Behaviour of biofuel addition on metallurgical properties of sinter

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Blast furnace gas yield is essentially controlled by a gas-solid reaction phenomenon, which strongly influences hot metal manufacturing costs. As a result of rising prices for reducing agents on the international market, Companhia Siderúrgica Nacional decided to inject natural gas into its blast furnaces. With more gas inside the furnace, the burden permeability became even more critical. To improve blast furnace gas yield, a new technological approach was adopted; raising the metallic burden reaction surface. To that end, a special sinter was developed with permeability being controlled by adding micropore nucleus forming agents, cellulignin coal, without, however, degrading its mechanical properties. This paper shows the main process parameters and the results from physicochemical characterisation of a sinter with controlled permeability, on a pilot scale, compared to those of conventional sinter. Gas flow laboratory simulations have conclusively corroborated the positive effects of micropore nucleus forming agents on enhancing sinter permeability.

Keywords: Sinter, Permeability, Cellulignin

Introduction

The blast furnace process is characterised essentially by the gas-solid reaction phenomenon. The metallic burden, in Companhia Siderúrgica Nacional (CSN)'s specific case, consists of ~70% sinter and 30% iron ore. At the same time, a CO gas flow, produced in the furnace lower area, combustion zone, rises to the furnace top, in a countercurrent flow. CO gas is generated from the reducing agents, metallurgical coke, charged into furnace top, and coal fines, injected from tuyères, which react with hot wind blown through the tuyères.

In this connection, one of the most important process parameters is the blast furnace gas (BFG) yield \( \eta \)-CO, which describes the extent to which BFG reducing power is being used, i.e. it tells us about the gas-solid reduction reactions. Essentially, as it is a gas-solid reaction phenomenon, gas yield is drastically impacted by the reaction kinetics, raw material reactivity in a reducing atmosphere, and furnace burden permeability, which in turn, depends upon raw material intrinsic permeability, degradation strength and burden distribution pattern.

The main cost components for hot metal production in a blast furnace are the reducing agents, i.e. coke, small coke and coal. For this reason, biomass such as sawdust can be introduced to successfully meet the challenges for increased demands in energy consumption while, at the same time, stabilising and/or reducing the greenhouse gas emissions of the metallurgical industries. Particularly over the last couple of years, reducing agent prices have soared, driven by a rising demand from the steel industry. Metallurgical coke price, for example, rose from some $70/t to over $500/t. Against this backdrop, achieving high BFG yield became a crucial factor for steelmakers to remain competitive.

According to CSN operational data, a 1% increase in BFG yield corresponds to a 7 kg reduction in coke rate (kg coke/tonne iron). In CSN’s case, whose annual output hovers ~5.35 m t⁻¹ per year hot metal, this represents annualised savings of ~$18.7m.

Typical BFG yield ranges from 45 to 52%. Higher figures would require a new technological approach.

The purpose of this project is to enhance sinter permeability, which accounts for ~70% of CSN blast furnace burden, without degrading its mechanical properties. It is also aimed at improving gas yield (\( \eta \)-CO) while cutting down on reducing agent consumption.

The aim is to produce a sinter with high specific surface area, preserving its mechanical properties, while ultimately enhancing reaction surface with CO flow during iron making. This is a particularly interesting solution because, with the increased gas volume by using natural gas, burden permeability becomes crucial.
Materials and methods

Micropore nucleus forming agents

The first phase of the study consisted of selecting the raw materials to be added to the blend, with a view to generating micropores in the sinter microstructure, micropore nucleus forming agents.

Just like conventional insulating refractory manufacturing process, these raw materials ought to be burned during sintering process, thus forming a micropore structure with controlled, uniformly distributed sizes, to increase the sinter permeability, without, however, degrading its mechanical properties. In this connection, particular attention should be paid to combustibility features as well as maximum particle size. There is also a need to specify materials with low volatile matter content to protect the electrostatic filter of the dedusting system. Conversely, in view of blast furnace process constraints, phosphorous, sulphur, zinc and alkali levels should be kept to a minimum.

As a result of the aforesaid characteristics, coupled with the need to lower costs, a cellulignin based coal supplied by the Department of Materials Engineering, Faenquil, was picked.

Cellulignin is a carbonaceous material, which stems from acid prehydrolysis of organic matter: wood, bark, bagasse and organic waste. This is a low cost, renewable raw material Biomass–Energy–Mass (BEM) Programme.2–4

To minimise impurities, the cellulignin used to was produced by 100% wood prehydrolysis, with potable water, and without later scrubbing. The coal, which was obtained at a later stage from cellulignin, was produced by carbonisation in a nitrogen atmosphere at a temperature of 400°C, the reason being the need to reduce volatile matter to a level commensurate with sintering process. The coal in question was obtained by using low temperature conversion (LTC) from wood residues.

Blend to be sintered

Blend raw materials, i.e. sinter feed, sinter fines (undersised, FSD), dolomite, limestone, coke breeze and lime, were thoroughly examined by means of the following laboratory techniques: screening, mercury porosimetry, helium picnometry, BET (specific surface area), chemical analysis, X-ray diffraction (XRD), SEM/EDS, and thermogravimetric and thermodifferential analysis.

Sintering pilot unit

To evaluate the addition efficiency and the effect of micropore nucleus forming agent, cellulignin coal, on sinter permeability and quality, sinter batches totalling 110 kg were produced on a pilot plant in a research department of CSN. Table 1 shows the CSN standard blend to be sintered, which was used as a reference parameter. Formulations were prepared ranging from the main sintering process parameters on a trial basis were determined as follows:

(i) sinter product yield (over 6.35 mm)/total sinter
(ii) blend yield
(iii) productivity (kg sinter product/min).

Sinter quality

The main metallurgical properties for the sinter produced on a trial basis were determined as follows:

(i) tumbler strength, reference standards: JIS-8712, ASTM-E-279
(ii) shatter test strength, reference standard: JIS-8711
(iii) reduction cegradation index (RDI) measures sinter fines generation in reducing medium, reference standards: ISO-4696-2 and ISO-3082-150

Furthermore, the sinter produced was also characterised in terms of chemical composition, specific surface area (BET), microstructure (SEM) and mineralogical composition (XRD).

Gas flow simulations

To directly evaluate the efficiency of micropore nucleus forming agents to increase sinter permeability, gas flow simulations were conducted at room temperature.

Results and discussion

Raw material characterisation of blend to be sintered

Chemical analysis

One of the factors to be highlighted in the chemical analysis of the granulometric fractions, picked from a number of raw materials, is the high silica concentration in sinter feed fine fraction, 0.106 mm and below. SiO2 content in these fractions amounted to 10%, i.e. 3–5% higher than those found in the other fractions. This may be ascribed to silica being less hard, which is more easily comminuted during ore dressing, thereby prompting a decline in Fe2O3 content between the granulometric fractions (Fig. 1).

Mercury porosimetry and helium picnometry

The combination of mercury porosimetry and helium picnometry techniques enabled an in depth characterisation of sinter pores. The intent was to combine raw materials used in the steel industry with those techniques
conventionally used in ceramic material study. Fundamental concepts, such as open porosity, closed porosity, pore surface area, structural specific mass, actual specific mass, etc. allow us to infer and correlate the dependence involving raw materials, process and final product.

The actual specific mass of sinter feed is $5.07 \text{ g cm}^{-3}$. Again, one should note the low values for the actual specific mass of sinter feed fine fractions $0-106 \text{ mm}$ and $<0-106 \text{ mm}$, equal to $4.52$ and $4.80 \text{ g cm}^{-3}$, respectively, compared to those of coarse fractions, which amount to $\sim 5.00 \text{ g cm}^{-3}$. As mentioned earlier, such results are due to the higher SiO$_2$ concentration, low density phase and, therefore, lower Fe$_2$O$_3$ concentration, high density phase, in these finer fractions of sinter feed, i.e. silica density: $2.56 \text{ g cm}^{-3}$; haematite density: $5.24 \text{ g cm}^{-3}$.

Figure 2 clearly shows the correlation between actual specific mass and iron oxide concentration in the various sinter feed fractions.

Regarding pore structure, there seems to be no significant difference between the various granulometric fractions of a single raw material, i.e. all of them follow the very same typical distribution standard for pore size and have similar actual, structural and apparent specific mass. In other words, ore dressing does not change pore distribution, pore structure is an intrinsic characteristic of each raw material.

**X-ray diffraction**

According to XRD results, sinter feed consists essentially of haematite, Fe$_2$O$_3$, and as minor phase quartz, SiO$_2$. Bearing out chemical analysis and helium pycnometry results, quartz presents the most intense fraction in sinter feed fine fractions, $0-106 \text{ mm}$ and $<0-106 \text{ mm}$ (Fig. 3).

Sinter fines consist essentially of haematite phases, Fe$_2$O$_3$, and magnetite, Fe$_3$O$_4$, and as secondary phases, monosilicate of calcium, CaSiO$_3$ and iron and calcium silicate CaFeSiO$_4$. These results are in line with the literature.

There seems to be no variation in the mineralogical composition of several fractions involving limestone and dolomite. According to X-ray diffractograms, limestone has in its main phase calcite, calcium carbonate, CaCO$_3$, and dolomite phase traces, double carbonate of calcium and magnesium, CaMg(CO$_3$)$_2$. Conversely, dolomite has in its main phase CaMg(CO$_3$)$_2$, and calcite traces, CaCO$_3$.

It is not economically viable to use the characterisation techniques mentioned earlier for raw material receiving control purposes. In addition to being costly, they require specialised personnel and are very time consuming in terms of sample preparation and char-
Characterisation of sinter produced on pilot scale

Yield

Table 3 shows the yield for a number of blends sintered on a trial basis.

It was found that by adding 0.5% cellulignin to the standard blend there was a 4.6% increase in sinter product/total sinter yield, while blend yield rose by 3.36%. Conversely, replacing 0.5% of coke breeze, which is a commonly used fuel, by cellulignin coal, there was a 5.41% decrease in sinter product/total sinter yield, while blend yield declined by 5.66%

Adding 0.5% cellulignin coal to the standard blend led to a 0.29% productivity increase. Conversely, replacing 0.5% of coke breeze by cellulignin coal caused productivity to drop by 0.73%. These results show that adding cellulignin coal to the standard blend to be sintered may be a good strategy to boost sintering productivity. Nonetheless, as we will discuss next, one should not lose sight of the effect that this additional fuel has upon the quality of the sinter to be produced. Depending on the characteristics of this fuel, the effect may adversely impact product’s quality.

Shatter, Tumbler, RDI and RI

Table 4 shows sinter test results for shatter, tumbler, RDI and RI.

It is interesting to note that adding cellulignin coal as extra fuel to the standard blend was also beneficial to product quality. By adding 0.5% cellulignin coal there was a 7.55% increase in the shatter sinter result and 0.94% for tumbler, i.e. increased tumbler strength and less sinter degradation. On the other hand, replacing 0.5% of coke breeze by cellulignin coal resulted in a 0.40 and 3.46% drop in the sinter results for shatter and tumbler, respectively.

In line with shatter and tumbler results, adding 0.5% of cellulignin coal reduced sinter RDI by 2.01%, while replacing 0.5% of coke breeze by cellulignin resulted in a 3.01% increase.

As one might expect adding cellulignin coal as extra fuel, resulted in sinter R1 being increased, i.e. mass loss increases by 0.89% for 0.5% cellulignin coal addition. Conversely, replacing 0.5% of coke breeze by cellulignin coal caused sinter R1 to drop by 4.90%. This result shows that cellulignin coal has a greater reactivity when compared to that of coke breeze. As cellulignin coal has a faster reaction, i.e. it burns more quickly; blend residence time under reducing atmosphere is lower. Hence, one can lessen reaction intensity of iron oxide reduction by CO and, therefore, reduce oxygen mass loss.

Chemical analysis

The sinter produced showed similar chemical composition and slag volume (%CaO+ %SiO2). Adding 0.5% cellulignin coal as additional fuel caused a 0.20% rise in FeO content.

On the other hand, replacing 0.5% of coke breeze by cellulignin coal led to a 0.60% drop in FeO content (see Table 5).

Scanning electron microscopy and energy dispersive spectroscopy

Figure 4 shows the microstructure of the sinter, composition image, coupled with X-ray mapping of silicon, calcium and iron.

As one can see, the aggregates, lighter phase, are iron and oxygen rich, consisting basically of thick, nucleus forming particles of sinter feed. In the matrix, silicon, calcium, iron and oxygen coexist, signaling the formation of calcium silicate phases, which bond sinter together.

The concept of nucleus forming particle, adhering is shown in Fig. 5. By inspecting the microstructure more closely, one can see that sinter pores are, for the most part, located in the matrix bonding phase, i.e. in the haematite grain boundary. This is the main reason for sinter permeability. Hence, one can assume that a low volume of liquid phase might cause sinter to lose its mechanical strength. Conversely, excessive liquid phase might render sinter impermeable. Therefore, there must
be a compromise involving liquid phase volume, sinter mechanical strength and permeability.

The fine particles of sinter feed iron oxide, which are picked up in the liquid phase, lead to the formation of iron and calcium silicate, and acicular crystals are shown in Fig. 6.

Effect arising from adding pore nucleus forming agents

Sinter

Figure 7 shows the pore distribution of standard sinter with larger pores, ranging from 50 to 200 μm, scattered throughout the microstructure, and a microporosity, which is concentrated in the bonding phase.

The effect of adding cellulignin coal is shown in Fig. 8. A new cluster of 5–10 μm pores is formed. These micropores are scattered throughout the matrix, generating, as planned, new reaction surfaces. It is interesting to note that the diameters of this new pore cluster are smaller than the size of cellulignin coal particles. Hence, one can assume that the voids created by coal combustion are partially filled by the liquid phases formed during sintering.

Specific surface area (BET)

The effect of this new micropore cluster, as a result of adding cellulignin coal to the specific surface area of sinter, is shown in Fig. 9. It is to be expected that these new reaction surfaces will lead to an increase in BFG yield.
Gas flow simulations

The most conclusive and direct measure of the effect arising from the addition of micropore nucleus forming agents on sinter permeability is related to the results of gas flow physical simulations. Corroborating all the results shown earlier regarding the formation of a new micropore cluster, with the consequent increase in sinter specific surface, gas flow simulations clearly show an increase in sinter permeability (Fig. 10). This permeability increase is closely associated with the coal concentration added to the blend.
Economic viability

To ascertain, on a preliminary basis, the economic viability of adding cellulignin coal to the blend to be sintered, average market prices were taken.

To estimate sinter manufacturing cost increase, a sinter output of 6-689 m t⁻¹ per year was considered and, conservatively, the use of other more costly fuels, in view of the fact that to produce cellulignin on an industrial scale and in the required amount to satisfy this application will take some time.

Figure 11 shows the rise in annual costs ($ m) to produce sinter, considering adding 0-25 and 0-5% of micropore nucleus forming agents to the blend to be sintered. Obviously, replacing cellulignin by other fuels is only an economic exercise, as its impact on sinter quality was not measured. Adding 0-5% of these fuels will entail a cost rise in sintering production to the tune of $6m per annum.

To check the economic viability of this project, the following assumptions were made: a hot metal output of 5-3 m t⁻¹ per year, and a decrease by 7 kg imported coke/ton hot metal for each 1% increment in BFG yield. Figure 12 shows hot metal manufacturing cost reduction with BFG yield increment. A mere 0-5% increment in BFG yield would render the addition of 0-5% of extra fuel to the blend economically viable. Besides the enormous potential for indirect reduction in hot metal manufacturing costs, adding cellulignin coal as extra fuel, to the blend to be sintered, showed, on a trial basis, the possibility of a slight increase in the productivity of the sintering machines.

Conclusions

The main conclusions arising out of this intense work, conducted on a trial basis, were as follows.

1. Silica, being less hard, tends to be concentrated in sinter feed fine fractions, during iron ore comminuting and dressing processes.
2. A typical sinter microstructure is essentially composed of thick, nucleus forming particles, consisting of haematite, its main phase, and magnetite, its minor phase. These thick grains are bonded by a calcium silicate-based matrix, bonding phase.
3. Under the effect of local high temperatures in front of combustion, calcium disilicate of bonding phase, initially formed, reacts with silica excess, causing calcium monosilicate to be formed.
4. Sinter pores are fundamentally concentrated in the matrix bonding phase in the haematite grain boundary. This is the main reason for sinter permeability. Low volume of liquid phase may lead to a decline in sinter mechanical strength and an excess may cause impermeability.
5. The characterisation techniques used in this study proved to be an excellent tool to support a mining plan.
6. The result of adding cellulignin coal to the blend is the creation of a new pore cluster in the sinter product, ranging from 5 to 10 \( \mu \)m in diameter, uniformly distributed, without degrading its mechanical properties. These micropores are scattered throughout the matrix, generating, as planned, new reaction surfaces. The voids created by coal combustion are partially filled by liquid phases formed during sintering.
7. These new reaction surfaces favour BFG yield increase, thereby contributing toward decreasing reducing agent consumption.
8. Corroborating all results obtained in this study, the gas flow simulations showed sinter permeability being raised as a result of adding micropore nucleus forming agents. The increased permeability is closely related to cellulignin coal concentration added to blend.
9. A mere 0-5% increment in furnace gas yield renders the 0-5% addition of extra fuel to the blend to be sintered economically viable. Besides the enormous potential for indirect reduction in hot metal manufacturing costs, adding cellulignin coal to the blend to sintered as extra fuel, showed, on a trial basis, the possibility of a slight increase in sintering machine productivity.

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