



# Article Batch Sintering of FeO·OH and Fe<sub>2</sub>O<sub>3</sub> Blends: Chemical and Metallurgical Characterization

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**Abstract:** A sample of goethite iron ore sinter feed (G\_SF) was employed as a raw material in a sintering bed. This sample partially replaced hematite sinter feed (H\_SF), which is currently used as raw material in a sintering plant in the state of *Minas Gerais*, Brazil. This substitution did not adversely affect the chemical and metallurgical proprieties of the sinter mix product, provided that the utilization of G\_SF was kept below 30% in weight. Despite the higher proportion of fines in G\_SF, the presence of argillaceous minerals in the sample led to an improvement in the granulation index (GI) of the sinter mix product. The GI value increased from 68.4 to 82.7% for the experiments conducted without the presence of goethite ore and with 40% of goethite ore in the sintering mix, respectively. Consequently, the qualities of both the process and the produced sinter product were not compromised. The raw materials and the various sinters produced were characterized through X-ray fluorescence (XRF) and X-ray diffraction (XRD), as well as thermal gravimetric analysis (TGA). The XRD results were used to perform a quantitative assessment of the mineral phase using the Rietveld method (RM). This technique allowed for the determination of goethite content in the studied sample, which was 35.5%. Finally, the incorporation of G\_SF in the sintering bed led to a 20% reduction in the cost of raw materials.

Keywords: ironmaking; iron ore; goethite; hematite; thermal analysis; Rietveld method

## 1. Introduction

The mineral processing of iron ore generates a large quantity of fines, considering particles under 5 mm in size [1,2]. Blast furnace (BF) ironmaking involves a vertical counter-current process designed to be fed with materials ranging from 5 mm to 50 mm [3]. Therefore, depending on the mineral-processing consequences over the particle size distribution, agglomeration unitary processes could be required to input specific fluid dynamics conditions, such as terminal velocity, to allow the raw material application in the BF ironmaking route. Under this perspective, sintering is an agglomeration process, based on thermal activated systems, used to transform the independent fine particles into a solid, aggregated material with adequate size and porosity, as well as with the mechanical properties required for efficient BF operation [3–6].

Brazil possesses substantial occurrences of Fe resources, with hematite (Fe<sub>2</sub>O<sub>3</sub>) being the primary mineral in these deposits [7]. The national commercialized production in 2022 was predominantly associated with the contributions of mines from the states of *Pará* (47.9%) and *Minas Gerais* (47.2%). The average Fe content in ores from the latter state



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). was measured at 48.9%, considering the reports from 2021 [8]. This number suggests the necessity of mineral processing for Fe concentration, and therefore, a significant amount of fine material is expected to be produced as the result of such unitary processes [1].

In the state of *Minas Gerais*, there is a specific region called *Quadrilátero Ferrífero*, which means Iron Quadrangle in English, where the occurrence of ores with a high content of goethite (FeO·OH) can be observed [1,7]. Regardless of their metallic Fe content, these resources are classified as marginal occurrences [1]. Their utilization by the Brazilian sintering plants poses a significant challenge, mainly due to their low grade, the increase in the coke requirements to promote thermal decomposition reactions [9], and the presence of deleterious elements, considering the content typically observed in Fe<sub>2</sub>O<sub>3</sub> ores [10]. The presence of goethite and the mentioned challenges often lead to a reduced market value, compared to rich hematite ores, resulting in frequent disposal or material storage in dump stocks. The increased demand for Fe ore has led to a shortage of good-quality Fe<sub>2</sub>O<sub>3</sub>, specifically for smaller BF plants. Therefore, these sites began to use granular low-grade material, produced from ores with smaller contents of Fe<sub>2</sub>O<sub>3</sub>, as input to BFs.

In general, studies have shown that increasing the goethite content in the sintering bed, often measured indirectly through lost on ignition (LOI), leads to improved permeability [11], particle contact [12], and moisture absorption capacity [11]. Consequently, these ores have been utilized to produce sinters with desirable chemical, physical, and metallurgical properties [13–15]. Furthermore, increasing the basicity of the sintering bed enhances the physical–chemical and metallurgical properties of the produced sinter [16,17]. Thus, the scarcity of high-quality hematite ore, the abundance of goethite in the *Quadrilátero Ferrífero* as well as the low market price of such a potential alternative source of Fe in Brazil create the technological motivation to investigate the development of a sintering operation considering two mineral sources of sinter feed. Hence, the present manuscript describes the results of batch sintering tests with blends of hematite sinter feed (H\_SF) and goethite sinter feed (G\_SF). The target is to produce a sinter mix product with physical, chemical, and mechanical properties required for its use as raw material for small BFs (volume under 193 m<sup>3</sup>).

## 2. Materials and Methods

## 2.1. Raw Materials

The goethite and hematite ore samples were extracted from two mines located in the Brazilian state of *Minas Gerais*. The fractions with particle sizes below 6.3 mm were utilized as feed materials in the sintering experiments. Limestone (CaCO<sub>3</sub>) and coke, from Brazilian steel industry suppliers, were also used in the experimental procedure; the characterization of these materials is detailed in the Supplementary Materials. The study was carried out in a pilot plant in an ironmaking company in the state of *Minas Gerais*. Hematite ore fines were used as the quality control comparison, as this is the currently employed raw material to feed the sintering plant at the ironmaking site.

## 2.2. Chemical and Metallurgical Characterization

## 2.2.1. X-ray Fluorescence (XRF)

The determination of the main element constituents of the sample was performed using XRF equipment manufactured by Thermo Scientific (model ARL Quant'x, Waltham, MA, USA).

One gram (1.000 g) of sinter was used to determine its iron (II) content (%FeO). The sample was mixed with 3 g of sodium carbonate (analytical grade—Synth—99.9%) and then digested with the addition of 30 mL of hydrochloric acid (16% v/v). Subsequently, 30 mL of phosphoric acid (50% v/v) was added to the solution. The iron (II) was then titrated with 0.1 N potassium dichromate solution using diphenylamine as the indicator.

#### 2.2.2. X-ray Diffractometry (XRD)

The XRD pattern for each of the particulate materials was obtained using a Malven Panalytical diffractometer (model Empyrean). The identification and quantitative analysis

of mineral species within the ore samples, as well as sinter products, were conducted through the software HighScore Plus (PDF-4+ database), with the latter study taken into effect employing the Rietveld method (RM), based on fundamental parameters. (Further information can be found in Supplementary Materials). The quantitative assessment of mineral phases followed the approach implemented for previous studies [18,19].

## 2.2.3. Thermal Analysis (TGA)

Non-isothermal thermogravimetry analyses were performed at a heating rate of 10 °C·min<sup>-1</sup>, utilizing nitrogen (N<sub>2</sub>—White Martins, 99.9990% in volume) at a flow rate of 60 mL·min<sup>-1</sup>. These experiments were carried out in a Mettler Toledo equipment (model Star System, Columbus, OH, USA).

## 2.2.4. Loss of Ignition (LOI)

This determination was performed in a muffle furnace at a temperature of 900  $^{\circ}$ C for 1 h, using approximately 1 g of the sample. The observed percentual mass loss was assigned here as LOI.

## 2.2.5. Sintering Tests (Pilot Scale)

The sintering test was carried out using a 0.022 m<sup>3</sup> sintering pan. (Dimensions and the design are described in Supplementary Materials). The gas temperature was measured at the outlet of the exhaust pipe using a K-type thermocouple. Negative pressure was measured using a water column. For the mixture materials, batch sintering experiments were performed using four raw materials, described below, in distinct proportions:

- (i) Goethite sinter feed (G\_SF);
- (ii) Limestone;
- (iii) Hematite sinter feed (H\_SF);
- (iv) Coke.

The mass contents of each one of these in the samples, as well as the designated names adopted for each experiment, are described in Table 1.

Table 1.	Mass	contents	of raw	materials	used i	n sintering	experiments	and the	e proportions	be-
tween th	lem.									

Experiments	Coke (kg)	H_SF (kg)	G_SF (kg)	Limestone (kg)	G_SF (%) *	H_SF (%) *
0%G_SF 10%G_SF 20%G_SF 30%G_SF 40%G_SF	5 5 5 5 5 5 5	89 79 69 59 49	0 10 20 30 40	6 6 6 6	0 10 20 30 40	100 90 80 70 60

\* Percentage calculated based solely on the iron-containing materials added.

Moisture content was determined using a moisture analyzer from Toledo do Brasil (model analisador de umidade MA 50.R). Homogenization and agglomeration tests were carried out using a concrete mixer operated at 5 rpm (0.4 m<sup>3</sup> and 2 hp engine). The homogenization process was started for 4 min, with the concrete mixer positioned parallel to the ground. Subsequently, to promote the agglomeration of the mix, the equipment was inclined at 30° from the initial condition, and water was added until it reached about 6% in weight. The mix was then stirred for 5 min.

A layer (bedding) was prepared at the bottom of the pan using 2 kg of granulated hematite iron ore (see Supplementary Materials—Figure S3). The sintering mix was added to the pan, and approximately 0.5 kg of charcoal, with a particle size below 4 mm, was placed over the mix to be ignited. The temperature and pressure of the sintering process were measured every 2 min.

#### 2.2.6. Shatter Test

The shatter test was performed according to the Brazilian standard (NBR 10633) [20]. In this test,  $20 \pm 0.2$  kg of dry sinter with a particle size between 9.5 mm and 50 mm was subjected to four 2 m fall experiments, and the fragmented material was sieved using a 9.5 mm sieve. Equation (1) was used to determine the shatter index (SI) of the samples.

$$SI = \frac{m_1}{m} \times 100 \tag{1}$$

where  $m_1$  is the mass of the resulting fragments with a particle size higher than 9.5 mm, and m is the initial mass of the sample.

#### 2.2.7. Slag Content (% Slag)

An important industrial parameter used to estimate the amount of slag generated in a blast furnace is the ratio between the oxides that will be reduced during the process and the total oxide content of the sinter. In this study, the X-ray fluorescence (XRF) technique was employed to determine the elemental composition of the sinter. This elemental composition was then converted to oxide composition using stoichiometric calculations. The following equation was used to calculate the slag content (% Slag):

$$\% Slag = \frac{\% CaO + \% MgO + \% SiO_2 + \% Al_2O_3}{\Sigma \% MeO}$$
(2)

where  $\sum$  %MeO represents the sum of the contents of all metal oxides identified in the sample using the XRF technique.

## 2.2.8. Granulation Index

The granulated sample was homogenized, dried, and sieved through a 1 mm sieve. After the last unitary procedure, the retained material was weighted, and with the observed mass results, the granulation index (GI) was calculated using Equation (3).

$$GI = \frac{Mass of particles retained on sieve}{Total mass of sample} \times 100$$
(3)

#### 2.3. Thermodynamic Data

All thermodynamic data used in this study were obtained from the HSC Chemistry software, version 6.1 [21], using the default database and reaction equations module.

#### 3. Results and Discussion

### 3.1. Chemical and Metallurgical Characterization of Raw Materials

The particle size distribution of raw materials is presented in Supplementary Materials (Tables S4 and S5).

The chemical analysis of the samples G\_SF and H\_SF are shown in Tables 2 and 3, respectively. In comparison to the iron content in Brazilian iron ores [1,7], sample G\_SF can be classified as a low-grade iron ore, while sample H\_SG can be classified as a high-grade iron ore. Despite the higher sulfur and phosphorus contents in the sample G\_SF, the results suggested that all types of pig iron (basic, foundry, and nodular) could be produced by using this ore as a blending raw material in the sinter pot.

The coke and limestone utilized in the experiments are current materials used for the sintering of the sample H\_SF, leading to the production of a high-quality sinter, based on the typical supply for the ironmaking industry. The characterization results of these materials are presented in Supplementary Materials (Tables S6 and S7). Figure 1 displays the observed and calculated diffractograms for the G\_SF sample, while Table 4 presents the content of the main minerals identified by the RM. It can be observed that FeO·OH was the major constituent of the sample. The results revealed that the total iron content, 52.2% in weight, was distributed among the following carriers in terms of weight: (i) 35.5% of goethite (FeO·OH) corresponding to 22.3% of Fe content in the sample;

(ii) 33.3% of hematite (Fe<sub>2</sub>O<sub>3</sub>) corresponding to 23.3% of Fe content in the sample;

(iii) 9.1% of magnetite ( $Fe_3O_4$ ) corresponding to 6.6% of Fe content in the sample.

Table 2. Chemical composition (weight percentage) of the sample G\_SF.

Fe *	SiO <sub>2</sub>	$Al_2O_3$	Mn	CaO	Cr <sub>2</sub> O <sub>3</sub>
54.8%	13.9%	2.7%	0.9%	0.02%	0.3%
TiO <sub>2</sub>	K <sub>2</sub> O	Р	S	MgO	LOI
0.10%	0.01%	0.07%	0.04%	0.09%	4.5%
* T-t-1 :					

\* Total iron content.

Table 3. Chemical composition (weight percentage) of the sample H\_SF.

Fe *	Cr <sub>2</sub> O <sub>3</sub>	Mn	CaO	S
60.3%	0.32%	0.05%	0.11%	0.02%
Р	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	FeO **
0.04%	6.3%	1.4%	0.04%	1.4%

\* Total iron content; \*\* iron II content.



**Figure 1.** XRD pattern of the G\_SF sample, considering [K] kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), [G] goethite, [Q] quartz (SiO<sub>2</sub>), [H] hematite, and [M] magnetite minerals.

Table 4. Mineralogical analysis of the sample G\_SF through RM.

Mineral	Hematite	Goethite	Magnetite	Quartz	Kaolinite
Content (% in weight)	33.3	35.5	9.1	18.7	3.4

Based on these results, it can be said that XRD findings agree with XRF, as the latter showed a total Fe content of 54.8% in weight.

On the other hand, Figure 2 exhibits the observed and calculated diffractograms for the sample H\_SF, while Table 5 displays the content of the main minerals identified. The principal mineral constituent of the sample H\_SF was  $Fe_2O_3$ , and among the identified minerals, iron was exclusively present in it. Based on the mineralogical analysis, the total iron content in the sample was 62.7% in weight. This inference is also in agreement with the values obtained by XRF (60.3% in weight).



**Figure 2.** XRD pattern of the H\_SF sample, considering [D] dickite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>); [C] chabazite ((Ca,K<sub>2</sub>,Na<sub>2</sub>)<sub>2</sub>Al<sub>4</sub>Si<sub>8</sub>O<sub>24</sub>.12H<sub>2</sub>O); [H] hematite; and [Q] quartz minerals.

Table 5. Mineralogical analysis of the sample H\_SF through RM.

Mineral	Hematite	Quartz	Chabazite	Dickite
Content (% in weight)	89.6	8.4	1.1	0.8

Finally, the minor difference between the iron content calculated by XRF and the one determined through RM using XRD can be attributed to the presence of Fe as an element of substitution within the crystalline structure of other mineral constituents of the sample.

Thermal analysis results are presented in Figure 3. The TGA curve for the sample G\_SF exhibited three thermal decomposition events, labeled here as [A], [B], and [C], while for the DTG curve, these same events were marked as [A'], [B'], and [C'].



Figure 3. TGA and DTG curves associated with the thermal decomposition of the sample G\_SF.

The event [A] was attributed to the thermal decomposition of the mineral goethite through Equation (4).

$$2\text{FeO} \cdot \text{OH} = \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}\,\Delta\text{G}^0 = -143.7\text{T} + 45,252\left(\frac{\text{J}}{\text{mol}\,\text{H}_2\text{O}}\right) \tag{4}$$

The temperature range, between 120 and 600 °C, for the thermal decomposition of this mineral is consistent with the values reported in literature [22–25]. Utilizing the calculated mass loss value in the TGA curve for event [A], it was possible to determine that the content of goethite in the sample was 34.6% in weight. This value aligns with the results obtained through RM (see Table 4). The slight disparity observed between the TGA and RM results (2.2% wt.) could be attributed to the potential presence of amorphous goethite in the sample, which could not be quantified through XRD, and/or the presence of water in the chemical structure of this mineral.

The literature indicates that certain goethite samples exhibit low crystallinity [22,26,27]. The event (B), on the other hand, was attributed to the thermal decomposition of the mineral hematite through Equation (4).

$$6Fe_2O_3 = 4Fe_3O_4 + O_2 \Delta G^0 = -340.2T + 586,770 \left(\frac{J}{\text{mol } O_2}\right)$$
(5)

The values of standard Gibbs free energy to the reaction, as observed in the literature [25], indicate that the thermal decomposition of Fe<sub>2</sub>O<sub>3</sub> will be spontaneous at temperatures higher than 1451 °C. This temperature level is considerably higher than the one observed in the experiments (near 1140 °C). Since the experiments were carried out using pure N<sub>2</sub> (99.9990% in volume), the implemented partial pressure can be estimated as  $10^{-5}$ . Thus, it is possible to estimate the thermal decomposition temperature of the hematite through Equation (6).

$$\Delta G = \Delta G^{0} + 2303 \text{RTlog} \left[ \frac{\left( a_{\text{Fe}_{3}\text{O}_{4}} \right)^{4} \times p \text{O}_{2}}{\left( a_{\text{Fe}_{2}\text{O}_{3}} \right)^{6}} \right]$$
(6)

Considering the activity of the pure solid as 1,  $pO_2 = 10^{-5}$ , and under equilibrium conditions, the calculated temperature value was 1072 °C, which is much closer to the level of temperature observed in the TGA curve for event [B]. This value was following the findings reported in literature [28,29]. Furthermore, considering the total thermal decomposition of the mineral goethite, the hematite content in the sample was 67.6% in weight, with 33.1% produced by the thermal decomposition of goethite, while the remaining 34.5% was already present in the sample. These values were calculated by RM and adjusted, considering the 3.5% mass loss observed in the event [A]. Thus, the mass loss resulting from the thermal decomposition of the mineral hematite in the sample was 2.25% in weight for the calculated mass loss for event [B]. This value is very close to those observed on the TGA curve.

Finally, event [C] was attributed to the thermal decomposition of the mineral magnetite, as described by Equation (7).

$$Fe_{3}O_{4} = 3FeO + \frac{1}{2}O_{2} \Delta G^{0} = -196.3T + 429,100 \left(\frac{J}{mol O_{2}}\right)$$
(7)

The values of standard Gibbs free energy showed that the reaction was spontaneous at temperatures higher than 1912.8 °C. However, considering a maximum partial pressure of oxygen of  $10^{-5}$ , following the same approach applied for event [B], the temperature values were calculated as 1480 °C for event [C]. This value follows the one observed in the experiment conditions and also agrees with values reported in the literature [26].

#### 3.2. Chemical and Metallurgical Characterization of Materials after Batch Sintering Experiments

Batch sintering experiments were conducted with varying quantities of G\_SF (see Table 1). The production of sinter using only the sample H\_SF, as an iron-containing raw material, is a daily routine experiment performed by the ironmaking site; an experiment without the sample G\_SF (labeled 0%G\_SF) was carried out and used as a reference experiment. XRF determined the chemical compositions of the sintering beds, and a reduction in iron content and an increase in silicon (Si) content with a higher amount of G\_SF in the sintering bed were observed (Supplementary Material—Table S8). It is important to mention that the chemical composition of all sintering beds studied in this manuscript fell within the typical range usually applied by various Brazilian ironmaking companies.

Table 6 shows the GI values before and after the granulation process for the studied sintering bed compositions, while Table 7 shows the chemical analysis of products using different sintering beds.

Experiment	0%G_SF	10%G_SF	20%G_SF	30%G_SF	40%G_SF
Before granulation	46.5	43.3	39.9	36.7	33.5
After granulation	68.4	72.0	76.3	81.2	82.7

**Table 6.** Granulation index (GI) for sintering beds with varying amounts of G\_SF.

Element	0%G_SF	10%G_SF	20%G_SF	30%G_SF	40%G_SF
Fe (%)	59.1	59.0	58.6	59.0	56.9
SiO <sub>2</sub> (%)	6.9	5.8	6.7	8.1	6.2
CaO (%)	3.6	3.7	3.5	3.8	3.32
Al <sub>2</sub> O <sub>3</sub> (%)	1.8	1.5	1.8	1.9	1.7
Cr <sub>2</sub> O <sub>3</sub> (%)	0.3	0.3	0.28	0.27	0.25
S (%)	0.03	0.013	0.024	0.014	0.013
P (%)	0.04	0.039	0.062	0.051	0.036
Basicity (B2)	0.52	0.65	0.52	0.47	0.53
% Slag	12.3	11	12	14	11.3

Table 7. Chemical analysis of the produced sinters with different amounts of G\_SF.

It can be observed that the GI increased after the granulation process for all conditions. Furthermore, the increase in the quantity of G\_SF contributed to the observed elevation in GI after the granulation process. The rise in the GI can be attributed to the presence of argillaceous minerals (e.g., kaolinite) (see Figure 1 and Table 6) and their capacity to retain moisture [30]. According to the literature, the granulation of the sintering mixture increases when ores with high iron content are mixed with ores exhibiting a high loss of ignition (LOI) [30]. Moreover, some researchers also declare that incorporating goethite in the sintering bed enhances the GI of the sinter product [31].

The results in Table 7 show that when the amount of G\_SF was increased, the Fe content in the sinter mix decreased, due to the lower iron content in this ore. Since the raw material that feeds the BF must contain at least 59% in weight of Fe, the sintering bed of 40% G\_SF cannot be employed in the current process.

The mineral phases identified by XRD were hematite, magnetite, and quartz, and the contents of these minerals in the different sinters produced are shown in Table 8. (Diffractograms are presented in Supplementary Materials—Figure S4). The RM refinement parameters for the calculated diffractograms were determined to be satisfactory, as the goodness-of-fit (GOF) and weighted R profile (Rwp) consistently registered values below 1.48 and 3.7, respectively.

Sinter	0%G_SF	10%G_SF	20%G_SF	30%G_SF	40%G_SF
Hematite (%)	66.3	68.5	63.8	43.5	59.3
Magnetite (%)	16.1	16.8	19.8	40.8	21.5
Quartz (%)	4.5	1.7	3.7	1.4	6.5
Amorphous (%)	13.0	13.0	12.2	14.3	12.7
Fe(total) (%)	58.0	59.0	59.0	60.0	56.9

 Table 8. Mineralogical analysis of the different sinters.

The total Fe percentage was calculated using the stoichiometric relation of this element in the minerals quantified by the RM and compared with values measured by XRF. The values obtained were remarkably similar; specifically, the maximum and minimum differences between these values were 1.9% and 0.02% for the samples 0%G\_SF and 10%G\_SF, respectively.

The results showed that the percentage of Fe in the sinter decreased when the amount of G\_SF in the sintering bed was increased; this reduction can be attributed to the low content of iron in the G\_SF when compared with the H\_SF. (The chemical composition of sintering bed can be found in Table S8.) In addition, increasing the amount of G\_SF in the sintering feed promoted the formation of a sinter richer in magnetite. This result suggests that the Fe<sub>2</sub>O<sub>3</sub> formed from the thermal decomposition of FeO·OH is easily reduced, due to its higher porosity.

The content of SiO<sub>2</sub> measured using both techniques (XRF and RM refinement) differed significantly. This disparity arises because the RM quantifies only the crystalline phase, while the XRF determines the total content of silicon in the sample. This difference between the analytical techniques explains the higher values obtained when determining the Si content using XRF. There was a clear correlation between the percentage of slag calculated by XRF and the content of the amorphous phase in the sinter (see Supplementary Material—Figure S5). The results suggest that RM refinement can be used as an analytical method to estimate the content of slag in sinter products. It is observed that the amorphous phase is consistently overestimated; this discrepancy could be attributed to the presence of unaccounted crystalline phases [32].

The negative pressure and exhaust gas temperature were measured as a function of the time in various sintering experiments (see Supplementary Materials—Figure S6). Figure 4A,B presents the corresponding values for sintering time, maximum temperature, and initial and final negative pressures.

The initial and final negative pressure values indicated that, for all studied sintering experiments, the permeability of the bed increased after the process. Furthermore, an increase in the amount of G\_SF led to an additional increase in the permeability of the sintering bed. As shown in the granulation results, the rise in the content of G\_SF in the sintering bed promoted an increase in the GI. The final negative pressure value measured in the exhaust gas pipe decreased slightly with an increase in the amount of G\_SF. This suggests that the presence of G\_SF could promote a slight improvement in the porosity of the sinter. The sintering time decreased with an increase in the quantity of G\_SF in the sintering bed. This can be attributed to the improved permeability promoted by the higher amount of G\_SF. The maximum temperature of the sintering bed increased when the percentage of G\_SF was raised in the process. This is a consequence of the improved permeability of the bed promoted by the addition of G\_SF, i.e., the increased permeability of the sintering bed, resulting from the addition of G\_SF, allowed for the more efficient combustion of the coke. Furthermore, according to previously published literature, the formation of magnetite increases when sintering is performed at temperatures higher than 1300  $^{\circ}$ C [33]. Thus, it is possible that the rise in the amount of G\_SF in the sintering enhanced the permeability, leading to higher temperatures. Consequently, an increase in the percentage of magnetite in the sinter was observed (Table 8).

Finally, the results showed that, despite the increase in the percentage of adherent particles in the sintering bed promoted by the addition of G\_SF, the effective performance of this sample in the granulation process allowed for a better permeability of the sintering bed to be reached. Consequently, the produced sinter exhibited chemical proprieties as

satisfactory as those displayed by the sinter currently used by the company. The results of the shatter test are shown in Table 9. The shatter indexes revealed that approximately 80% of the sinter retained a particle size greater than 9.5 mm, and overall, the shatter index values remained consistent. Furthermore, all the sinters produced exhibited sufficient mechanical resistance for transportation within the company and to support the charge inside BFs.



Figure 4. (A) Initial negative pressure and final negative pressure at different sintering experiments and (B) maximum temperature and total time of the sintering experiments.

Table 9. Shatter index of the various sinters.

	0%G_SF	10%G_SF	20%G_SF	30%G_SF	40%G_SF
Shatter Index (%)	82.5	81.3	81.1	82.1	78.4

Finally, it is crucial to highlight that the cost of the sintering process was reduced when the G\_SF sample was used as raw material. The reduction in this value was estimated based on the cost of a sintering process operation performed using only H\_SF as raw material (X). Table 10 shows the reduction in the value brought about by this alteration, which is a consequence of the low price of G\_SF when compared to H\_SF.

Table 10. Cost of the sintering bed with different amounts of G\_SF.

Bed	0%G_SF	10%G_SF	20%G_SF	30%G_SF	40%G_SF
Cost	Х	0.93X	0.86X	0.79X	0.72X

## 4. Conclusions

The studied goethite sinter feed (SF\_G) sample contained 35.5% in weight of goethite, the main constituent. The TG curve obtained from the sample's thermal decomposition revealed three main decomposition events: (i) goethite decomposing to hematite, (ii) hematite decomposing to magnetite, and (iii) magnetite decomposing to wustite.

Sintering tests performed using different ratios of goethite sinter feed (G\_SF) and hematite sinter feed (H\_SF) showed that: (i) The presence of argillaceous minerals in the

goethite sinter feed (G\_SF) sample contributed to an improved granulation index (GI) and consequently enhanced the permeability of the sintering bed, compared to the bed prepared solely with the hematite sinter feed (H\_SF). The GI value increased from 68.4 to 82.7% for the experiments conducted without the presence of goethite sinter feed and with 40% of goethite sinter feed in the sintering bed, respectively. (ii) The G\_SF can substitute up to 30% of the H\_SF without a significant loss in the physical, chemical, and metallurgical properties of the sinter, and (iii) the cost spent on raw materials was reduced by ~20% through the substitution of the more expensive H\_SF with G\_SF.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/met14050598/s1, Figure S1. Dimensions (mm) and layout of the sinter plant; Figure S2. Sintering pilot plant; Figure S3. Bedding of granulated iron ore; Figure S4. Observed and calculated diffractogram to the different sinters; Figure S5. Correlation between the % of slag and the % of amorphous in the sinters.; Figure S6. Sintering bed negative pressure and temperature of the gas at the windbox; Table S1. Acquisition configurations for the X-ray experiments; Table S2. Models employed for the Rietveld refinement; Table S3. Particle size distribution of the sample G\_SF and H\_SF; Table S4. Particle size distribution of limestone and coke; Table S5. Specifications for the structural materials used in the sinter plant; Table S6. Coke characterization; Table S7. Chemical composition of the limestone; Table S8. Chemical analysis of the mixes used as feed material in the sintering process; References [32,34–42] are cited in the supplementary materials.

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