Effect of high petroleum coke additions on metallurgical coke quality and optical texture

Abstract

The objective of the present study was to evaluate the effect of high additions of petroleum coke on the rheological properties of coking coal and the quality of cokes produced on pilot scale at the Usiminas R&D Center. For this purpose, blends using petroleum coke additions of 5%, 10%, 20%, 30% and 40% were produced. The results showed that the blends were able to satisfactorily absorb up to 30% of petroleum coke, keeping the quality (DI, CRI and CSR) similar to the industrial mixture. The observed main textural components were: mosaic, fragmentary, fusite and anisotropic inert. In general, before CRI, cokes showed good cohesion, with the petroleum coke having been absorbed by the coke matrix. After the reaction with CO$_2$, there was verified a preferential consumption of the textures fusite, fragmentary and anisotropic inert due to the Boudouard reaction, besides the deterioration of the interfaces between the petroleum coke and coke matrix. In addition, the results showed that the increase of mosaics contributes to the increase of cokes DI and CSR. Finally, for the coal blend employed, it is suggested the utilization of a maximum of 30% additions of petroleum coke.

Keywords: petroleum coke, inerts, optical texture, cokemaking.

1. Introduction

Metallurgical coke, obtained by carbonizing an appropriate blend of coals at temperatures up to 1100°C is the most suitable reducing agent for the blast furnace. However, decreasing availability of prime coking coals and problems related to supply, have led coking companies to look for alternative raw materials and to redesign blends with lessened properties (Flores et al., 2017). In this scenario, petroleum coke (PC) became an interesting additive to cokemaking because of its properties and availability (Menéndez et al., 1997).

It is often assumed that petroleum coke behaves as inert material in cokemaking; thus, its inclusion in coking blends has an important influence on the properties of metallurgical coals (Alvarez et al., 1995; Zubkova, V. V., 1999). Over the years, petroleum coke has been used in various proportions for the production of metallurgical cokes, ranging from 5 wt.% to 40 wt.% (Menéndez et al., 1996). However, in many cases, it is not clear how and why metallurgical coke properties are affected by the addition of petroleum coke. Contradictory reports concerning the beneficial (Menéndez et al., 1997; Pis et al., 2002; Zorin et al., 2015) or detrimental (BCRA, 1974; Kiran et al. 2013) effect of PC on coke quality can be found in literature.

At Usiminas, Brazil, the use of petroleum coke in coking blends is a practice which started in the 1970s. At the time, due to commercial availability, PC was limited to 5% of the coal blends, substituting low volatile American coals. However, studies carried out at Usiminas R&D center in 2012 indicated the possibility of using values greater than 20% of petroleum coke in coal blends (REIS et al., 2012).

Moreover, in recent years several South American steelmaking companies have successfully increased the additions of petroleum coke in their blends, achieving participations varying around 30 wt.% to 40 wt.%. Despite this, predicting the maximum amount of petroleum coke that can be added beyond which the quality of the metallurgical cokes is impaired is quite difficult. Moreover, most studies dealing with the fundamentals of the petroleum coke effect on coke quality do not investigate such high addition levels.

In this scenario, the present study aimed to determine the limit of petroleum coke additions for an industrial metallurgical coke and investigate the fundamental aspects regarding the influence of petroleum coke over coke quality.
2. Materials and methods

2.1 Raw Materials

Two American coking coals (H and L), two Australian coals (M1 and M2), one Canadian coal (M3) and Brazilian petroleum coke (PC) were selected for the preparation of coking blends for coke production at a semi-pilot scale. All selected coals and PC are available at the international coal market and the Brazilian internal market, respectively. Materials were characterized by proximate analysis (ASTM D7582), ultimate analysis (ASTM D4239) and total sulfur (ASTM D4239). Coals were also analyzed by petrography (ISO 7404/S) and Gieseler plastometry (ASTM-D2639). The main characteristics of the selected coals, classified as high-volatile (H), medium-volatile (M1, M2 and M3) and low-volatile (L), according to ASTM D388, together with the petroleum coke (PC) properties, are summarized in Table 1.

Table 1 - Raw materials main characteristics.

| Coal  | Geographical Origin | Volatile Matter (wt% db) | Ash (wt% db) | Vitrinite reflectance -Rr- (%) |
|-------|---------------------|--------------------------|--------------|------------------------------|
| H     | USA                 | 37.1                     | 7.41         | 0.90                         |
| M1    | Australia           | 20.9                     | 9.36         | 1.22                         |
| M2    | Australia           | 22.3                     | 9.32         | 1.25                         |
| M3    | Canada              | 21.4                     | 9.84         | 1.30                         |
| L     | USA                 | 18.0                     | 4.86         | 1.59                         |
| PC    | Brazil              | 11.1                     | 0.10         | -                            |

Ultimate Analysis (wt% db)

| Coal  | C       | H       | N      | O       | S       |
|-------|---------|---------|--------|---------|---------|
| H     | 78.5    | 5.08    | 1.77   | 6.41    | 1.01    |
| M1    | 80.1    | 4.41    | 1.56   | 4.73    | 0.51    |
| M2    | 79.9    | 4.40    | 1.29   | 5.47    | 0.47    |
| M3    | 80.5    | 4.32    | 1.28   | 3.99    | 0.45    |
| L     | 85.2    | 4.31    | 1.21   | 4.02    | 0.79    |
| PC    | 91.3    | 4.00    | 1.83   | 1.32    | 0.73    |

Gieseler Parameters

| Coal  | Maximum Fluidity -Fmax- (ddpm) | Maximum Fluidity -Fmax- (log ddpm) | Softening temperature (°C) | Fmax temperature (°C) | Resolidification temperature (°C) | Plastic range (°C) |
|-------|---------------------------------|-------------------------------------|-----------------------------|-----------------------|-----------------------------------|--------------------|
| H     | 64997                           | 4.81                                | 380                         | 424                   | 471                               | 91                 |
| M1    | 4.0                             | 0.60                                | 422                         | 448                   | 469                               | 47                 |
| M2    | 6.0                             | 0.78                                | 422                         | 453                   | 482                               | 60                 |
| M3    | 6.5                             | 0.81                                | 427                         | 458                   | 481                               | 54                 |
| L     | 35.0                            | 1.54                                | 440                         | 472                   | 500                               | 60                 |
| PC    | -                               | -                                   | -                           | -                     | -                                 | -                  |

Maceral Composition (vol% mmf)

| Coal  | Vitrinite | Liptinite | Semifusinite | Inertinite | Reactives | Inerts |
|-------|-----------|-----------|--------------|------------|-----------|--------|
| H     | 68.5      | 22.1      | 9.8          | 22.1       | 81.1      | 18.9   |
| M1    | 51.6      | 0         | 32.7         | 48.4       | 62.5      | 37.5   |
| M2    | 45.8      | 0         | 34.2         | 54.2       | 57.2      | 42.8   |
| M3    | 53.7      | 0         | 31.5         | 46.3       | 69.4      | 30.6   |
| L     | 70.3      | 0         | 19.4         | 29.7       | 76.8      | 23.2   |

*Obtained by difference, bSemifusinite was considered as 1/3 reactive and 2/3 inert.
For Canadian coal was considered 2/3 reactive and 1/3 inert.

2.2 Coal blends and carbonization at pilot-scale

To evaluate the effect of PC on coke quality and establish some practical limits, additions at the levels of 5%, 10%, 20%, 30% and 40% were carried out partially substituting the coals majorly responsible for coke quality (H, M1 and M3), while the proportions of coals M2 and L were kept constant. The blend compositions can be seen in Table 2. Additionally, a reference coal blend, industrially applied at Usiminas at the time, was used for comparison. The latter allows evaluating new PC addition limits with changing coal blend composition.
The carbonization tests were carried out using a pilot coke oven (360 mm H x 440 mm L x 250 W) with electrical heating and 34 Kg capacity. The crushed coals (85% < 3 mm for coals H, M1, M3; 90% < 3 mm for coal M2; and 95% < 3 mm for PC) were dosed, blended and charged at a pre-heated oven at 1000°C. During carbonization, the temperature of the walls was maintained constant at 1000°C. The coking time was nearly 9 hours, reaching 960°C in the center of the charge. The cokes obtained were water quenched and subsequently dried at 120°C for 9 hours. After that, cokes were stabilized by three falls from 2 m height using a shatter apparatus. The carbonization tests were carried out in duplicate, with moisture as close as possible to 8 wt% and charge density around 850 kg/m³.

### Table 2 - Relative wt% proportion of coals in the coking blends.

|       | H | M1 | M2 | M3 | L | PC |
|-------|---|----|----|----|---|----|
| Ref.  | 36| 7  | 7  | 7  | 14| 14 |
| PC-5  | 40| 18 | 7  | 20 | 10| 5  |
| PC-10 | 35| 18 | 7  | 20 | 10| 10 |
| PC-20 | 30| 15 | 7  | 18 | 10| 20 |
| PC-30 | 25| 12 | 7  | 16 | 10| 30 |
| PC-40 | 20| 10 | 7  | 13 | 10| 40 |

### Table 3 - Additional classification besides ASTM D5061 regarding organic inerts.

| Component          | Appearance                                      |
|--------------------|-------------------------------------------------|
| Anisotropic Inert  | Anisotropic domain formed from fusinite, semifusinite or micrinite |
| Fusite             | Slightly anisotropic domain from fusinite and semifusinite |
| Fragmentary        | Isotropic or slightly anisotropic domain from micrinite, |
| Petroleum Coke     | High anisotropic large domains                  |

### 3. Results and discussion

#### 3.1 Raw materials quality outline

Considering the characteristics shown in Table 1, coal volatile matter varied between 18.0 wt.% and 37.1 wt.%, with vitrinite reflectance (Rt) from 0.9% up to 1.59%. With respect to maceral composition, coals showed moderate to high vitrinite (45.8 vol% to 70.3 vol%) and moderate to high inertinite (22.1 vol% to 54.2 vol%) contents. Moreover, with the exception of coal H, significant quantities of semifusinite, ranging from 19.4 vol% up to 34.2 vol%, were observed.

Regarding the coal thermoplastic properties, coal H has a quite high maximum fluidity (around 65000 dppm) and a wide plastic range (91°C). Such properties are usually valued by the cokemaking industry due to their higher capacity for absorbing inert materials, such as inerinite, mineral matter and additives like PC. In comparison, coals M1, M2, M3, and L have relatively low maximum fluidity, below the inferior limit of the fluidity window (from 100 dppm to 1000 dppm) established by Miyazu et al. (1974). The latter is accepted as a good parameter for coal blend strategies to obtain coke with sufficient quality. Regarding other technological parameters, coal ash and total Sulfur contents varied from 4.86 wt.% to 9.84 wt.% and 0.45 wt.% to 1.01 wt.%, respectively.

In contrast to coals, PC is accepted to be an inert material, i.e. it does not pass through a plastic stage during pyrolysis. Additionally, PC presents almost no ash, which is always desired for coal blends, especially for blends utilizing high ash coals. According to Diez et al.14, coke ash influences slag volume and composition in the blast furnace. The industrial experience indicates that 1 wt.% decrease of ash in the coke reduces the coke rate by 2 wt.% to 3 wt.. Another advantage of the PC selected is its low volatile matter content (11,1%) and sulfur (0.73%), which is crucial to achieving higher participation levels in coking blends as this allows for
increased productivity.

In order to establish some practical limits for the use of PC in a coke oven battery, the coal blends proposed in Table 2 had the objective of maximizing PC additions, which increases coke/coal yield, also optimizing the proportion of coal H, the major item responsible for the blend’s fluidity. Comparatively, the reference coal blend, with 28 wt% of PC and 35 wt% of coal H, was already achieved at industrial scale and its optimization is aimed.

### 3.2 Pilot scale coke quality

Table 4 presents the quality of the cokes produced at pilot scale. Overall, the better coke was obtained from PC additions of 5 wt.%, resulting in higher cold mechanical strength (DI) and especially lower reactivity towards CO\(_2\) (CRI). The CSR of the coke PC-5 was a little inferior to that of the Reference coke. As the participation of PC increased up to 30 wt.%, all parameters were slightly impaired, although quality still remained within the range of industrial practice (Díez et al., 2002, 2016). Moreover, when PC reached 40 wt.% of participation, coke quality was sharply reduced, especially regarding DI and CSR. These results show that, in comparison to the reference coke, it was possible to obtain good quality coke with the addition of 30% PC in this coal blend, also reducing coal H content from 36 wt.% to 25 wt.% and increasing the participation of coal M1 from 3 wt.% to 12 wt.%.

| Coke   | DI (%) | CRI (%) | CSR (%) |
|--------|--------|---------|---------|
| Ref.   | 85.8   | 18.0    | 67.7    |
| PC-5   | 87.1   | 14.4    | 66.5    |
| PC-10  | 86.3   | 21.3    | 66.2    |
| PC-20  | 85.1   | 23.2    | 63.5    |
| PC-30  | 84.6   | 24.0    | 62.0    |
| PC-40  | 66.0   | 26.5    | 58.1    |

Similar tendencies of coke quality reduction due to the addition of PC were reported by Kiran et al. for additions up to 20%. In contrast to this, Menéndez et al. (1997), Pis et al. (2002) and Zorin et al. (2015) have obtained an improvement of coke quality for similar levels of PC. Thus, the use of PC may affect coke quality differently, depending on a combination of factors, such as the quality of the parent coals, the type of petroleum coke and the levels of additions evaluated. Moreover, no studies utilizing PC in proportions higher than 20%, or superfluid coal like coal H, were found for comparison, which incentivates further investigations. In the present study, it is believed that coke quality and the resultant limit of 30% PC addition were more related to the quality of the parent coals used and the composition of the coal blend, which may have obtained sufficient fluidity to incorporate the PC.

**3.3 Relation between coke quality and coal maximum fluidity**

Usually, metallurgical coke properties depend on several factors, which fall into two categories: the nature/quality of the precursor materials (i.e. coal properties and coal blends) and the parameters of the coking process. Since the cokes were produced using the same experimental conditions, the differences in quality can be majorly attributed to the changes in the coal blends.

The drop of coke quality with PC may be explained, to some extent, by the known negative effect of inerts over the rheological properties of the blends (Guerrero et al., 2015). Figure 1 (a) shows the expected reduction in maximum fluidity of the blends calculated by an additive model based on coals maximum fluidity (log ddpm). From that, a sharp and continuous reduction of maximum fluidity is observed, from 2.4 log ddpm to 1.34 log ddpm, which correlates well with the coke quality parameters measured (see Figure 1 (b)). Such good correlations occur since any variation in the viscosity, temperatures of the plastic interval and/or amount of volatile matter release during the plastic interval affects the final microstructure of the metallurgical cokes (Pis et al., 2002).

![Figure 1](image-url) - (a) decrease of fluidity due to PC addition by additive model, (b) its relationship with coke properties and (c) comparison between actual and calculated maximum fluidity for a binary blend.
If the fluidity window (Miyazu et al., 1974), (2 to 3 log ddpm) would be considered as a quality determining factor, and blends would be limited to about 20% PC additions. However, the utilization limit for PC was experimentally determined to be 30 wt.%. If further amounts of PC would be used, the caking and coking quality of the blend may be improved by increasing the participation of coal H. The inconsistency between the results obtained and the fluidity window may occur due to the additive model (Fig. 1 (a)) disregarding any possible interaction between PC and coal during the plastic stage. Although petroleum cokes are considered inert when submitted to rheological tests, they are not completely inert materials during the plastic stage of a carbonizing blend. The volatile matter released from the PC is able to interact with the fluid matrix in such a way that the agglomeration of the PC particles improves and shows less fissured interfaces than in the case of a completely inert material (Valia et al., 1992; Menéndez et al., 1999). The latter may contribute to smooth the negative effect of PC over coal maximum fluidity. Similar to this, Figure 1 (c) shows a previous investigation comparing the maximum fluidity of binary blends (medium volatile American coal and PC) measured with the Gieseler plastometer and calculated by an additive model. It can be seen that the model overestimates the negative effect of PC on the blend fluidity, always obtaining smaller values than the actual ones. This shows the importance of determining blend properties experimentally, while the models can be used to determine occurring interactions between blend constituents.

### 3.4 Coke microstructure and texture

Since petroleum coke has a great influence on the rheological properties of a given coking blend, coke microstructure and microtexture were evaluated in order to understand the fundamental aspects influencing coke quality. Figure 2 presents the evolution of coke porosity in relation to PC addition and its correlation with coke quality parameters. As expected, coke PC-5 showed the highest porosity among cokes produced due to its higher content of coal H. High volatile and fluid coals, like coal H, usually produce elevated porosities and large pores, which are known to be detrimental to coke mechanical strength (Kubota et al., 2011). Moreover, a reduction of coke porosity can be seen up to 20% PC, however, for higher participation levels a subsequent increase of porosity takes place. Similar results were shown by Pis et al. (2002).

![Image](Figure 2 - (a) evolution of coke porosity due to PC additions and (b) the relationship between porosity and coke properties.)

The initial drop of porosity may be related to the amount of volatile matter released during the plastic stage, which is responsible for the formation of most of the pores (Hays et al., 1976; Smedowski et al., 2013). According to Pis et al. (2002), for coal/petroleum coke blends, the amount of volatile matter release during carbonization is lower than when there is no petroleum coke. With this, the rate of volatile matter release is slower and volatile matter can be incorporated within the plastic matrix in an easier way, contributing to form cokes with higher densification. Otherwise, the effect responsible for increasing coke porosity for PC additions higher than 20% may be related to coke cohesion. As the quantity of PC in the blend increases, two effects occur at the same time: (I) the decrease of the maximum fluidity of the blend (Figure 1) and (II) the increase of inert surface area. If sufficient dilatation is not achieved, the structure formed will have little coherence, producing a weak and friable coke due to the poor contact between reactive and inert particles. This may also increase coke porosity due to the lack of binder phase material, which could explain the sharp decrease in quality obtained for coke PC-40. Besides this, coke porosity has shown quite weak correlations with coke properties (Figure 2 (b)), indicating other parameters may be more significant to coke quality with high inert participation.

In addition to coke microstructure, Table 5 gives the quantification data of the textural components of the coke, before and after, the determination of reactivity towards CO₂ (CRI). In the table, the variation of microtexture due to gasification is compared side by side (Before/After).

![Image](Firstly, regarding the microtexture before gasification, the binder phase (matrix) of all cokes was composed of circular structures. The formation of anisotropic and incipient components, which are usually related to high volatile coals, were not identified. The binder phase of cokes varied from around 75 vol% for coke PC-5 down to 41 vol% for coke PC-40, according to PC participation in the blends. Concerning the filler phase components, similar amounts of anisotropic inert, fusite and fragmentary structures were observed for all cokes, indicating that these structures may be majorly formed from coals M3 (high content of inertinite macerals) and L, which were kept constant throughout the coking blends. Moreover, as expected, the texture component from PC increased in the cokes as its proportion was increased in the blends.

Regarding microtexture after coke gasification (Table 5), a reduction in the proportion of the filler phase with a subsequent increase of binder phase was observed. This indicates that for CRI around 20%, the filler phase is consumed preferentially in the binder phase. Additionally, according to several authors, the size of texture domains has a direct
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The influence of petroleum coke on the reactivity towards CO₂ (Smedowski et al., 2013). With this, since circular components alone formed the matrix of the cokes studied, which have relatively narrow size range (from 0.5 μm to 2 μm), changes in CRI and CSR may be more related to the proportions of binder and filler phases. Besides this, PC reactivity towards CO₂ was also relatively low, since its volume percentage increased after reaction due to the consumptions of other inerts. Thus, among the different inert components observed, those formed from coals (anisotropic inert, fusite and fragmentary) may have a greater influence on CRI and CSR when compared to PC.

Table 5 - Texture components (vol% mmf) for coke samples (results Before/After gasification).

| Metallurgical Cokes | Binder Phase (vol% mmf) | Filler phase (vol% mmf) |
|---------------------|-------------------------|------------------------|
| PC-5                | 74.8/81.9               | 6/3.9                  |
| PC-10               | 66.9/78.5               | 6.2/2.1                |
| PC-20               | 59.5/64                 | 6.6/2.1                |
| PC-30               | 48.9/56.9               | 5.3/1.5                |
| PC-40               | 40.7/47.5               | 6.8/0.7                |

Figure 3 presents the relationship between the coke properties and the amount of binder and filler phase obtained by the microtexture analysis. Good correlations were observed for all technological parameters, in special for CRI and CSR, with lower volumes of the binder phase being prejudicial to the coke quality. It is interesting to see that the sharp decrease of cold mechanical strength (DI) occurred at the point where the proportion of binder phase became smaller than the filler phase. This shows the fundamental importance of the coke matrix to develop good quality coke, also corroborating the results shown in Figure 2 (b). When the relationship between the binder and filler phase becomes too low, the quality of the binder phase needs to be enhanced in order to absorb and sustain such high inert additions. However, the negative effect of PC on blend fluidity complicates the task, indicating that optimal adjustment of the coal blend needs to be carried out in order to further increase the additions of PC for coke production. In addition to that, the substitution of coal M2 in the blends may be quite beneficial to coke quality, since this coal presents a high quantity of inertinite macerals, which showed to be worse than PC for coke quality.

Figure 3 - Correlation between coke properties with the volume of (a) binder phase and (b) filler phase.

4. Conclusions

The influence of petroleum coke on the quality of cokes produced on a pilot scale and the fundamental aspects involved in the evolution of the coke properties were investigated.

The limit of utilization for PC in the coking blends proposed, also targeting the reduction of coal H₂, was determined to be 30 wt.%, with the blend having the capacity to incorporate PC in its structure. Further additions sharply impaired coke quality due to the lack of sufficient fluidity to incorporate such a high proportion of inert material. The latter also negatively influenced coke porosity and cohesion, although porosity showed quite poor correlations with coke properties.

Furthermore, the overall changes in coke quality were accessed through the blend’s maximum fluidity and coke’s microtexture, which showed high correlations to coke’s structural strength (DI) and reactivity towards CO₂ (CRI). The petroleum coke, being an inert material, highly impaired coal fluidity, although some interaction with coal can occur due to PC volatile matter release, which smooths its negative effect.

Moreover, no major influence of PC on the type of coke texture was observed. All coke matrices (binder phase) were
formed by circular textural components, whose proportion reduced as the participation of PC increased. Additionally, coal inerts revealed to be more reactive towards CO₂ in comparison to PC, being consumed first. The latter, together with the negative effect of PC in coke structure and cohesion may be determinant to achieve the CSR requirements for the blast furnace.

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