2. Ash chemistry in %

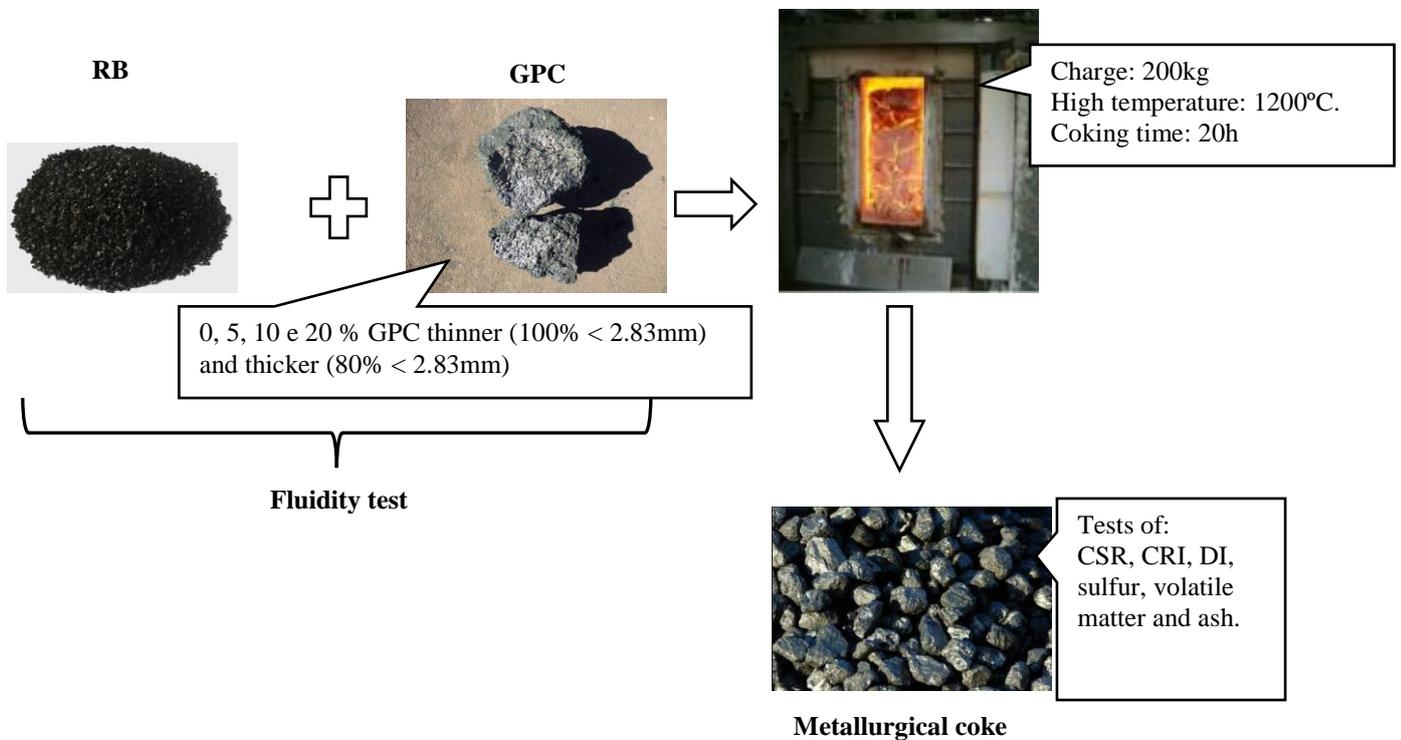
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	P ₂ O ₅	MgO
RB	52.38	33.21	8.13	2.69	1.29	0.32	0.53	1.45
GPC	50.21	25.32	6.19	2.62	0.85	0.69	1.13	0.63

Were realized seven (07) pilot oven tests composed by RB and different fractions of GPC among some particle sizes, as showed below.

Table 3. Blend Composition

Blend	RB (kg)	GPC (kg)	GPC < 2.83mm (%)
1	250.00	0.00	-
2	237.00	12.50	100.00
3	225.00	25.00	100.00
4	200.00	50.00	100.00
5	237.00	12.50	80.00
6	225.00	25.00	80.00
7	200.00	50.00	80.00

The tests were done at 1200°C and the time of coking were 20h for each test. After coking period, the coke was cooled by water and, after that, were sampled 80kg of coke for each sample composition. The collected materials were sent to lab where realized metallurgical coke analysis. There is a flowchart of process below.



The tests followed the usual current standards as detail in table 4.

Table 4. Analysis standards for coals and blends

Analyzes and tests	Content	Method
Samples preparation	Lot Representation	JIS M 8811
Immediate analysis	Ash	ASTM - D – 3174
	Volatile matter	ASTM - D – 3175
	Sulfur	ASTM - D – 2492
	Moisture	ASTM - D – 3173
Ash chemical composition	Fe ₂ O ₃ , SiO ₂ , Al ₂ O ₃ , MnO ₄ , CaO, MgO, P ₂ O ₅ , ZnO, Na ₂ O, K ₂ O, TiO ₂	Atomic Absorption
Sole heat oven	Contraction / expansion (pressure Coq. - psi)	ASTM - D – 2014
Plastometry gieseler	Fluidity Log (DDPM)	ASTM - D – 2639
Optical microscopy	Maceral composition; Reflector power	Standards adaptation ASTM - D - 2798 e ASTM - 2799
Bulk density	Bulk density	ASTM - D – 291

2.1. Fluidity

This test followed ASTM D2639 standard. A 5g coal sample with particle size smaller than 35 meshes was put in pot. A small stirrer coupled to a motor with 300 rpm and a dial with 100 divisions (Readings up to 30.000 ddpm) positioned in the middle of coal is subjected to a constant torque. The sample was heated in the absence of air at 3°C/min between 300°C and 500°C. When the temperature reached a value in the range of 350°C to 420°C, the stirrer started to rotate very slowly. Its speed increased when increase temperature and reached a maximum between 430°C and 480°C. The speed decreased too fast and the stirrer finally stopped at a temperature below 500°C.

2.2. Coke reactivity index (CRI)

This test follows ASTM Standard D5341-99. In this test a 200g coke sample dried with particle size between 19 and 21 mm were put in a reactor (under N₂ flow) and were introduced in an electric oven at 1100°C. After temperature stabilization in the reactor center at 1100°C, the coke is subjected by CO₂ flow at 5l/min for 120 min. After reactor cooling until 40°C, the weight lost percentage by the sample give the CRI index.

2.3. Coke strength after reaction rate (CSR)

The remaining coke of the CRI test is subjected to 600 revolutions (20 rpm) in a spinning cylinder and then analyzed by particle size. The retained in the 9.52 mm sieve (percentage on the weight after reaction) gives the resistance index of the coke after reaction.

2.4. Drum index (DI)

In this test were used 10kg of coke with particle size between 25 and 100 mm. This sample was paced in a drum (MICUM) and was subjected to 150 rpm. After this step, the coke is sifted in 15 mm; the percentage of coke retained in the screen by initial coke mass gives DI.

2.5. Volatile matter (VM) and ash

The volatile mater and ash tests were executed almost together because both test used the same sample in the same equipment, the TGA. This test is performed in duplicate. For each analysis 1.0g of sample is used, with particle size smaller than 0.250 mm. This sample were placed in a pot without cap and taken to TGA. Firstly the sample was heated at 150°C (under N₂ flow) for removal humidity. After that, the equipment measures the material new mass. A cap is

placed on the pot and the material is heated to a temperature of 950°C, also under N₂ flow. The material is subjected to this temperature for 7 minutes. The equipment then measures the new mass and records the volatile matter by mass difference. After this step, the TGA decreased the temperature to approximately 600 °C, then cap's put is removed and the sample is heated, under N₂ flow for 2h, and the ash percentage was obtained.

2.6. Sulfur

The sulfur content is determined by infrared radiation. A sample of 3.0g with particle size smaller than 0.250 mm was placed in a pot then in an oven. The sample was burned in an O₂ atmosphere at 1137°C. While this step, the sulfur is oxidized to SO₃ so measure by infrared detector.

3. RESULTS

3.1. GPC and metallurgical coke micrography

Were realized microstructural analysis using an optical microscope, the images are showed below.

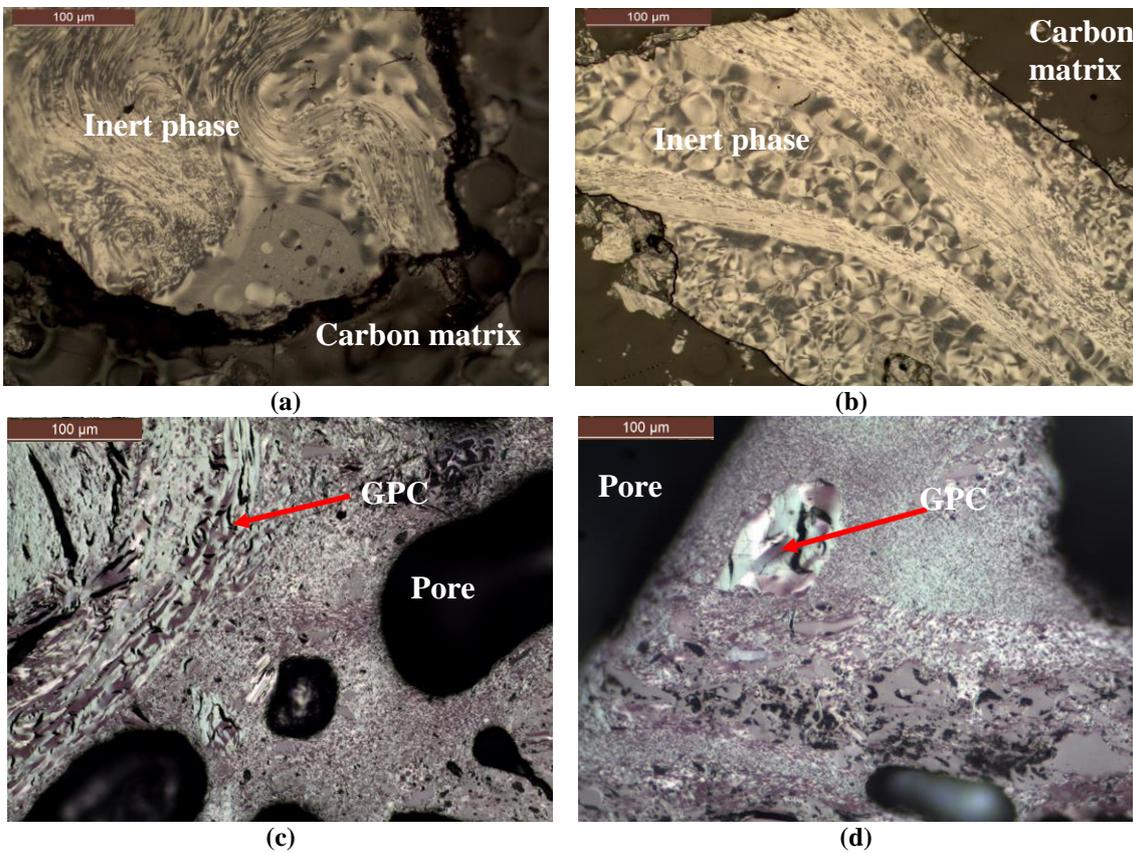


Figure 1. Green petroleum coke micrography (a) and (b), metallurgical coke micrography (c) and (d)

In (a) and (b) we can observe GPC microstructure where the light coloration represents the inert phase whereas the dark coloration represents the carbon matrix. In (c) and (d) we can observe how the GPC is distributed in metallurgical coke matrix.

3.2. Fluidity

For the fluidity analysis were analyzed four (04) samples. The first one were only composed by mineral coal blend (RB), while the second, third and fourth one were composed by 5, 10 and 20% of GPC respectively. The results obtained are showed in Figure 2.

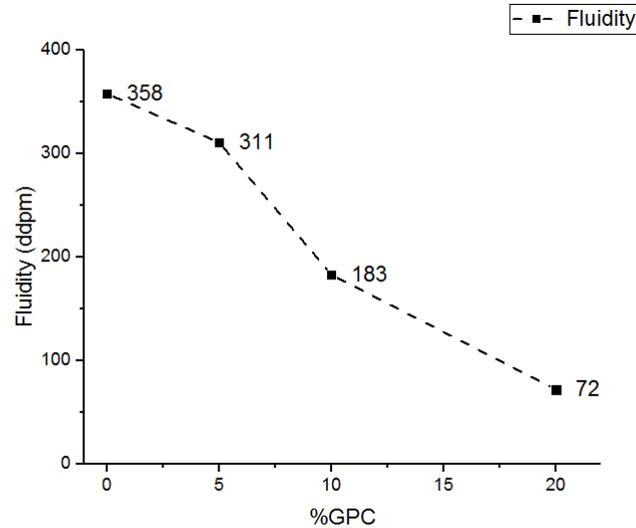


Figure 2. Diagram shows fluidity behavior when GPC is added (Fluidity = f (% GPC))

By the fact that the GPC be an inert material, the fluidity drop was already expected. Despite the fluidity drop be a negative point, other factors were analyzed for to know how much harmful is this drop.

3.3. CRI

The CRI index can be observed in Figure 3.

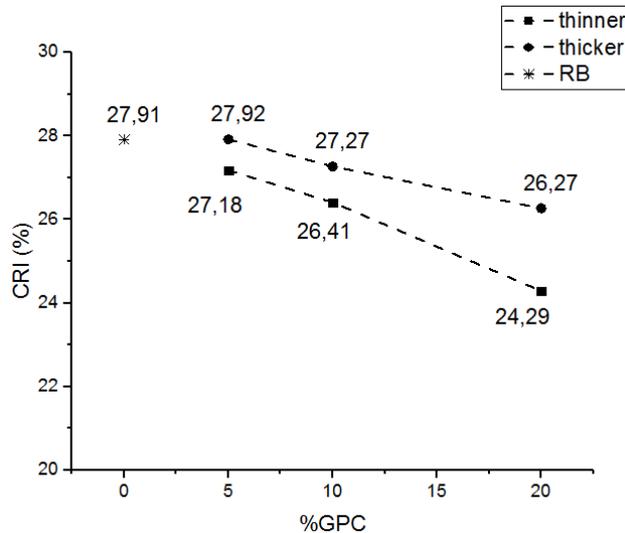


Figure 3. CRI variation with GPC added (CRI= f (% GPC))

In this case we can observe that the use of GPC decrease the coke reactivity in both situations, but the better results occurred when was used a smaller particle size. It is explicated because there are stronger bonds between thin particles and mineral coal, so we've a metallurgical coke with less porosity, which reduces CRI values. This phenomenon is explicated by the fact that the contact surface between coal and carbon dioxide is smaller.

Besides that in both cases, GPC thinner (100% < 2.83mm) and GPC thicker (80% < 2.83mm), how bigger the GPC fraction, better are the CRI values, almost getting 13% reduction in CRI value in RB + 20% GPC.

As well as CSR case is observed an increase in CRI gap with an increase of fraction of GPC. Because of that, the difference between CRI value using particle size thinner or thicker is bigger in 20% GPC when compared the others.

3.4. CSR

The CSR variation with GPC utilization is showed in Figure 4.

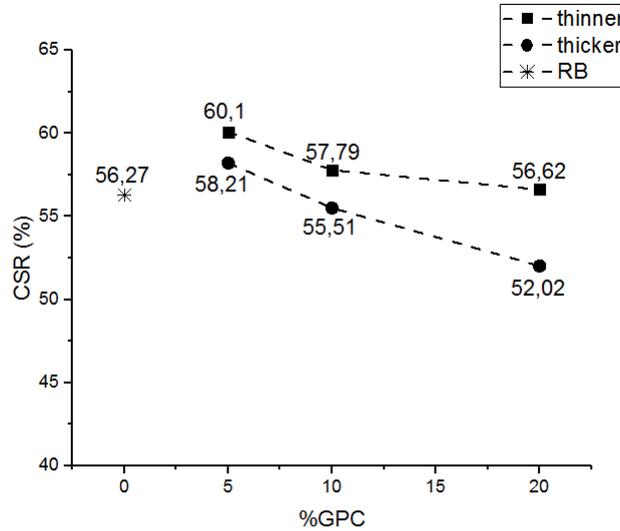


Figure 4. CSR variation with GPC added (CSR = f (% GPC))

Analyzing the results is noted that when compared to RB, the better results are until 5% GPC in both particle sizes. From 5% GPC we can observe a decrease in CSR value, but is important to emphasize that GPC thinner in all test had satisfactory results when compared to RB.

The results obtained proved that the particle size has influence in CSR because all GPC thinner results are higher than GPC thicker. It should also be noted that the delta between both particle sizes increase while GPC is added.

3.5. Drum Index (DI)

The DI results are showed in Figure 5.

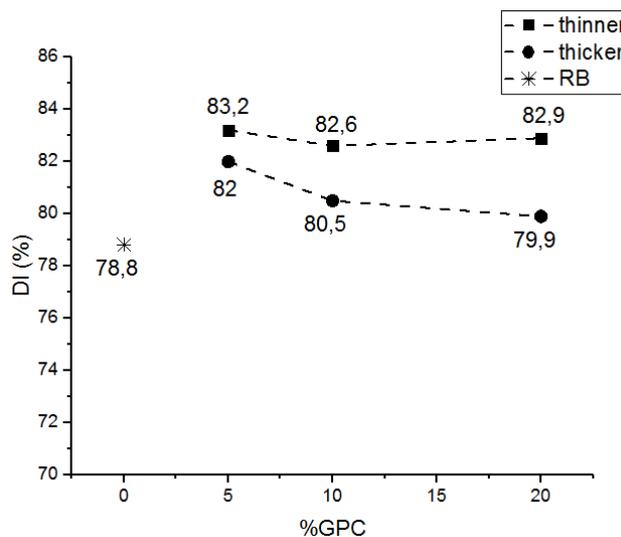


Figure 5. DI variation with GPC added (DI = f (% GPC))

As in the case of CRI, an improvement of DI in all situations was observed, and the best results occurred for 5% GPC. This may have occurred because the blend had a deficiency of inerts, which was filled when 5% GPC was

added. However, when more GPC was added, the amount of inerts that the blend could absorb was extrapolated, reducing the DI value.

3.6. Volatile Matter (VM)

The Figure 6 shows VM as a function of %GPC added.

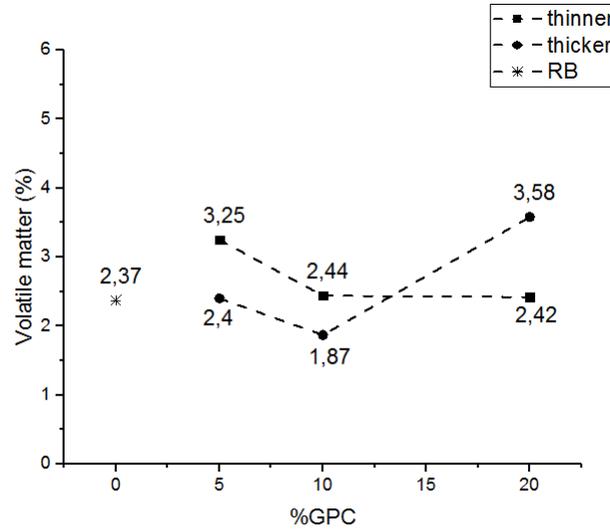


Figure 6. VM as a function of %GPC added (VM = f (% GPC))

From obtained results was possible to observe that occurred the cokemaking of the blend. Before the test, the volatile matter of the blend was approximately 25%. Therefore during the coking process the blend lost approximately 22% of VM, what was expected. We can observe that the VM values does not fluctuated too much, and we can to conclude that the GPC use doesn't influence significantly in volatile matter of metallurgical coke.

3.7. Ash

The Figure 7 shows ash as a function of %GPC added.

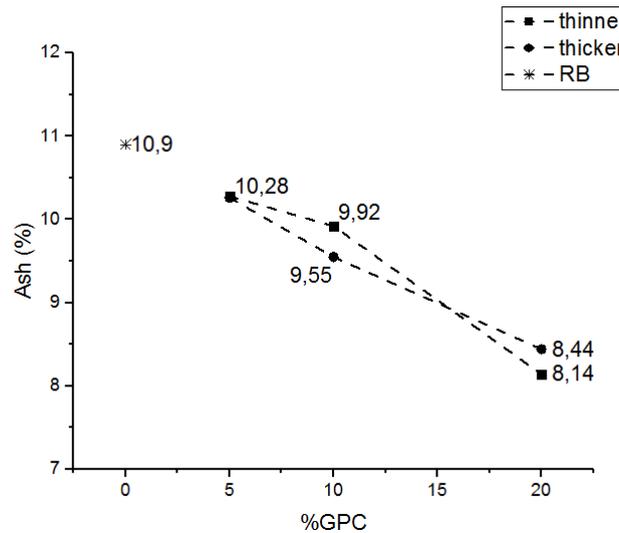


Figure 7. Ash as a function of %GPC added (Ash = f (% GPC))

From these results is notorious an improvement of ash level in all situations, how higher is the %GPC added, lower is the ash level. This was already expected because the ash contained in GPC is much lower than the average ash content of the mineral coals (while the GPC ash is below 0.5%, the average of the coals is 8.5%). With this reduction in

ash level, it is possible to use coals with higher ash level in the same mixture, which represents a cost reduction, since coal with higher ash has a lower price than a mineral coal with lower ash.

3.8. Sulfur

This tests were made in duplicate and the results are showed below in Figure 8.

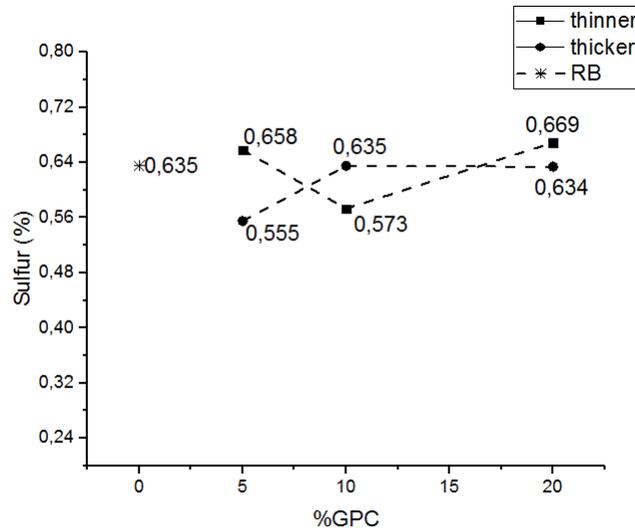


Figure 8. Sulfur as a function of % GPC added (Sulfur = f (% GPC))

It was possible to observe that the use of GPC did not present significant variation in metallurgical coke sulfur, even observing that the behavior of thinner GPC and thicker GPC were opposite. All situations presented sulfur close to blend 1.

As there wasn't change in the sulfur content, another aspect called attention, the sulfur content of the GPC was higher than the mixture, for the sulfur content to remain constant we must have a GPC desulphurization during the coking process. To prove this assumption were realized the same test with now 20kg of blend, using GPC thinner.

Table 5. Desulphurization test

Desulphurization test						
Material	VM (%)	Yield (%)	Sulfur GPC (%)	Sulfur expected (%)	Sulfur Coke (%)	Desulphurization index (%)
GPC thinner	12.63	89.52	0.719	0.803	0.654	16.95
Metallurgical coke with GPC	2.15					

The GPC volatile matter was 12.63% and coke volatile matter was 2.15%. Thus, it was concluded that there was a yield of 89.52% during this cokemaking process. As the sulfur content of GPC was 0.719% and the yield was 89.52%, if there wasn't desulphurization of GPC, it was expected to find 0.803% sulfur in the metallurgical coke obtained. However, this did not occur and the sulfur content found in metallurgical coke was 0.654%, which shows a desulfurization rate of 16.95%.

4. CONCLUSIONS

From the obtained results it was possible to conclude that the GPC is a great additive when used in a smaller particle size. Although the use of GPC reduces the coal blend fluidity, it keeps metallurgical coke quality equal to or greater than metallurgical coke without GPC, even in fractions until 20%. Besides that, the GPC contributes to decreasing the ash content that allows to use coals cheaper than decreasing the coal blends costs.

5. ACKNOWLEDGEMENTS

We would like to thank the steelmaker Gerdau S.A. and the IFMG-Ouro Branco for the opportunity to develop this research in their dependencies and for the technical and financial support.

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