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Iron Ore Agglomeration Technologies

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Abstract

Until the 1950s of the last century, the oxidized iron ores that were loaded into the blast furnace had granulometries within 10 and 120 mm. However, the depletion of high-grade iron ore sources has made necessary the utilization of concentration processes with the purpose of enriching the iron ore. Because of these processes, a fine granulometry is produced, and thus iron agglomeration process is necessary. There are several agglomeration processes including: briquetting, extrusion, nodulization, pelletizing and sintering, although pelletizing and sintering are the most widely used, and especially sintering process (70% blast furnace load). Apart from obtaining an agglomerated product, the objective is reaching the suitable characteristics (thermal, mechanical, physical, and chemical) in a product that is then fed into the blast furnace, achieving a homogeneous and stable operation in this furnace with economical profitability.

Keywords: iron ore, sintering, pelletizing, solar energy, environment

1. Introduction

Iron and steel are widely used in modern societies despite the appearance of new materials. In this way, there is a growing tendency in the production of steel as according to the historical data, around 200 Mt were produced in 1950, 595 Mt in 1970, 760 Mt in 1990, 848 Mt in 2000 and 1630 Mt in 2016 [1, 2]. There is an irregular distribution of steel production worldwide as most of the steel is produced in Asia (more than 50%, mainly in China), followed by Europe (205 Mt in 2013), Russia, and USA. In the same line, Asia was the place where the steel production grew more in the last 40 years (from 121 Mt in 1970 to 1123 Mt in 2013), while in Europe the production remains stable in around 200 Mt, and in North America (USA and Canada) decreased from 131 Mt in 1970 to 102 Mt in 2013 [1, 2]. This growing tendency has led to the depletion of high-quality iron ore resources, and the use of concentration processes to increase

the iron content, but also the agglomeration processes to achieve a homogeneous material's size that could ensure a suitable operation in the furnace.

Until the 1950s of the last century, oxidized iron ores with a granulometry within 10 and 120 mm were loaded into the blast furnace (lower sizes led to permeability problems in the furnace bed) [3]. However, nowadays, 70% of the blast furnace ferrous bed belongs to sinter [4], and is for that reason the main agglomeration process. As we said previously, the depletion of the high-quality iron sources has caused the utilization of concentration operations after size reduction processes, having as objective enriching the ore by eliminating the gangue, but causing a fine granulometry that makes necessary the utilization of agglomeration processes, such as nodulizing, briquetting, extrusion, pelletizing, and sintering. Concentration processes can be classified into four categories according to the properties of the materials to separate them from the gangue [5]: *classification*, based on particle size; *gravimetric concentration*, based on density and/or volume differences; *flotation*, based on superficial properties; and, *magnetic or electrostatic separation*, based on magnetic susceptibility or electric conductivity. The obtained product is rich in iron but with a fine granulometry, making necessary the utilization of the previously mentioned agglomeration processes. However, increasing the particle size is not the single aspect that makes necessary the utilization of agglomeration processes. Nowadays, the existence of a global iron ore market with ores with different precedence and quality is responsible of that the raw material that reaches the iron and steelmaking factories has neither the same chemical composition nor the same granulometry. This question could affect blast furnace behavior, when a stable and homogenous operation is pursued with the objective of achieving economic efficiency, consistency in the pig iron and minimal coke consumption [6].

2. Iron ore agglomeration technologies

Five iron ore agglomeration technologies can be defined: briquetting, nodulization, extrusion, pelletization and sintering. Sintering and pelletization are the most important agglomeration technologies, in this way, in the EU-27, 14 countries operate 34 iron ore sinter plants with 63 iron ore sinter strands, producing in the first decade of the twenty-first century 130 million tons of sinter annually, on its behalf, 6 pelletization plants produce 27 million tons of pellet annually [7]. Here we are going to describe all these agglomeration technologies, with special dedication to pelletizing and sintering as they are the most used worldwide.

2.1. Briquetting

Briquetting is the simplest agglomeration process. Fine grained iron ore is pressed into two pockets with the addition of water or some other binder agent (molasses, starch, or tar pitch) to form briquettes [8]. A traditional application is the agglomeration of coal [8], other example is the agglomeration of ultrafine oxidized dust produced in the ferroalloys industry [9].

2.2. Nodulization

Nodulization is a process like sintering as it does not need a binder agent. The iron ore concentrate is mixed with carbon, and fed into a rotary kiln, where the material is tumbled at

high temperature to form nodules [8]. Reached temperature is enough to soften the ore but not to fuse it. Problems of the nodules are the considerable differences in composition and density (they are too dense), and the lack of a well-developed porosity (permeability) which is of great importance for the operation in the blast furnace. This process, as briquetting, is mainly used for the recycling of iron ore wastes in steel plants.

2.3. Extrusion

Extrusion is a process widely used in the ceramic industry, but it has begun to be used in the ironmaking and steelmaking industry in the agglomeration of powders generated in the factories as Basic Oxygen Furnace and Electric Arc Furnace powders. A certain level of moisture is required, as well as a binder agent, for instance bentonite or Portland cement. The mixture is sent to the extrusion machine to obtain the agglomerated product [8].

2.4. Pelletization

Pelletization is an agglomeration process of iron ore concentrates with a granulometry lower than 150 μm and low concentration of impurities [10, 11]. This iron ore is mixed with water, bentonite (or other organic binders less expensive and contaminant [12]), and lime and treated in a furnace at temperatures of around 1200°C, with the purpose of obtaining a product of 10–20 mm in diameter with suitable physical, chemical, and mechanical properties to be fed into the blast furnace or to the production of DRI (Direct Reduction Iron) [10]. Sintering raw mixes with a high proportion of fines (<150 μm) deteriorates the operation of the Dwight-Lloyd sinter machine, and for that reason pelletizing is the best method for treating this kind of material. The formation of liquid phases, which agglomerate the iron ore, in pellets is achieved by an external source of energy (fuel, natural gas or pulverized coal), as opposed to sintering, where liquid phases are consequence of the combustion of coke breeze [2].

Chemically, pellets are characterized by (approximately): 94% Fe_2O_3 , 3.3% SiO_2 , 1.0% CaO , 0.20% MnO , 0.50% MgO and 1.0% Al_2O_3 , and as we mentioned previously, a granulometry of 10–20 mm [2]. According to this question, it is possible to say that pellets are characterized by [10]: great uniformity regarding the size (10–20 mm in diameter); high mechanical strength; almost inert behavior facing to water as a consequence of the low CaO content that makes possible storing and transporting pellets outside; good reducibility; and, high iron content.

As in the case of the sintering, mixing is an important step to obtain homogenous pellets. This mixing is easy when the materials to be mixed have the same particle size and physical properties, however, binder additions (around 1%) are necessities and they are less dense than the ore. For that reason, segregation between particles must be considered when mixing the materials in the production of pellets.

Bentonite clay is the most common binder agent in iron ore pelletization as we mentioned previously, and is added at levels of 0.5–1.5% by weight [8]. There are others, that can be classified into two categories: organics (do not add impurities to the pellet and can be added in amounts of 1/10 of the equivalent in bentonite, although sometimes do not provide sufficient strength to the indurated pellets), and inorganics (usually result in strong pellets, which is good for shipping and handlings, but have the problem of impurities) [8]. Examples of

inorganic pellets are: bentonite, sodium carbonate, calcium carbonate or calcium hydroxide; while examples of organic pellets are: carboxymethylcellulose (CMC), other CMC-based polymers, corn starch, wheat flour or molasses [8].

Regarding pelletizing technologies, it is possible to mention two that are used at industrial scale: rotary drum and rotary disc. The rotary drum is a large drum-shaped cylinder that is elevated at one of its ends ($3\text{--}4^\circ$). The mixture (iron ore-binder) is fed at the elevated zone of the drum and leaves the drum at the lower zone, where it is classified into three groups, the undersize pellets (which are recirculated), the oversize pellets (which are recirculated after crushing), and the final product [8]. The pelletizer discs are the second technology, having as advantage if compared with the rotary drum that there is no recirculation. The mixture is fed to an inclined large disc ($40\text{--}60^\circ$ to the horizontal), and the rotation of the disc causes the formation of balls, which remain in the disc until they reached the adequate pellet size. The variables that should be controlled are the disc angle, feed rate, water addition, and rotation speed [8].

Once the green pellet is obtained, it must be subjected to induration as it is too weak for its application. Pellets are for that reason processed at high temperatures to strengthen them. Three types of furnaces are used: shaft furnace, traveling grate, and grate-kiln, and temperature will depend on the kind of pellet. Pellets can be classified into three groups:

- *Blast Furnace grade.* They are dried at $105\text{--}120^\circ\text{C}$, and then indurated at high temperature ($1200\text{--}1400^\circ\text{C}$, depending on the kind of both ore and binder, the same for the time), allowing for a strong pellet that can resist shipping, handling, and processes in the blast furnace. This kind of pellets can have certain level of impurities since all constituents of the iron feed are melted during the process in the blast furnace, and they can float as slag above the reduced iron (being then removed). Typically contain 58–65% Fe and size range of 9–12 mm [8].
- *Direct Reduction grade.* As opposed to blast furnace process, direct reduction of iron oxide happens in solid state (components are not melted). For that reason, impurities are necessary to be controlled. They are first dried at $105\text{--}120^\circ\text{C}$, and then indurated at high temperature ($1200\text{--}1400^\circ\text{C}$, depending on the kind of both ore and binder, the same for the time, as in Blast Furnace grade pellets), allowing for a strong pellet that can resist shipping, handling, and steelmaking processes [8].
- *Rotary Heating Furnace pellets,* or iron ore-coal composite pellets. This kind of pellets does not require high strength as in the other two types, since in the same vessel that the green pellets are fed, they are transformed into direct reduction iron. The resistance is required only for feeding as they are dried in the first part of the furnace and then are reduced without requiring more handling than that to feed them into the furnace [8, 13].

2.5. Sintering

Sintering is a thermal process ($1300\text{--}1400^\circ\text{C}$) by which a mixture of iron ore, return fines, recycled products of the iron and steel industry (mill scale, blast furnace dusts, etc.), slag-forming elements, fluxes and coke are agglomerated in a sinter plant with the purpose of manufacturing a sintered product of a suitable chemical composition, quality (physically) and

granulometry to be fed into the blast furnace, ensuring a homogenous and stable operation in the blast furnace [2]. This definition proposed in [2], describes the sintering process, but prior to sintering there is an important process called granulation that is deeply reviewed also in [2]. Granulation is the homogenization of the iron ore mixture in a rotatory drum with 7–8% water having as objective the obtaining of a pre-agglomerated product, which is then delivered as a layer over a continuously moving grate or “strand” (Dwight-Lloyd machine) to obtain the sintered product. This process that takes between 30 and 60 min. (including the addition of moisture, granulation and feeding to the sintering machine) has a fundamental role as it ensures an adequate sinter bed permeability and hence good productivity [2].

Dwight-Lloyd technology is the main iron ore sintering technology. Basically, this equipment consists in a sintering grate that is a continuous chain of large length and width, which is formed by the union of a series of pallet cars making the sintering strand. The process in the Dwight-Lloyd machine begins with each pallet car passing below the charging hopper. Feeding is carried out in two layers: the hearth layer that protects steel grates from over-heating during the sintering process, which is formed by sinter of coarse granulometry (10–20 mm, with a granulometry not enough to be sent to the blast furnace) in a layer of 3–6 cm [14, 15]; and the layer of fine material (0–8 mm) granulated to be sintered (fine material, return fines, fluxes, and coke). Once charged, the pallet car passes below an initializing furnace, causing the combustible ignition on the surface of the mixture, and being at the same time the mixture subjected to downdraught suction through the load. The combustion of the coke breeze (or alternative combustible in the corresponding case) does not take place in the whole thickness of the bed instantaneously, on the contrary, combustion happens as a horizontal layer that moves vertically through the bed. In this way, permeability is important, and for that reason granulation is a fundamental step [16]. This movement of the combustion zone defines several zones in the sinter bed (from the lower to the upper zone) [16]: *cold and wet zone*, is the zone of the sinter mix to be sintered at a temperature lower than 100°C; *drying zone*, zone at temperatures between 100 and 500°C where the vaporization of moisture and dehydration of hydroxides take place; *reaction zone*, where the maximum temperatures are reached during the combustion of coke (exothermic), decomposition of carbonates (endothermic), solid phase reactions, reduction and re-oxidation of iron oxides and reactions of formation of the sintered mass take place; and finally, *cooling zone*, is the zone where the cooling and re-crystallization of the sintered product take place. The high thermal efficiency is consequence of the heat accumulation in a partial layer called sintering zone or flame front (which progresses at 10–30 mm/min) toward the sintering grate, and in this way a 500–600 mm bed height would be sintered in around 25 min [16, 17]. Finally, the flame front reaches the bottom of the layer at the end of the strand, where the sintered product is discharged and subjected to cooling, crushing, and screening, being three kinds of product finally obtained: 0–5 mm (or 0–10 mm depending on the author, see [16]), called return fines and sent back to the beginning of the sintering process; 5–20 mm (or 10–20 mm or 10–15 mm depending on the author, see [16]), used as hearth layer in the sinter strand with the functions previously mentioned; and, > 20 mm (or >15 mm depending on the author, see [16]), sent to the blast furnace directly. Maximum sizes around 50 mm [18].

As we mentioned, flame front is the region limited by the moment where the coke begins to combust and the moment where the coke burned [19]. There are other definitions that can be

read in [16]. The temperature at which the coke begins to burn depends on the size, oxygen partial pressure, volatile content, and component types in the coke. The ideal flame front thermal profile is characterized by short heating time (1.5 min) up to the high temperature zone (1100°C) to avoid the formation of important amounts of FeO due to the low partial pressure of oxygen, and long cooling times (3–5 min) down to the room temperature to avoid a strong sinter structure by the formation of a gangue matrix [16]. Anyway, maximum temperature and heat distribution should be uniform to obtain a homogenous sinter with suitable quality, and with the maximum process efficiency. In this way, a double layer sintering is used in some plants to satisfy this question, the upper layer would have higher coke content than the lower one, and under that conditions the tendency of T_{\max} of being higher in the lower layer is avoided [16].

There is a strong relationship between sinter structure and sinter characteristics. Sintering process is based on rising the temperature with the objective of producing a molten phase, which, during the cooling period, will crystallize or solidify into several mineral phases and will agglomerate the mixture. In this way, from a mixture whose main constituents are Fe_2O_3 , CaO , SiO_2 and Al_2O_3 , it is possible to obtain a product having the following constituents: Fe_2O_3 , Fe_3O_4 , FeO , metallic iron, calcium ferrites and silicates. Calcium ferrites and silicates bond metallic oxides. It is, for that reason, possible to establish five categories of constituents that we can find in the sinter structure [20]: *hematite* (Fe_2O_3), primary (original mineral) and secondary or recrystallized (directly crystallized, formed by oxidation of magnetite crystals in liquid phase or formed by magnetite oxidation in solid phase); *magnetite* (Fe_3O_4), formed from the minerals or crystallized from the liquid phase; *wüstite* (FeO), formed by precipitation from the liquid in low potential of oxygen (typically associated to excesses of coke in the sinter, retained carbon grains or magnetite reduction in solid state); *calcium ferrites* ($x\text{SiO}_2 \cdot y\text{Fe}_2\text{O}_3 \cdot 5\text{CaO} \cdot z\text{Al}_2\text{O}_3$ with $x + y + z = 12$), they are difficult to define as there is partial replacement of Ca^{2+} by Mg^{2+} , Fe^{2+} by Mn^{2+} , Fe^{3+} by Al^{3+} and Si^{2+} , etc., so they include several chemical compounds formed by crystallization of the liquid phase according to the reaction above mentioned, and they are known as silico-ferrites of calcium and aluminum (SFCA); and, *silicates*, which include olivine, fayalite, and calcium silicates. Reactions involved in the formation of these constituents are described in [16, 20]. It is obvious that each constituent has a certain influence in the quality of the sinter produced, in this way, for instance primary hematite is considered beneficial for the sintered product as improves reducibility index, and SFCA are also beneficial for the sinter structure as they have good reducibility, improve shatter index and tumbler index [20]. The optimum sinter structure for sinter reducibility in the blast furnace would be hematite nuclei (un-melted) surrounded by an acicular ferrite network [21, 22]. Considering the temperature of operation, the best sinter quality (maximum percentage of ferrites, high primary hematite, good porosity, and good quality indices) is reached when sintering at 1225–1275°C [23].

2.5.1. Sinter quality indices

As it was mentioned previously, blast furnace operators require a homogeneous product with the suitable thermal, chemical, physical, and mechanical properties to be fed into the blast furnace, ensuring the highest productivity and performance. The main quality indices are:

Softening melting test: this test was developed in Japan and UK to simulate the behavior of iron ore materials in the cohesive zone of the blast furnace (defined as the zone of the blast furnace where the load formed by coarse mineral grains, sinter and pellets begins to soft [20]). See [20] to enlarge information.

Tumbler Index (TI) (% > 6.3 mm) (min. 63, max. 79, typical > 74 [20]): this test was developed with the purpose of knowing the cold strength of the sinter, and in this way, evaluating the tendency to the formation of fines during the handling and transportation of the sinter from the sintering machine to the blast furnace throat (obviously informing about the losses of material as fines). The Tumbler index depends on the strength of each component, as well as on the strength of the bonding matrix components and ore composition [24]. Standards to calculate this index are IS 6495:2003 and ISO 3271:2015. There are other indices used with the same purpose as for instance Micum and Irsid indices. The generation of fines was studied by using a method different from TI in [25]. They simulated different steps of handling and transportation by using customized drop and vibration tests and considering sinter size, drop height and conveying time [25].

Low temperature degradation tests: degradation that happens during reduction in the low temperature zone has harmful effects on burden strength in the blast furnace (loss of permeability to reducing gas and increase of coke consumption [26]). To have more information about the tests you can read [20]. Low Temperature Breakdown Test (LTB) was developed by the British Iron and Steel Research Association (BISRA) and Luossavaara-Kirunavaara AB (LKAB) with the purpose of evaluating the abrasion resistance of iron bearing materials under reducing conditions, simulating those in the upper zone of a blast furnace stack [20].

Reducibility index (RI) (R_{60} , %) (min. 49, max. 78 [20]): this test informs about the ability of the sintered products for transferring oxygen during the indirect reduction process in the blast furnace stack. The porosity (non-occluded porosity is the surface available for gas–solid contact) and the mineralogical composition. RI is related with FeO content in the sinter (the higher the FeO content, the lower the reducibility) as FeO reacts with SiO_2 to form calcium ferrites, which are difficultly reduced. There are eight tests to calculate the reducibility: Midrex-Linder, HYLSA Batch, VDE (Verein Deutscher Eisenhüttenleute), Japanese Industrial Standard, Gakushin, ISO Relative Reducibility Test, ISI test, and HYL-III test. They are described in [20].

Reduction Degradation Index (RDI) (% < 3 mm) (min. 27, max. 33, typical < 33 [20]): This test gives a measure of the sinter strength after the partial reduction of the material, and provides information about the degradation behavior in the lower part of the blast furnace stack [20].

Coke consumption (min. 39 kg t^{-1} sinter, max. 54 kg t^{-1} sinter [20]) is one important factor, as nowadays is the main combustible for the sintering process (around 88% [7], there are other traditional combustibles such as anthracite (with low volatile matter content), and other modern combustibles (biomass, biochar, etc.) developed in an attempt of reducing CO_2 , NO_x and SO_x as coke breeze (<5 mm) has 0.42–1% S and 1.06–1.23% N [7]) and for that reason it is necessary to guarantee the coal for coking production. The problem is that coking coal is only available in some regions, but also rises in coke price, unstable supply of anthracites and global warming by CO_2 [2, 16, 27]. Size is an important factor in sinter productivity and reducibility,

being the best results found when coke size is 0.25–3 mm [28]. The fraction 1–3.15 mm is more economical in terms of consumption [28–30]. The reduction in coke breeze consumption is being carried out mainly by replacing coke breeze by new renewable solid fuels as biochar, biomass, or charcoal [31–33].

Fe total (%) (min. 51, max. 61, typical > 56 [20]): iron ore market is mainly composed by hematite (Fe_2O_3), goethite ($\alpha\text{-FeOOH}$) and magnetite (Fe_3O_4), with low impurities content (alkalis, sulfur and phosphorus) and iron average content of 60–65% in 2016 (around 40% in 1940) [2]. However, the depletion of rich iron ore mines will lead to exploitation of complex chemistry ores and low-grade iron ore mines, considering in some cases the bioprocessing [5].

Basicity index (typical 1.70 [20]): reduction degradation index (RDI) decreases when basicity increases [20]. Obviously, basicity index has importance in the hardness and reducibility of the sinter as expresses the relation CaO/SiO_2 . See [20] for a deeper explanation on sinter basicity index and sinter structure.

FeO content (%) (min. 4.0, max. 11 [20]): this parameter informs about the thermal state of the sintering process [20] and about coke rate. RDI is reduced when FeO content is increased [20, 34]. The problem is that increasing FeO content affects coke rate, deteriorates the sinter reducibility [35, 36], and can also affect blast furnace productivity [35].

Al_2O_3 content (%) (min. 0.6, max. 1.8, typical 1.35 [20]): sinter quality is related with Al_2O_3 content as when Al_2O_3 content is increased, RDI is higher. This point is under discussion as Kumar et al. observed that with 10–10.5% CaO an increase of 0.1% in Al_2O_3 increases RDI 2 points [34], while Hiesch observed no relation between RDI and Al_2O_3 [37]. Alumina is also related with reducibility, but the same as for RDI, there are different opinions, Yu et al. observed that maximum reducibility is reached when Al_2O_3 content is 2.5% in the sinter ore [38], while Umadevi et al. observed that reducibility increased when alumina content is raised from 2 to 5.5% [39].

MgO content (%) (min. 0.7, max. 2.2, typical 1.65 [20]): MgO is related with the obtaining of an optimum blast furnace slag (flowability and desulphurization). For that reason, MgO is added as dolomite or dunite, directly or through the sinter. It was observed an increase in the utilization of dolomite (containing CaO and MgO) or other MgO-bearing materials with low SiO_2 (as dunite) due to the use of iron ores with high SiO_2 content. There are mixed opinions regarding how this constituent affects reducibility, RDI, Tumbler and productivity. Umadevi et al. observed that reducibility was decreased with increasing MgO addition (in low and high silica iron ore fines) [40]. Kalenga and Garbers-Craig observed an increase in Tumbler index and coke rate with increasing MgO content [41]. Bhagat observed that varying MgO content within certain limits (1.5–2.5%) did not affect productivity and Tumbler, while coke breeze consumption was reduced [42]. On their behalf, Umadevi et al. observed that increasing MgO content from 1.4 to 2.6% increased heat consumption, and productivity was reduced [43]. And Yadav et al. observed that raising MgO content from 1.75 to 3.25% caused a deterioration in productivity and an increase in Tumbler index [44]. With regard to how MgO content affects RDI, there are several opinions, and in this way, [41, 43, 45] observed that RDI improved when

MgO content was increased, but [42] observed that MgO did not affect RDI, and [44] observed that increasing MgO increased RDI.

Alkalis content (%) (min. 0.11 [20]): they are mainly K and Na compounds and enter in the blast furnace with the charge materials (sinter, 32–58%; coke ash, 21–33%; pellets, 16–37% [46]). They cause several problems in the blast furnace performance: decrease coke hot strength, deteriorate sinter RDI, weak refractory lining and facilitate the formation of slag crusts, scarfolding and burning of the tuyeres [47].

2.5.2. Multivariate statistics in the sintering process

Data analysis is nowadays widely used with the purpose of correlating variables and, in this way, evaluating the effect of them in a certain process, whose have a higher influence, and how changing them will affect the sintering process. We have studied what variables are and what weight have them on three sinter quality indices as Tumbler Index, Reduction Degradation Index, and Reducibility Index. The objective of our work was to estimate them by using multivariate statistics, and thus avoiding long and expensive laboratory tests. Once each index was defined by a mathematical equation whose parameters are easily measured, we used fuzzy inference to develop a fuzzy control system that could warn in case of deviations from the conditions that ensured the best quality indices.

For our work, we used real data from a sintering machine. The variables with a higher weight for each quality index are: **RDI** ($\% < 3.15 \text{ mm}$): fines (%), fluxes (%), Fe_2O_3 (%), FeO (%), CaO (%), S (%), 10–20 mm (%), average particle size (mm), productivity (t/h), basicity index, and abrasion ($\% < 0.6 \text{ mm}$); **Tumbler Index** ($\% > 6.35 \text{ mm}$): Fe_2O_3 (%), CaO (%), MgO (%), MnO (%), P_2O_5 (%), 0–10 mm (%), 10–20 mm (%), basicity index, and maximum temperature in box prior to sinter discharge ($^{\circ}\text{C}$); and, **RI**: Recoveries from other stages of the ironmaking and steelmaking process (%), FeO (%), P_2O_5 (%), MgO (%), S (%), Al_2O_3 (%) and $>50 \text{ mm}$ (%).

We elaborated a mathematical equation that correlated the RDI, the TI and the RI with those variables mentioned above, and in this way, it is possible to predict the indices by using these easily measured variables.

2.5.3. Environmental issues

Avoiding or minimizing pollutants is of large importance in nowadays environmental industrial policies, but also the objective is reducing the ecological footprint of the sintering process. In a second plane, environmental improvements will enhance the profitability of the sintering process from the economical point.

Sintering process is also used in the ironmaking and steelmaking as recycling system as apart from using iron ore fines and additives (such as fluxes and coke breeze), mill scale, collected dusts (and to a much lower extent sludges) from gas cleaning, other recycled by-products of steel manufacture and recycled sinter particles from sinter screening are treated in the sintering machine. Air pollutants are the most significant and are presented here:

Carbon dioxide: primary metal production is responsible for around 5% of the total world anthropogenic greenhouse gas emissions, while the iron and steel industry accounts for around 70% of this 5% [48], around 200 kg CO₂/t sinter are generated in European plants [49] mainly as a consequence of fossil fuels combustion and carbonate's decomposition. JFE Steel Corporation developed a hydrogen-based gas fuel injection technology, reducing CO₂ emissions by 60,000 tons/year [50]. Yabe and Takamoto proposed a process that used pre-reduced iron ore as sinter raw material (produced by reducing the iron ore to the degree of wüstite with blast furnace gas [51]). Coke breeze consumption is reduced (40,000 tons/year less of coke breeze in integrated plant of 4 Mt/year hot metal production) and 50,000–12,000 tons CO₂/year less by using 10% pre-reduced iron ore.

NO_x: NO_x emissions can be reduced by using low nitrogen content combustibles as 90% vol.% of NO_x comes from the fuel [52]. Using additives to inhibit the NO_x generation: hydrocarbons (1% sugar addition) reduced NO_x emissions from 533.8 g/t sinter to 283.3 g/t sinter [53]; or increasing Ca-Fe pellets in sintering bed [54]. End of pipe technologies could be other option but the huge volume of gas to be treated makes this option expensive. Flue gas recirculation lead to a significant reduction of pollutants emissions: 35–45% dust, 20–45% NO_x, 60–70% dioxins, 25–30% SO₂ and 40–50% CO reduction [55].

SO_x: sulfur is present as sulfide and sulfate (FeS₂, CuS, BaSO₄, MgSO₄, etc.) in iron ore fines and as elemental sulfur and organic sulfur in solid combustibles, which is oxidized and enters sinter flue gas as SO₂, but low SO₂ content in flue gas (400–1500 mg/Nm³, [56]) is responsible of low desulphurization efficiency of desulphurization processes. Li et al. studied the behavior of SO₂ in different zones of sintering bed for flue gas circulation sintering, and observed that moisture condensation zone and sinter mix zone are characterized by a strong SO₂ absorption ability, mainly by reaction of SO₂ with CaO [56].

Particulate matter (PM_{10/2.5}): the sintering process is the main contributor to PM emissions in an integrated steel factory [57, 58], around 45% of the total emissions. Due to the temperatures reached during the sintering process, components with noticeable vapor pressure like alkalis and heavy metal chlorides are volatilized and then re-condensed in the off-gas system resulting in a high fraction of PM_{10/2.5} in the dust emission of sinter plants [59]. End of pipe measures include electrostatic precipitators high-quality filter bags, etc. [7, 59]. Gan et al. observed that from over-wetted layer to the burning through point is the main area of PM₁₀ emitting [57]. Ji et al. observed that increasing moisture content and extending granulation time the emission concentration of PM_{10/2.5} is reduced, while increasing coke breeze rate increases the emission concentration of PM_{10/2.5} the same as adding recycled materials [58].

Dioxins: sintering has been recognized as an important source of organic micro-pollutants such as PCDDs and PCDFs [7, 60–63]. The mechanism of PCDD and PCDF formation in sinter plants is complex and associated to a de novo synthesis process [64]. The range of PCDD/F emissions in the EU-25 in 2004 is from 0.15 to 14.64 µg I-TEQ/t sinter expressed on an annual average basis [7], with most plants in the range 0.2 to 6.0 µg I-TEQ/t sinter [7]. The best option in the problem of dioxins is minimizing their formation instead of end of pipe treatments as is the most effective method. Several primary measures are considered in [65], we want to emphasize the addition of urea in the raw mix to inhibit the dioxin formation. In this way,

Long et al. observed that with 0.05% urea, it was achieved a decrement of 63.1% in urea emission if compared with sinter without urea [66]. Lechtanska and Wielgosinski proposed the use of ammonium sulfate as inhibitor of dioxin formation [67].

Heavy metals: metals and heavy metals emissions are other important problem in the iron ore sintering, specially associated with $PM_{10/2.5}$. See in [65] the sources of heavy metals.

PAH (Polycyclic Aromatic Hydrocarbons): are generated by the inhomogeneous and incomplete combustion processes. Several techniques are described in [7] to reduce PAHs emission concentrations from 591.7 mg/t sinter to 0.2 mg/sinter.

Measures to enhance air quality can be divided into three categories [65]: primary measures, based on preventing or minimizing the release of pollutants; secondary measures, consist in basically end-of pipe treatments; tertiary measures, consist in treating polluting wastes and raw materials in a single facility, concentrating there the source of pollutants.

Sintering is an energy and polluting intensive process in integrated steelworks. Around 9–12% of the energy consumed in an integrated steelwork is consumed in the sintering process, and 75–80% of this energy is produced by using contaminant solid fuels, such as coke breeze, anthracite, etc. [68]. These fossil fuels generate diverse pollutants, mainly CO_2 , SO_x and NO_x , and have made researchers to focus on studying more ecological alternatives as biochar, straw, or charcoal [65]. These new fuels are CO_2 -neutral, and lead to a significant reduction in SO_x and NO_x emissions. Other possibility is using blast furnace dust, as it has 24–40% carbon [69], although the amounts that are possible to recycle are limited fundamentally because of the zinc emissions.

Secondary measures, as we mentioned, have the objective of reducing pollutant emissions in sinter plants. They have been applied since the last decades of the last century [65], in general combined with other primary measures. In this way, for instance, in an attempt of reducing PCDD/Fs in Servola sinter plant (Italy), they used urea (primary measure) and the WETFINE (Wet electrostatic Precipitator, secondary measure or end of pipe measure), reaching <0.4 ng I-TEQ/ Nm^3 when using both systems (around 2 ng I-TEQ/ Nm^3 when using only one) [70].

Secondary measures are deeply described in [65], but the main technologies of this group of end of pipe technologies are: WETFINE system, MEROS process, EOS system, AIRFINE system and EFA process.

2.5.4. Solar energy in the ironmaking and steelmaking

Solar energy when properly concentrated offers a great potential in applications where high temperature is required as for instance metallurgical processes [71]. Even when the possibility of using concentrated solar energy in the sintering process is very limited because of the large volume of material to be treated, it could find a great potential in iron recovery from metallurgical wastes such as slags or other by product. In our basic researches in this field, we used iron oxide (III) mixed with carbon, and a 1.5 kW medium size vertical axis solar furnace at the laboratory PROMES-CNRS (Font Romeu-Odeillo-Via, France). Sun radiation is concentrated in a spot of 12.2 mm in diameter, being controlled the power by means of a venetian blind. 14 samples were prepared by mixing iron oxide (III) (100% Fe_2O_3 , $d_{50} = 6.7$ μm) with different

carbon (100% C, $d_{50} = 10.2 \mu\text{m}$) excesses (10, 25 and 40%) over the stoichiometric. Samples of 0.8–2.5 g were loaded into crucibles of 75 mm length, 12 mm width and 8 mm depth, with three thermocouples placed at the bottom of the crucible. This crucible is then placed below the solar beam and displaced at a controlled speed of 0.25–0.76 mm/s.

Samples were analyzed by x-ray diffraction and SEM–EDX. It was observed that the main phases were Fe_2O_3 , Fe_3O_4 and in some cases FeO . This indicates that a transformation took place during the experiments, carbon was mainly burnt during the process, so it was not used as reductant agent [71], and for that reason, the appearance of Fe_3O_4 and FeO takes place because of thermal decomposition of the iron oxide. It is possible to see in **Figure 1** the influence of displacement speed and power in the formation of magnetite.

From SEM–EDX, it is clearly observed that the disperse constituent is magnetite (white), while the matrix constituent is a phase formed by silica and alumina (both coming from the crucible [72]), iron and oxygen (see **Figure 2**). There are, for that reason, both diffusion and melting phenomenon during the process.

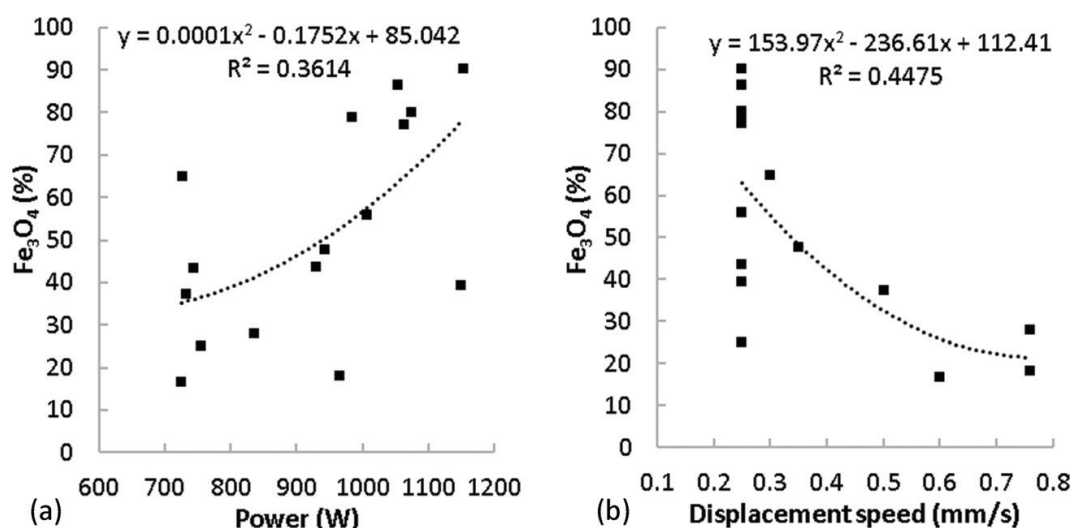


Figure 1. Magnetite formation as a function of power (a) and displacement speed (b).

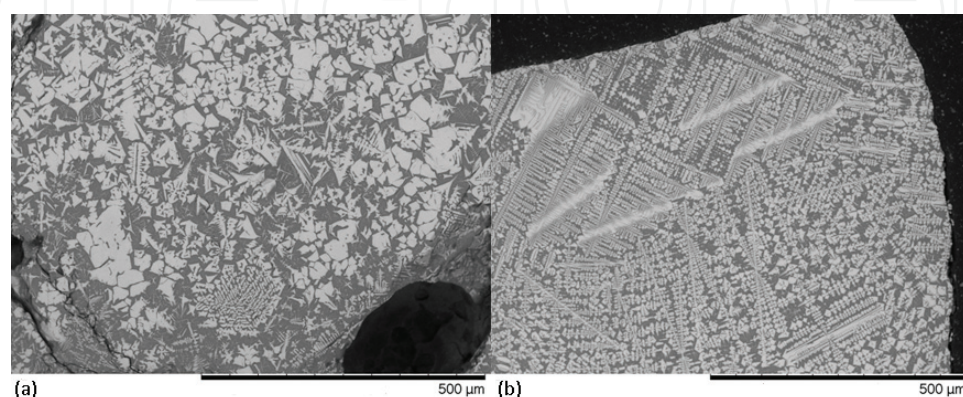


Figure 2. Micrographs obtained with an electronic microscope (E34 P2 (a) and E25 P2 (b)).

Knowing that the formation of magnetite is easily achieved by using concentrated solar energy, it is possible to think in recovering iron from wastes of the metallurgical industry containing iron as oxide, as for instance slags.

2.5.5. Other alternative processes to sintering and pelletizing

2.5.5.1. HPS process: hybrid pelletized sinter

This process was developed by the Nippon Kokan Keihin company (nowadays JFE Steel Corporation) with the objective of using fine iron-rich ores in their plants. The process is based on using pelletizing discs to obtain green pellets that are then coated with coke breeze before their disposal over the sinter strand. A commercial plant with an annual capacity of 6 million tons is working using HPS process at Fukuyama (belonging to JFE Steel Corporation) [18].

2.5.5.2. MEBIOS: mosaic embedding iron ore sintering

In 2001, Iron and Steel Institute of Japan began a research project on porous meso-mosaic texture sinter with the purpose of incorporating Australian goethite/limonite ores (characterized by a high proportion of ultrafine particles, up to 30% <150 μm) [16]. In this way, the purpose was to use important amounts of fine ores by controlling the void structure of the sinter bed structure (achieving a good sinter bed permeability and sinter yield). Consequence of the project is the MEBIOS process [73], which organizes dense granulated pellets in a conventional sinter mixture, allowing for obtaining well-developed voids and few pores that define a ventilation route, where the aging bed is based on Marra Mamba ore (fine ore and coarsely granulated material) while the induction bed is based on pisolitic limonite ore blended with coke and CaO [16]. In this way, dense large pellets support sinter bed and avoid sinter shrinkage, allowing the appearance of ventilation routes that improve permeability [18].

This process has another version known RF-MEBIOS (Return Fine-Mosaic Embedding Iron Ore Sintering). It was applied on Number 3 sinter plant in the NSSMC Kashima Steel Works, and then it was installed on three commercial sintering machines (Kashima, Wakayama, and Kokura) belonging to Sumitomo Metal Industries Ltd [18].

2.5.5.3. CAP: composite agglomeration process

Sinter and pellets are loaded in the blast furnace together, but this causes several problems associated to two aspects: spherical shape of pellets (responsible of the tendency to flow toward the center of the furnace, causing unstable operation); and, higher bulk density of pellets, making them to sink into the coke layer during the burden descent [74]. Jiang et al. developed the Composite Agglomeration Process with the purpose of solving the problems caused by the spheroidal shape of pellets and the increase in the supply of fine grained ores [74]. The process consists in: part of fine grained iron ore is transformed into 8–16 mm green pellets, while the rest and the coarse fine ores are mixed with fluxes, fuels and return fines, and then granulated (primary mixture); green pellets and primary mixture are blended (secondary mixture) and then fed to the sintering machine; the mixture is transformed into the composite

agglomerate by ignition and down draft firing; finally, the composite agglomerate is crushed and screened, being the fraction <5 mm considered as return fine.

The process was used for first time in 2008 by Baotuo Iron and Steel Company, and improvements in sinter bed permeability, decrements in fuel consumption and increases in productivity were observed [75]. Other authors studied the use of CAP in specularite ores [76], titanomagnetite concentrate [77] or fluorite iron concentrates [78].

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