Original Article

Influence of pellets quaternary basicity on softening and melting properties

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Abstract

The softening and melting zone is deemed the most critical region within a blast furnace. It is in this region that iron ore commences its softening and melting process, thereby obstructing the flow of ascending gases. The formation of a liquid phase within the ore or agglomerate, a phenomenon referred to as exudation, is intricately complex and strongly tied to the chemical composition of the burden material. Despite the challenges in replicating the conditions of the softening and melting zone at a laboratory scale, numerous studies have endeavored to establish a correlation between these chemical characteristics of the burden and its metallurgical properties. Through an extensive series of pellet tests, an investigation was conducted to determine such correlations taking into consideration the VALE's Ferrous Technology Center database. The findings revealed that quaternary basicity serves as the most accurate predictor variable for describing the softening and melting properties of the pellets. This study supports the existing literature, suggesting that burdens with higher basicity exhibit a higher softening temperature and, consequently, a greater degree of indirect reduction. Conversely, more acidic pellets demonstrated a lower softening temperature, coupled with an extended softening interval. In conclusion, it was discovered that burdens with higher basicity also yielded lower maximum pressure values and pressure drop areas.

Keywords: Iron ore; Softening; Melting; Blast furnace.

1 Introduction

The Blast Furnace (BF) is a system designed to obtain primary iron in the form of hot metal by means of high temperature and a reducing atmosphere rich in CO gas. The BF reactor can be divided into some zones such as: the granular, cohesive, dripping, raceway and hearth zones. The cohesive zone is responsible for the higher pressure drop inside the blast furnace, and it is also in this zone where the softening and melting of the metallic burden occurs [1].

The softening and melting zone is below the granular zone and is determined by the softening start temperature and the final melting temperature of the metallic burden. Due to the fact that the ferrous materials are in a physical transition from solid to liquid phase, this region establishes a high resistance to the gases flow, being responsible for a high-pressure loss in the blast furnace column [2]. So, this zone can determine the BF performance according to its thickness, shape and position. A comprehensive knowledge of the shape and position of the zone is essential for the BF operation, as these factors directly impact the fuel consumption, gas flow, burden displacement and kinetics of chemical reactions.

Until now, tests for analyzing the behavior of metallic burden at high temperatures are not completely standardized. There are few centers that have proper laboratory or pilot scale equipment's able to simulate the softening and melting zone. Usually, organizations that have this kind of equipment present their own methodologies according to their technical and operational culture [3]. However, several works [4-12] that have tried to correlate the results of softening and melting tests with theoretical aspects of the burden can be compared and studied. Most of them aimed to understand the exudation mechanism and liquid phase generated from the ferrous burden during the melting and based their analysis and findings from properties such as burden porosity and chemical quality.

The understanding of the softening and melting behavior of pellets in a blast furnace is crucial for optimizing blast furnace operations and improving overall performance. In a study conducted by Mikko Iljana and his team at the University of Oulu, they used computational thermodynamics to study the softening behavior of blast furnace pellets [13]. They found that the main slag-forming components (SiO_2, MgO, CaO, and Al_2O_3) significantly impact the formation of liquid phases. By altering the chemical composition of a commercial acid pellet, they suggested several practical means for postponing liquid formation at higher temperatures. These include reducing the SiO_2 content, increasing the MgO content, reducing the Al_2O_3 content, and choosing suitable CaO contents for the pellets. Another study observed the interaction between pellets at high temperatures under load [14]. The results showed that the looser the structure was, the better the reducibility will be. The compact structure and good reducibility led to a high expansion rate [15]. This suggests that the physical characteristics of the pellets, such as their structure and reducibility, can significantly influence

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their softening and melting behavior. Moreover, a study on the effect of MgO content in sinter on the softening–melting behavior of the mixed burden based on fluxed pellets showed that a low MgO content in sinter is conducive to reduce the MgO content in blast furnace slag. When the MgO content increased from 1.31% to 1.55%, the melting temperature of sinter increased to 1521°C [16].

In this context, the present work aimed to present a critical analysis about a database of softening and melting Vale's tests of pellets correlating the parameters obtained with the chemical quality of the pellets, more specifically their quaternary basicity.

2 Development

2.1 Softening and melting test procedure

The database that was used in the work came from the results obtained with the Vale's Softening and Melting apparatus installed at the Ferrous Technology Center (CTF) in Nova Lima, Brazil. This device is based on two Tamman type furnaces, the upper one with a power of 45 kW and the lower one with 55 kW.

In the lower part, the gaseous compound is preheated and inserted into the upper furnace, which is capable of reaching a maximum temperature of 1700 °C. The sample is fixed in the center of the upper furnace, where it is exposed to the thermal profile as showed in Figure 1. Each furnace has a thermocouple, and in addition there is a thermocouple located inside the piston that compresses the sample. Each oven is particularly supervised by a PID (Proportional Integral Derivative) that is related to the cascade control.

The sample is placed in the middle of two layers of coke in a graphite crucible (100mm in diameter and 180mm in height) which is situated in the center of the upper furnace. The sample fraction is determined by the height of the sample in the crucible (70 mm) and the density of each material. Each layer of coke has a thickness of 20 mm and the bottom of the crucible is designed for the dripping of the molten material.

Initially, the sample is heated in a nitrogen environment at a flow rate of 34 NL/minute at a heating rate of 10 °C/minute until reaching a temperature of 800 °C. Upon reaching the temperature of 800 °C, a pressure of 98 kPa is imposed on the sample and the injection of the reducing gas begins (CO = 29.5%, H_2 = 3.5% and N_2 = 67.0%), also at a flow rate of 34 NL/minute. Upon reaching 1000 °C the heating rate of the upper oven is reset to 5 °C/minute and heating continues until reaching 1600 °C. The lower furnace continues at 10 °C/minute up to 1700 °C. From the temperature of 800 °C onwards the outlet gas is constantly evaluated allowing continuous determination of the degree of reduction of the sample. A system makes it possible to monitor the displacement of the graphite piston, marking the shrinkage of the softening and melting stages.

At the end of the process, the material is dripped into molds on the turntable, located in the lower region of the equipment. The spin starts automatically as soon as the first drop is detected.

The information that is monitored during the test is: lower and upper oven temperature, sample temperature, drip temperature, gas mixture inlet flow, exhaust gas composition, sample contraction, sample pressure drop, sample mass and sample degree of reduction. In the results of the Softening and Melting test, different parameters referring to the burden are reported, as can be seen in the Table 1.

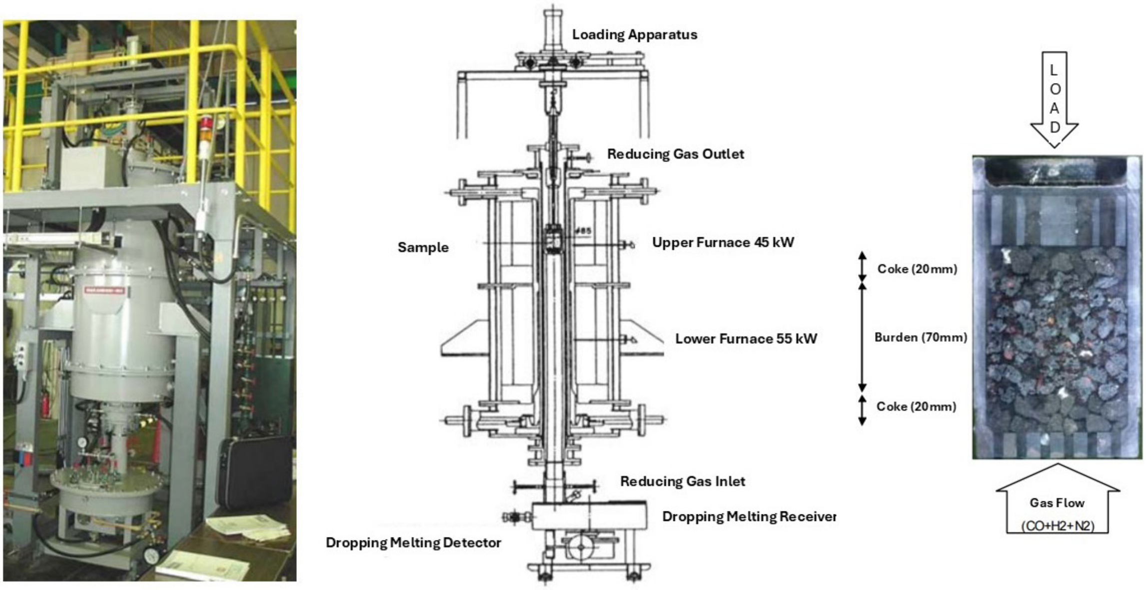

Figure 1. Vale's Ferrous Technology Center softening and melting furnace.

Table 1. Chemical analysis of ores and mixture evaluated in the study.

Parameters	Description
R1000 (%)	Reduction degree at 1000 °C.
R1100 (%)	Reduction degree at 1100 °C.
R1200 (%)	Reduction degree at 1200 °C.
Area S (kg°C/cm²)	Area under the pressure drop curve.
Rs200 (%)	Degree of reduction when a pressure drop of 200 mmH_2O is reached. Total indirect reduction.
Ts200 (°C)	Temperature when a pressure drop of 200 mmH_2O is reached. Beginning of the cohesive zone.
dT (°C)	Difference between Ts200 and Te200.
Te200 (°C)	Temperature when a pressure drop of 200 mmH_2O is reached again. End of cohesive zone.
Td (°C)	Dripping temperature.

Based on the CTF's procedure, softening, and melting tests are performed in duplicate for each sample. When the results obtained in tests "A" and "B" diverge beyond the expected coefficient of variation for each parameter, then a test "C" is performed, and the final result is obtained by the median of the three tests. When the additional test is not required, the final result of each sample is given by the average of the "A" and "B" results.

2.2 Database refining

The database used in this study covers all softening and melting tests ran in CTF based on single burden composed by pellets from 2010 to 2019.

The database was prepared in Excel® from 2010 to 2019 with the results of all tests performed, the database contains sample names, year of tests, sample chemistry, binary basicity, quaternary basicity, and the output parameters from each experimental point (appendix).

After consolidating the database, Minitab® program was employed to support the correlations analysis considering the chemical constituents with the response variable (output parameters of the softening and melting test). In Minitab®, the fitted line plot was utilized, which includes three lines: the regression line, the confidence interval, and the forecast interval. The points of the results align with the regression lines. In the first approach was observed that in some cases the points were outside the limits of the lines shown in the graph, these points it can be called "outliers" [17].

Any statistical analysis that has analyzed a real data set is likely to encounter outliers. The ill-considered explanation of an outlier would be an observation of "a point out of the curve".

One of the mechanisms for identifying outliers is the data that arise from two distributions. The first is the basic distributions, where it generates "good" data distributions, and the second is the contaminating distribution where it generates the contaminating data called outliers [18,19].

After analyzing the fitted line plots, it could be possible to identify outliers that had significant impacts on the results. To address these outliers, it was opted for the approach of excluding them from the data sample.

Finally, after treating all outliers and re-analyzing the graphs, we noticed that several chemical constituents did not have a strong correlation. On the other hand, it was observed that quaternary basicity carried a well fit correlation and then we focused on it to explore the results and understanding.

3 Results and discussion

The original database of single burden composed of pellet softening and melting results contained 139 results. Initially, a simplification of data was made from the consolidation of results from the same pellet (chemical quality) and later in function of the outliers found, as mentioned in the methodology chapter.

The graphs in the figures below demonstrate the results of the softening and melting test that made up the strong correlations with the quaternary basicity. It is possible to verify that the R^2 values were not so high, and this can be explained by the fact that there are other parameters, in addition to the quaternary basicity, that also play an important role in the softening and melting mechanism. Other factors that can be mentioned in this case: the product porosity, the mechanical strength of the agglomerate, the microstructure and the morphology of the iron ore.

Figures 2 and 3 present, respectively, the parameters of Ts200 and Rs200 for the pellet samples according to the quaternary basicity. It can be noted, as the basicity increases, the softening temperature also increases and, consequently, the Rs200 raises up. This is because a higher softening temperature means that the material will have more time to reduce in the granular zone, leading to a greater indirect reduction. This may be related to the possible formation of compounds that have a high melting point, as the content of basic oxides increases. These new phases such as dicalcium silicate (Ca_2SiO_4) or periclase can be easily formed due to this low Gibbs free energy. On the other hand, with the presence of acidic oxides such as SiO_2, the fayalite form tends to have a low melting point and contributes to the premature start of the softening of the burden. These results noted in this study are aligned with other literatures. For example, Ritz et al. [4], studied the effect of ternary basicity (B3) on softening and melting properties, concluding that the correlations between the ternary basicity (B_3) and the beginning of softening temperature, the end of melting temperature and permeability

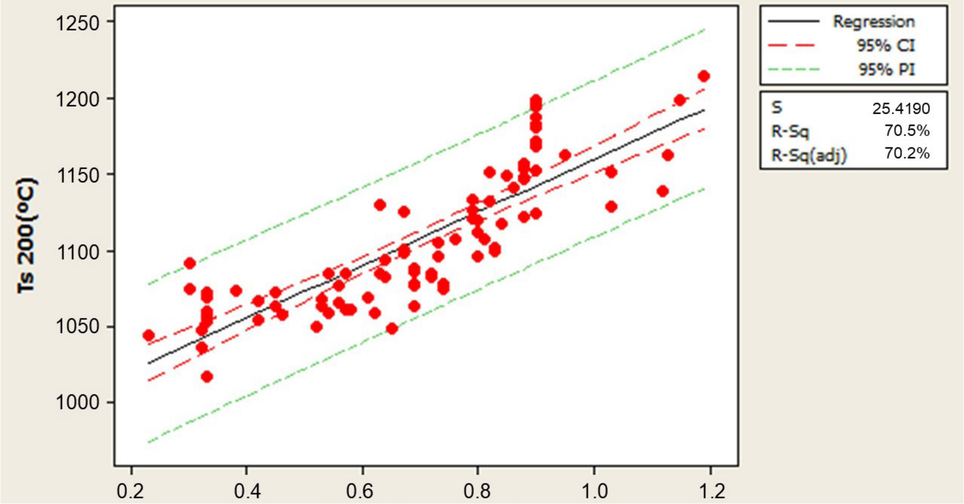

Figure 2. Correlation between the start of softening (Ts200) and the Quaternary Basicity.

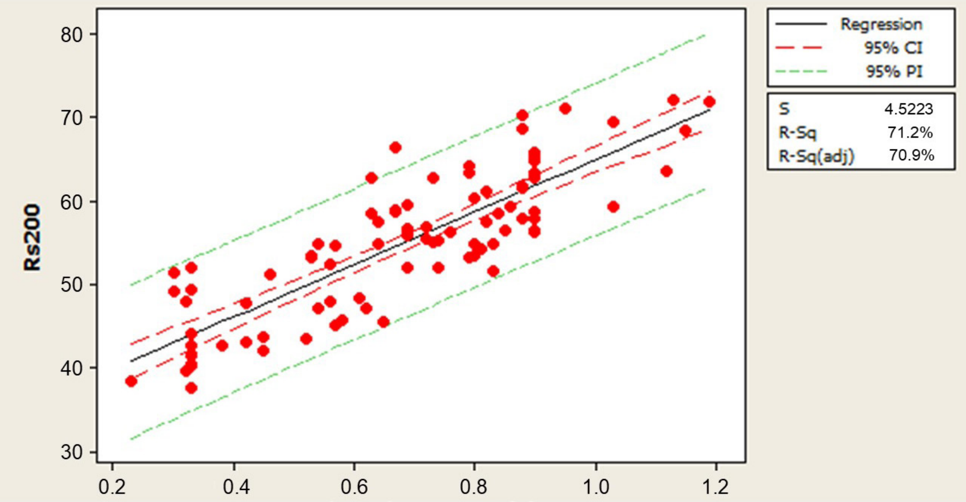

Figure 3. Correlation between the Rs200 and the Quaternary Basicity.

in the cohesive zone are directly proportional. Besides that, according to Nogueira [9], the FeO-CaO-SiO_2-Al_2O_3-MgO system presents a larger solid region as the MgO content increases due to its characteristics whose melting point is significantly higher.

Equations 1 and 2 show, in order, the expressions of the lines that represent the variation of the parameter Ts200 and Rs200 as a function of quaternary basicity (B_4):

$$Ts200(°C) = 986.4 + 172.8 * B_4 \quad (1)$$

$$Rs200(\%) = 33.6 + 31.3 * B_4 \quad (2)$$

Figure 4 shows the variation of the dT parameter as a function of quaternary basicity. This parameter can be understood as the limits of the cohesive zone, as it is estimated based on the difference between the temperatures of Ts200 and Te200, which symbolize in the test, respectively, the temperature of beginning and end of softening and melting of the burden. As can be seen in Figure 4, the higher the quaternary basicity, the lower the dT of the test. This result reflects the trend of basic burdens to start softening later than acid pellets. The value of Te200 does not vary much as a function of basicity, as it is expected that all slag phases that may be formed in the system are already liquid around 1350 °C. However, Figure 5 demonstrates a slightly higher final melting temperatures for acid pellets, which may be due to the formation of more complex slag phases with the dilution of Al_2O_3. Khaki et al. [11] also found a similar trend where the fluxing pellets with high CaO and MgO content tends to reduce the dripping

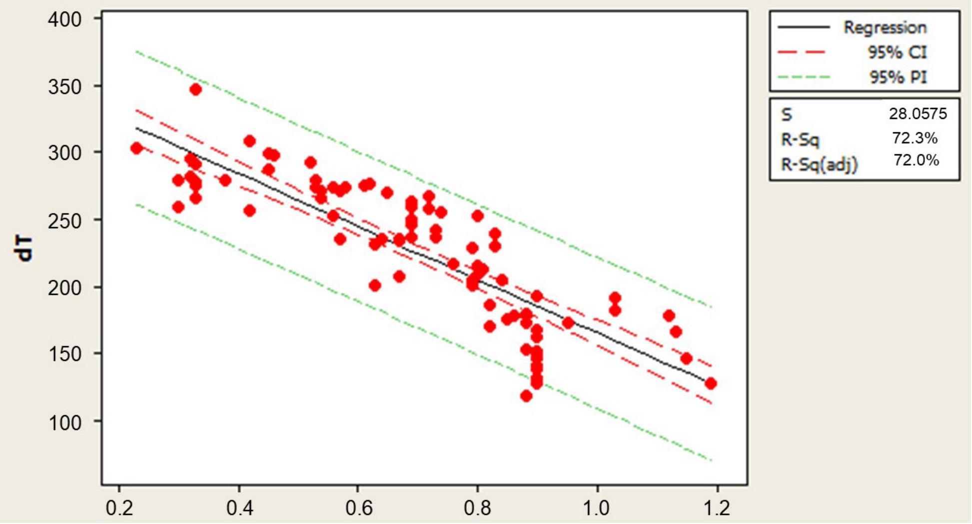

Figure 4. Correlation between the delta T (dT) and the Quaternary Basicity.

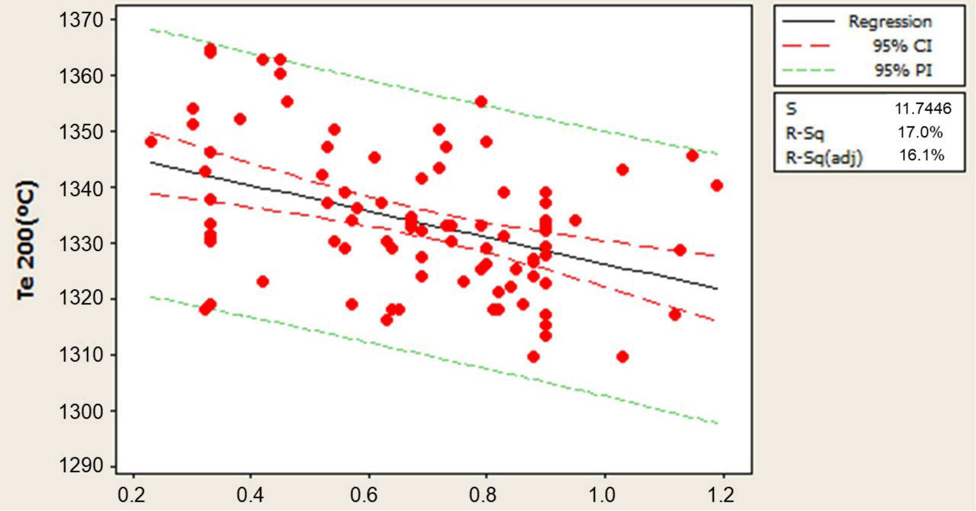

Figure 5. Correlation between the Te200(°C) and the Quaternary Basicity.

temperature. Clixby [12], pointed that the acidic burden presented an interval from softening to final melting higher than the other materials.

Equation 3 presents the expression that represents the variation of the parameter dT as a function of quaternary basicity (B_4):

$$dT = 364.4 - 199.5 * B_4 \tag{3}$$

The maximum pressure drop (dPmax) and Area S variation graphs are shown in Figures 6 and 7 and corroborate all the results of the other parameters. It is pointed that the higher the quaternary basicity, the lower the value of Area S and the lower the dPmax. As the pressure loss phenomenon is directly linked to the amount of liquid phase formed as well as its distribution in the burden bed, it was to be expected that the acid pellets that have a greater temperature range and softening and melting interval would present the highest values of dPmax and Area S.

Equations 4 and 5 show, in order, the expressions that represent the variation of the parameter dPmax and Area S as a function of quaternary basicity (B_4):

$$dPmax\left(mmH_2O\right) = 7777 - 4578 * B_4 \tag{4}$$

$$Area\ S\left(kg\ °C / cm^2\right) = 142.0 + 127.6 * B_4 \tag{5}$$

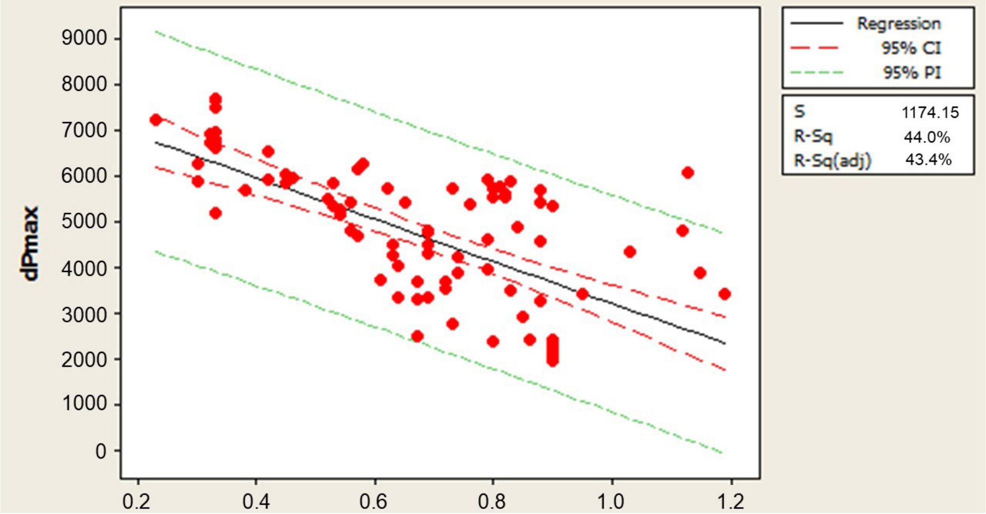

Figure 6. Correlation between the dPmax(mmH_2O) and the Quaternary Basicity.

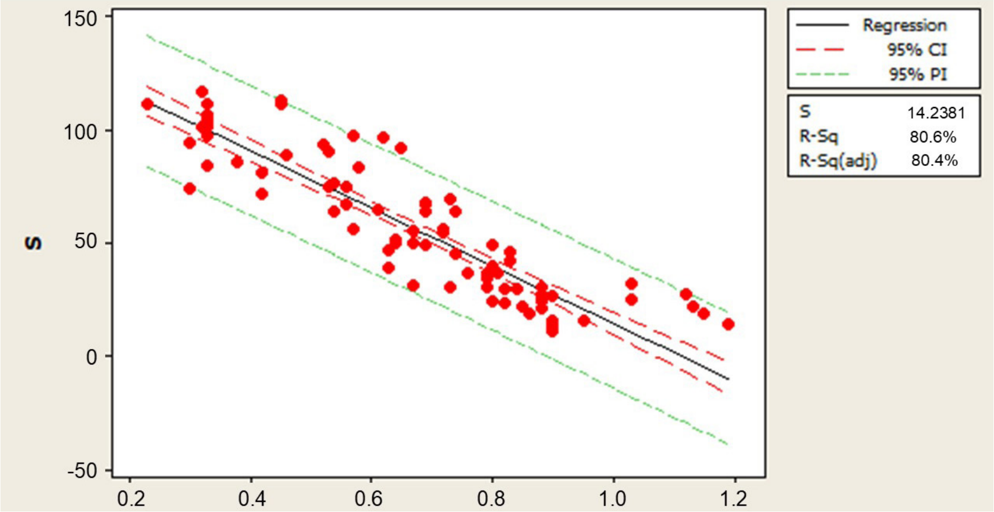

Figure 7. Correlation between the Area S(kg°C/cm^2) and the Quaternary Basicity.

4 Conclusions

The study of the softnening and melting results from pellets burden in Vale's database were in accordance with the literature on the subject. Based on these tests, some observations were made:

- Pellets with high quaternary basicity showed greater resistance to start softening which implies in a higher reduction degree before the melting when compared to the acid pellets. Therefore, pellets with higher quaternary basicity presented a higher Ts200, Rs200 and a smaller Area S and dPmax. These kind of materials are more rich in CaO and MgO compounds which tend to show a higher liquidus temperature what can explain its later starting of cohesive zone. According to the literature this can be related with the mainly compounds with SiO_2 and Al_2O_3 in systems with FeO reaching low melting points.

- The properties found in the high basicity pellets as high Rs200 and Ts200 and low area S and Dp máx. tend to contribute to a greater reduction of iron oxide, which potentially reduces fuel consumption, due to the direct reduction of iron oxides. Besides that, with this better cohesive zone formation is expected a good permeability and stability of the blast furnace.

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