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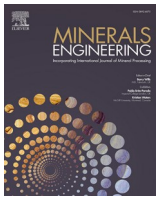

Three-dimensional characterization of porosity in iron ore pellets: A comprehensive study

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ABSTRACT

This paper presents a comprehensive study on the production and reduction of high-quality iron ore pellets characterized by a basicity index nearing 0.5 and diameters ranging from 1 to 2 cm. The reduction process was carried out in a hydrogen atmosphere at temperatures spanning 800–1000 °C and a pressure of 8 bar. Initial findings revealed substantial variations in pellet density and compressive strength, attributed to their mean dimensions. To delve into the microstructural transformations occurring during reduction, meticulous micro-tomographic analyses were conducted on each pellet before and after the reduction process. The research assessed reducibility factors such as porosity, pore size, and tortuosity adjustments across diverse reduction conditions. The study highlights the intimate connection between the reduction process rate, processing parameters, and pellet microstructure. Furthermore, the metallization tendencies were explored through extensive reduction experiments involving multiple pellets. These findings offer crucial insights into optimizing iron ore pellet performance during production and reduction processes, contributing to advancements in industrial applications.

1. Introduction

Iron ore and steel products are essential components of modern society, and their production efficiency is critical for sustainable development. In the steelmaking process, iron ore undergoes reduction to become primary iron, which is further refined to yield the final product. Before entering the steelmaking phase, iron ore must undergo several processing steps to eliminate impurities, increase concentration, and modify granulometry (Cavaliere, 2019). During this process, the ore is categorized into three granulometry types: granulated ore, with a size ranging from 31.0 to 6.3 mm; sinter feed, sized between 0.15 mm and 6.3 mm; and pellet feed, with a granulometry below 0.15 mm (Biswas et al., 2023). The granulated ore requires suitable granulometry for furnace reduction, whereas sinter feed and pellet feed, being fine ore fractions, cannot be directly used due to potential furnace clogging and gas transport impediments (Mohammad et al., 2023).

For a long time, the coarse ore fraction was loaded into blast furnaces, while the fine fraction accumulated in piles without economic value. To make use of this ore fraction, agglomeration technologies such as sintering and pelletizing were developed. These processes shape the material into the required form and size (usually several centimeters for sinter and approximately 12 mm, with variations from 10-16 mm, for pellets) (Reddy et al., 2023). Consequently, the iron ore charge for blast furnaces can comprise a mixture of ore lump, iron ore sinter, and iron ore pellets. The pellet manufacturing process involves three main stages: raw material preparation, raw pellet formation, and pellet hardening through heat treatment (Zhang et al., 2023). The final product should possess porosity to enhance heat transfer and facilitate the reduction process while maintaining mechanical strength (Cavaliere et al., 2023; Cavaliere et al., 2023; Cavaliere et al., 2023). Achieving the right balance between reducibility and strength is crucial in assessing pellet quality. Reducibility refers to the ability of the pellets to be reduced to metallic iron in the blast furnace, while strength refers to the ability of the pellets to withstand mechanical stresses during handling and transportation (Metolina et al., 2023).

Iron ore pellets, alongside lump ore and sinter, are fundamental raw

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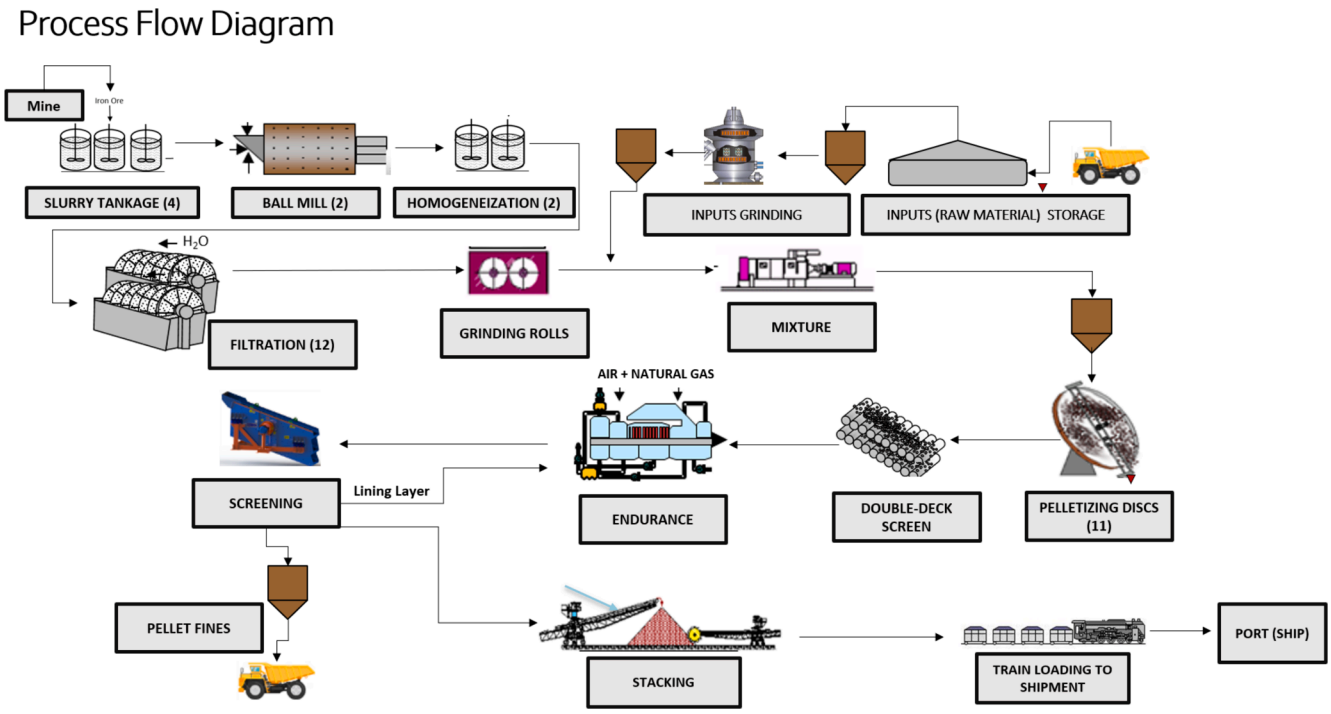

Fig. 1. Pellets production flow diagram.

materials for steel production, generated through the pelletizing process (Singh et al., 2023). The porosity developed during pellet manufacturing is a critical attribute. It enables internal gas flow, enhancing reducibility and process efficiency (Kim and Sohn, 2023). Nevertheless, porosity also impacts the physical integrity of the pellets, which must endure various stresses during handling, transportation, and processing. Thus, the quantity, size, shape, and distribution of pores are essential aspects of pellet quality control. Traditionally, porosity characterization relied on techniques like mercury intrusion porosimetry (PIM) and optical microscopy (OM) (Korobeinikov et al., 2023; Zhang et al., 2023). PIM, however, solely assesses surface-connected pores, while OM is confined to two-dimensional space, potentially yielding unrepresentative data.

To overcome the limitations of PIM and OM, recent advancements in technology have introduced more sophisticated methods for porosity characterization. One such method is X-ray microtomography (micro-CT), which allows for a non-destructive three-dimensional analysis of the internal structure of iron ore pellets. This technique provides a comprehensive understanding of the pore network, including the connectivity and tortuosity of the pores (Ju et al., 2023). Furthermore, micro-CT can quantify the size, shape, and distribution of pores with high accuracy, thereby offering a more reliable assessment of pellet quality.

In addition to micro-CT, computational modeling and simulation techniques are also being employed to predict the behavior of iron ore pellets under various conditions (Augusto et al., 2015; Ljung, 2010). These models take into account the physical and chemical properties of the pellets, as well as the environmental conditions during handling, transportation, and processing. By simulating these conditions, researchers can optimize the pellet manufacturing process to achieve the desired porosity while maintaining the physical integrity of the pellets. Recent advances have seen the application of MicroCT-based porosity characterization, offering three-dimensional insights into iron ore pellets. MicroCT, a form of 3D microscopy, provides comprehensive internal and external structural information without extensive sample preparation (Tang et al., 2023). Thus, our aim is to develop a porosity characterization methodology for iron ore pellets, potentially complementing or replacing conventional techniques. We acknowledge the limitations of each approach (Bezerra and Augusto, 2020).

To obtain primary iron, two commercially viable production routes exist: blast furnace reduction, yielding liquid pig iron, and direct reduction, which produces solid iron sponge or DRI (direct reduced iron) (Cavaliere, 2019; Cavaliere, 2019). DRI encompasses metallized products derived from the solid-state reduction of iron ore (granules and pellets) in direct reduction reactors (Nurdiawati et al., 2023). DRI is primarily composed of metallic iron, residual iron oxides, and reactor contaminants such as silica, alumina, and calcium. DRI reoxidation, particularly during storage and transport, presents ignition risks, requiring specialized handling as water is ineffective for extinguishing reoxidation-induced fires (Bersenev et al., 2022; Li et al., 2021). Certain pellets exhibit a greater propensity for self-ignition during direct reduction, likely due to altered process conditions (Yazir et al., 2021; Hamadeh et al., 2018). Despite these observations, current laboratory test methodologies, standardized by ISO, do not adequately address this behavior or provide insights into predicting autoignition occurrences (Anameric and Kawatra, 2007). In direct reduction, iron oxides are solid-state reduced to metallic iron without melting, resulting in increased porosity and fine generation (Pfeiffer et al., 2023). The removal of oxygen leaves a highly porous structure (Meshram et al., 2022; Man and Feng, 2016), and both raw materials and reduction temperature influence DRI porosity (Cavaliere et al., 2023; Cavaliere et al., 2023; Cavaliere et al., 2023).

Despite these technological advancements, challenges remain in accurately characterizing and controlling porosity in iron ore pellets. In addition, the heterogeneous nature of these materials hinders complete description through stereological methods (Shen et al., 2023). This study is aimed to propose a three-dimensional porosity characterization methodology for iron ore pellets, leveraging X-ray microtomography (MicroCT) and image analysis to study open and closed pores separately. Factors such as predominant phase fractions, pore distribution, morphology, and phase connectivity are pivotal in understanding pellet behavior during the process (Ju et al., 2023).

This study aims to develop a three-dimensional porosity characterization methodology for iron ore pellets, enabling the separate study of open and closed porosity. We seek to compare the results with classical

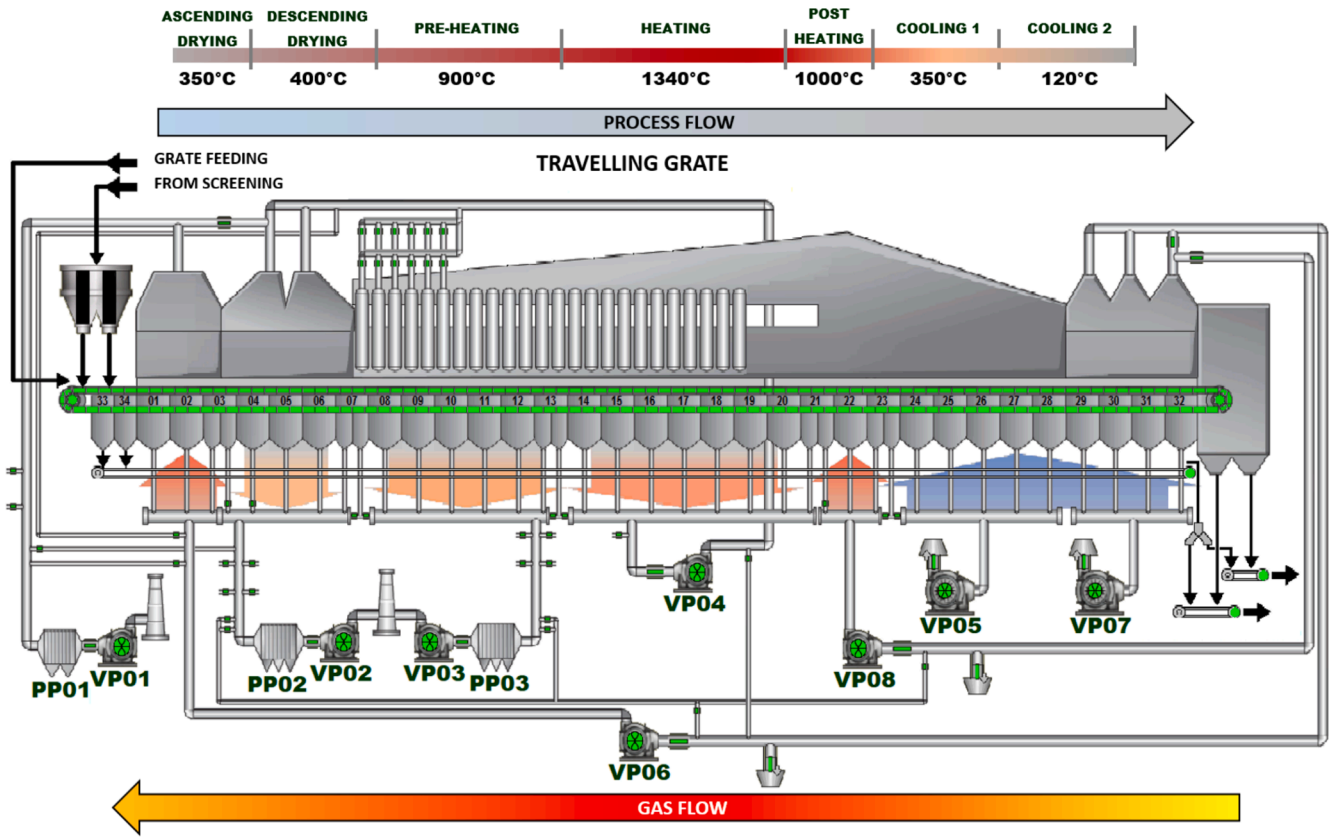

Fig. 2. Endurance procedure schematic with (in scale) the indication of the different stage temperatures. PP = Precipitator, VP = Vacuum Pump.

Fig. 3. Customized shaft furnace.

porosimetry techniques, especially in assessing porosity evolution and pore geometry during direct reduction in a hydrogen atmosphere. Our methodology involves acquiring MicroCT images of iron ore pellets in different geometric configurations, comparing lower and higher resolutions, and subsequently processing and analyzing these images for qualitative and quantitative material assessment.

2. Experimental procedure

2.1. Mining and pelletizing procedure

The examined pellets were supplied by VALE (Brazil), and the pelletization process is illustrated in Fig. 1.

The iron ore pelletizing plant starts with the grinding stage, where the ore is combined with a precise solid content and grinding balls of different sizes. The plant is equipped with several ball mills, each of which has a considerable capacity for processing the ore. The most important quality parameter at this stage is the specific surface area (Blaine), which is usually in the range of 1,500 to 1,600 cm^2/g. After the grinding process is completed, the material passes through vacuum filtration. The filters used in this stage are characterized by their large diameter and provide a large filtration area. After the filtration stage, the material undergoes a treatment with high pressure grinding rolls (HPGR), which further improves the quality parameters. The HPGR process is characterized by its capacity and uses rollers with specific dimensions in terms of diameter and width.

The material is then fed to the pelletizing discs, with each disc providing a different capacity. The plant has several discs, and both the discs and the screens have specific dimensions in terms of their diameter and width. Finally, the material is subjected to a continuous treatment, as shown in Fig. 2.

At the end, the pellets go through a filtration step to remove fines less than 5 mm. This thorough process culminates in the production of iron

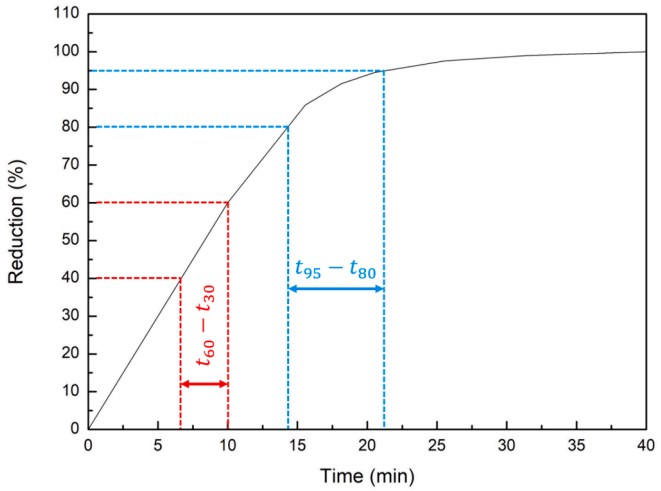

Fig. 4. Rates of reduction indexes calculation.

ore pellets, which serve as an important resource for various industries.

2.2. Characterization procedure

The composition of the pellets was studied by energy dispersive X-ray spectroscopy (EDS) in a Zeiss EVO 60 scanning electron microscope. To determine pellet density, seven pellet diameters were measured and the average diameter was calculated. Subsequently, this average diameter was employed to calculate the pellet density by weighing the pellets accurately using a balance with a resolution of 0.0001 g. The pellets were then weighed with a balance. In addition, the surface microstructure of the pellets was examined using a scanning electron microscope (SEM) to quantify the surface pores. The compressive strength of the pellets was measured using a Zwick/Roell Z100 standard testing machine at a speed of 0.5 mm/min (the example movie of the performed tests is shown in Supplementary Material). A specially designed shaft furnace was used for the comminution experiments of the pellets, which is shown in Fig. 3.

2.3. The gas composition was 100 % H2 hydrogen

From the reduction curves, which represent the percentage of reduction versus time to reduction, we calculated the kinetics constants and the reduction rates. The kinetic constant was calculated through the three dimensional diffusion model (Eq.1):

$$k = \frac{[1-(1-\alpha)^{\frac{1}{3}}]^2}{t} \quad (1)$$

and through the three dimensional phase boundary controlled reaction (Eq.2):

$$k = \frac{1-(1-\alpha)^{\frac{1}{3}}}{t} \quad (2)$$

where α is the fraction reacted (0–1) and t is the time at which a given fraction of the material reacts (Man and Feng, 2016).

The reduction rate is analyzed through the definition of two indexes described in Equations 3 and 4:

$$\frac{dR}{dt}_{40} = \frac{33.6}{t_{60} - t_{30}} \quad (4)$$

$$\frac{dR}{dt}_{90} = \frac{13.9}{t_{95} - t_{80}} \quad (5)$$

with t_{95}, t_{80}, t_{60} and t_{30} being the time required to reduce the pellets by 95, 80, 60 and 30 %. This is schematized in Fig. 4.

The morphology and evolution of particle pores were analyzed by microtomography using General Electric's Phoenix v/tome/xs system. Microtomography data were then analyzed using Image J software to characterize the porosity of the material. Selected pellets were completely metallized during the reduction process and then reheated in a heat treatment furnace at 200 °C to 700 °C for different times to determine their reoxidation behavior. All CT scans were performed at 150 kV and 10 W, with the sample rotated 360° during imaging. Factors such as exposure time and number of projections directly affect the overall analysis time. Binding is a process that involves grouping pixels, which also affects analysis time; It increases the signal-to-noise ratio but

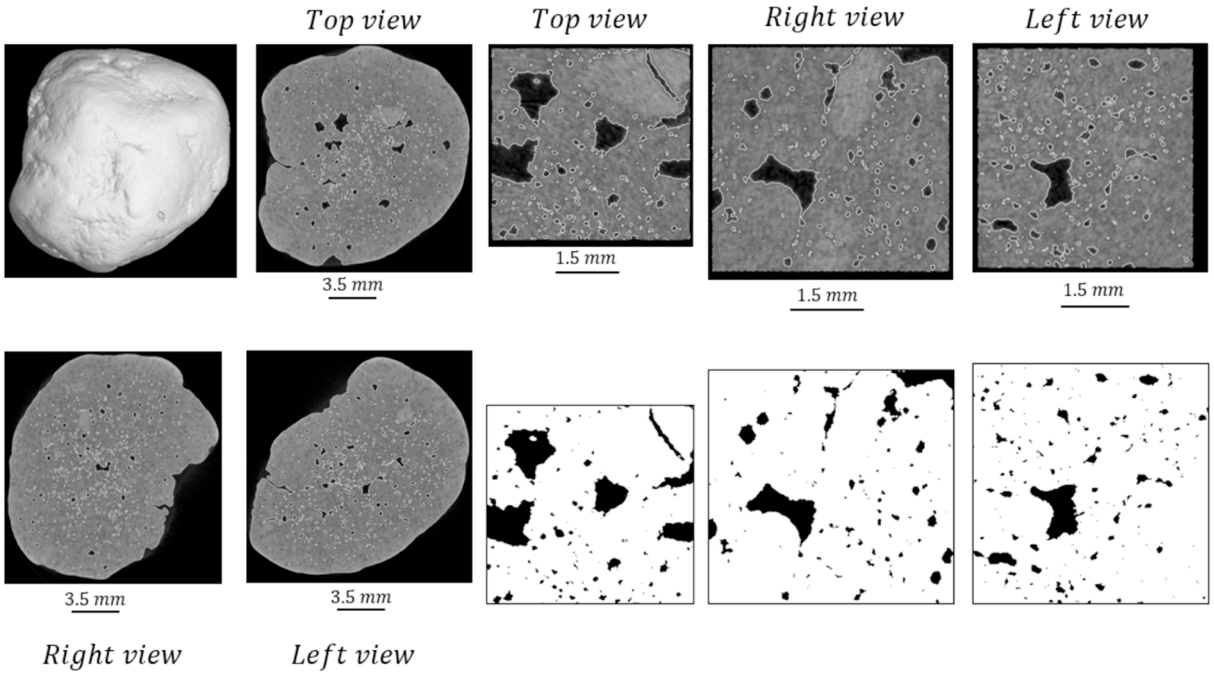

Fig. 5. Tomography analyses example performed on the studied pellets.

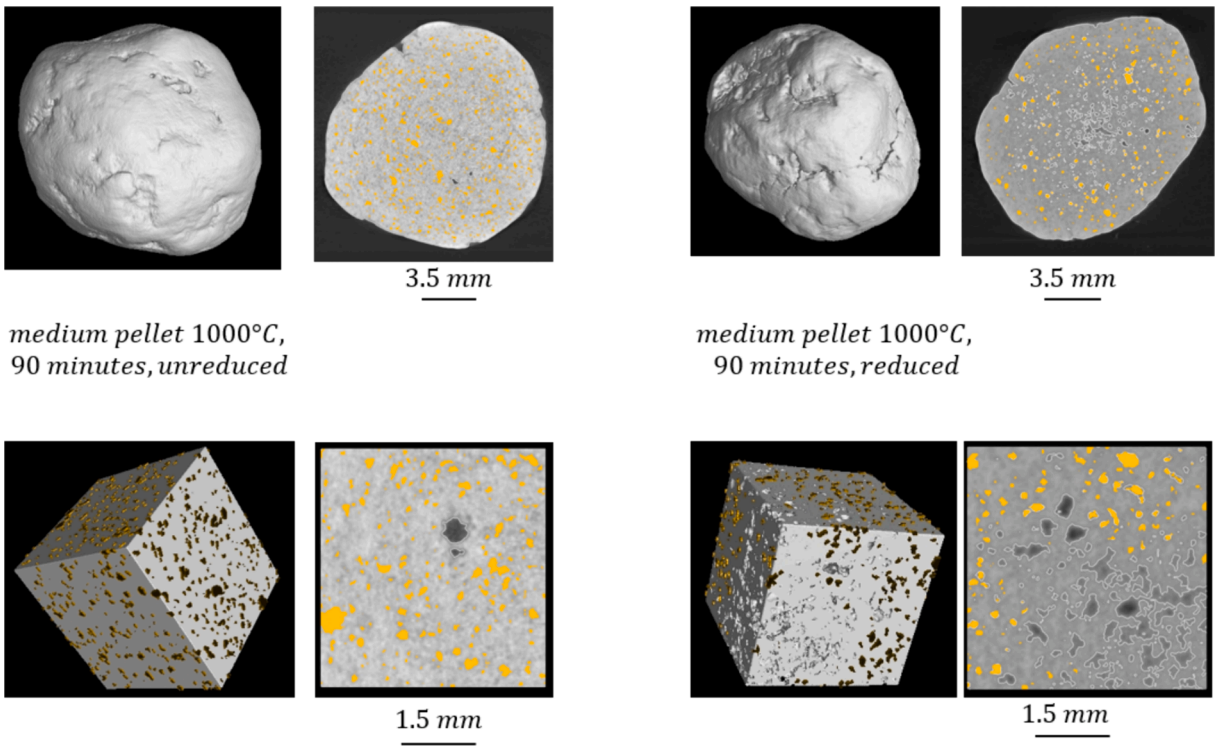

Fig. 6. Pellets structure analysed selecting different volumes sections.

reduces the resolution, thus affecting the pixel size.

In all acquisition processes, a filter type suitable for the analysis of dense samples requiring high energy products is used. Filters are used to eliminate lower-energy X-rays that would otherwise be preferentially absorbed near the surface of the sample. This selective absorption, known as beam hardening, can generate artifacts that degrade the image quality, making the edges of the sample appear denser. The choice of filter was based on the transmission value, which is a ratio between the X-ray signal received with the sample and without the sample. For image preprocessing, open-source software FIJI/ImageJ was used. In an effort to optimize analysis conditions with respect to image quality and acquisition time, various parameters were experimented with, including different geometric configurations during acquisition, which inherently altered image resolution, as well as reductions in the number of projections and the angular range of sample rotation, from the standard 360° to 180°.

3. Results and discussion

X-ray microtomography was used to analyze the pellets. Pellets were classified into three groups based on their mean diameter: small (up to 1.1 cm), medium (1.1 to 1.5 cm), and large (with a diameter greater than 1.5 mm). Individual pellet reduction tests were performed, with reduction times set at 5 min, 30 min, and 90 min, to follow the evolution of porosity. Various parameters were calculated, including the variation of porosity and tortuosity under different reduction conditions for each individual pellet. All tomography images of the monitored pellets are included in the Supplementary Material, which can be accessed via an online link. X-ray computed microtomography is a nondestructive technique that allows internal and three-dimensional visualization of a sample exposed to ionizing radiation and requires minimal physical and chemical sample preparation (Nie et al., 2023). It works on the same principle as conventional radiography, where different parts of a sample absorb radiation to different degrees. Consequently, it allows the nondestructive examination of two-dimensional cross sections, which can be reconstructed using mathematical principles to create a corresponding three-dimensional model of the sample. This in turn allows visualization and quantification of the internal structure of the material (El-Zoka et al., 2023). Computed tomography produces an image that closely approximates reality by displaying the average attenuation of each small volume element, ordering the attenuation data, and providing quantitative information, as shown in Fig. 5.

After the post-processing step, the image finally goes to the attribute extraction in which the quantitative data of interest are obtained (Fig. 6).

The numerical data contained in the images can be acquired and analysed, allowing subsequent steps of classification and pattern recognition. Pore segmentation was performed using the freely available software FIJI /ImageJ. A lower threshold was determined visually to exclude some pores from selection, and an upper threshold was set above which non-filled pores were selected, but also above which segmentation of solid partial remnants began. This threshold (either maximum or minimum) was consistently applied to all sample layers. The determination of this threshold is of critical importance, as it significantly affects the calculation of the porosity fraction in iron ore pellets. The images have well-defined contrast, which allows better segmentation of tonal variations. To distinguish between open and closed porosity, a novel pore discrimination method based on the calculation of Euclidean distances (EMD) was used to delineate the pellet edge (Ignacio et al., 2022). The minimum edge distance (MDE) of the filled object provides a hue reference where each object is assigned a hue based on its distance from the pixel to the object edge. The lowest hue values are related to connected pores, since this type of pore is in contact with the edge. Consequently, after calculating the MDE, a graph of minimum intensity is created, with the smallest values corresponding to connected pores.

Segmentation is done interactively by applying a fixed threshold to each 2D layer of the model. The selection of the separation cutoff tone value affects the number of pixels. To determine the porosity percentage and segmentation of iron ore pellet images was still difficult even after all previous steps, we used five different segmentation thresholds for each sample, with a difference of 5 tons between them. Then,

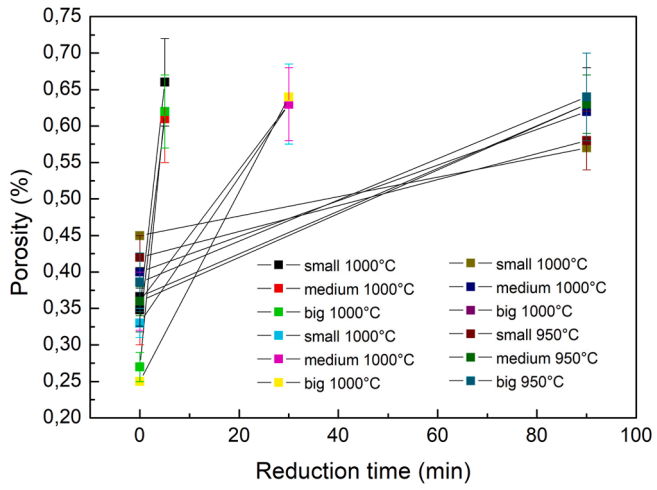

Fig. 7. Porosity as a function of temperature and reduction time for different size pellets.

segmentation is performed using these values and the pore volume is subtracted for each volume obtained. Therefore, the estimated value of the porosity of each sample falls within the scope of determining these thresholds (Wei et al., 2019).

Porosity is generally the rate limiting step of the reduction process (Fig. 7).

Pores in materials can be grouped based on how easily they can be reached by outside fluids. Closed pores are entirely isolated from external fluids and other pores, influencing macroscopic properties like density, elasticity, mechanical strength, and thermal conductivity. However, they are irrelevant in processes involving fluid flow and gas adsorption. Pores that have a communication channel with the external surface of the solid are referred to as open pores (Mishra, 2020). Open pores have various designations, including "pore-through," which features an open channel starting at one point on the surface, passing through the particle, and emerging at another surface location. Another type is "blind-pores," which have an opening at only one end. Pores with slight surface irregularities are technically considered blind-pores, but it's better to treat them separately as a distinct characteristic known as surface roughness (Yi et al., 2013).

The main factor influencing the process is the porosity of the pellets in terms of dimensions, tortuosity, and pore distribution (Ghadi et al., 2016). This is closely related to the specific volume of hydrogen reacting with the pellet's internal surface. In cases of low porosity and small surface pore dimensions, gas encounters numerous obstacles in penetrating the pellet. Consequently, solid-state diffusion from the surface becomes more significant but operates at orders of magnitude slower rates than gas diffusion. As a result, all chemical reactions are driven by hydrogen adsorbed on the pellet surface (Ma et al., 2021).

This aspect is crucial for the swelling behavior of pellets within industrial reactors (Huang et al., 2012). In fact, porosity and pore dimensions significantly affect the kinetics of direct reduction, and when porosity decreases due to pellet compression within DRI reactors, the time required for complete reduction is substantially prolonged (Ghadi et al., 2023). Therefore, the microstructural characteristics of iron ore pellets play a pivotal role in evaluating factors that influence their behavior during reduction processes. Porosity, for instance, must be adequate to enable gas flow, enhancing process efficiency, without sacrificing mechanical strength, essential for transportation and handling. Thus, the distribution of pore size and shape are vital aspects of pellet properties. The volumetric fraction and morphology of each phase present also contribute to the pellets' metallurgical quality (Lei et al., 2023). Conversely, resistance increases with decreasing porosity. To achieve both high strength and high reducibility at the same time, a potential solution is to produce pellets with open pore structures or closed pores near the surface but with low overall porosity (Rao et al., 2023).

Porosity tends to increase as the reduction processes take place Fig. 8).

As the reduction process progresses, this phenomenon tends to speed up the reaction rate. Considering that diffusion can often be the limiting step, porosity and pore dimensions have a significant impact on the reduction process (Zheng et al., 2023). This is because both porosity and

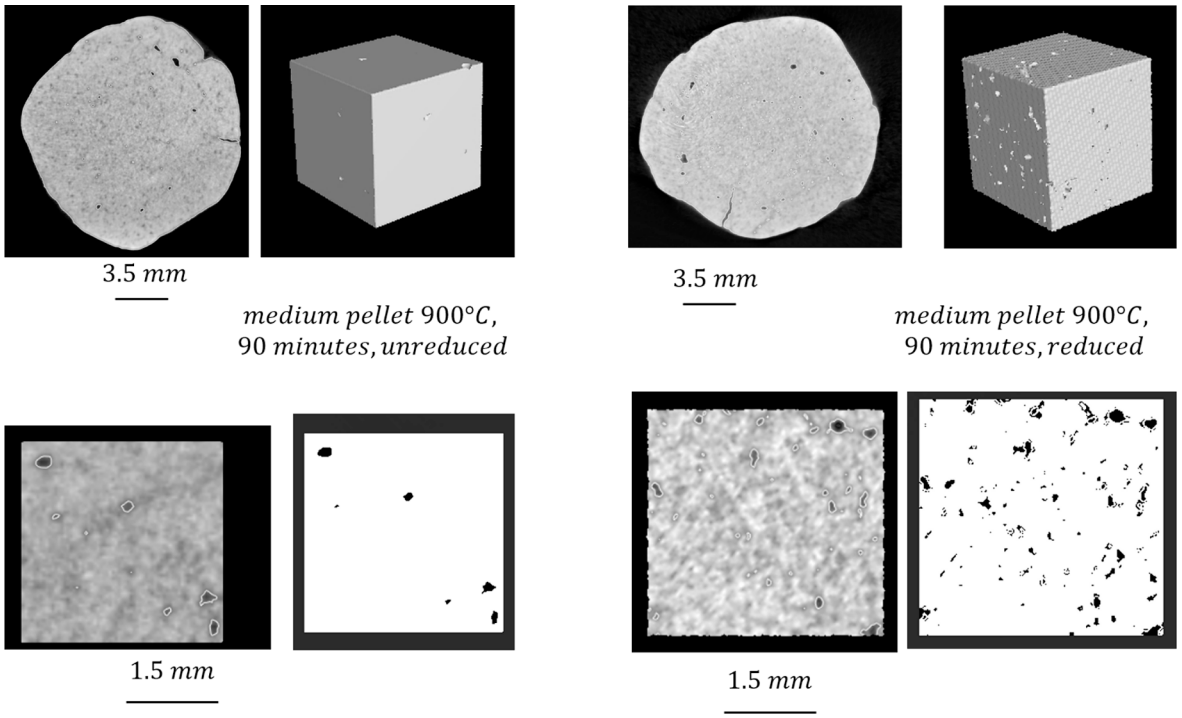

Fig. 8. Porosity analyses for selected pellets.

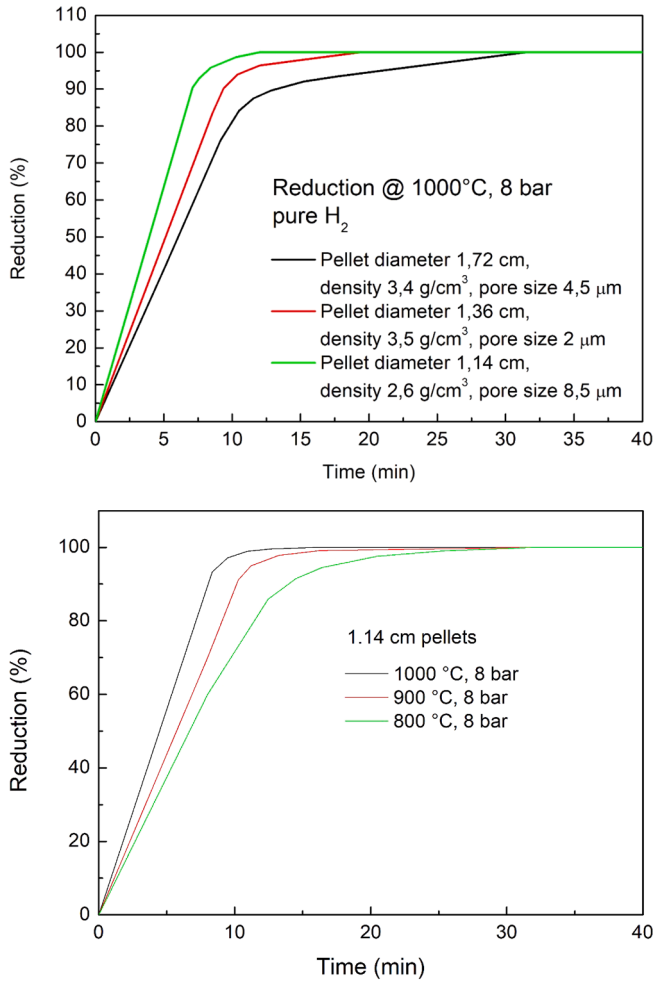

Fig. 9. Reduction curves for selected pellets.

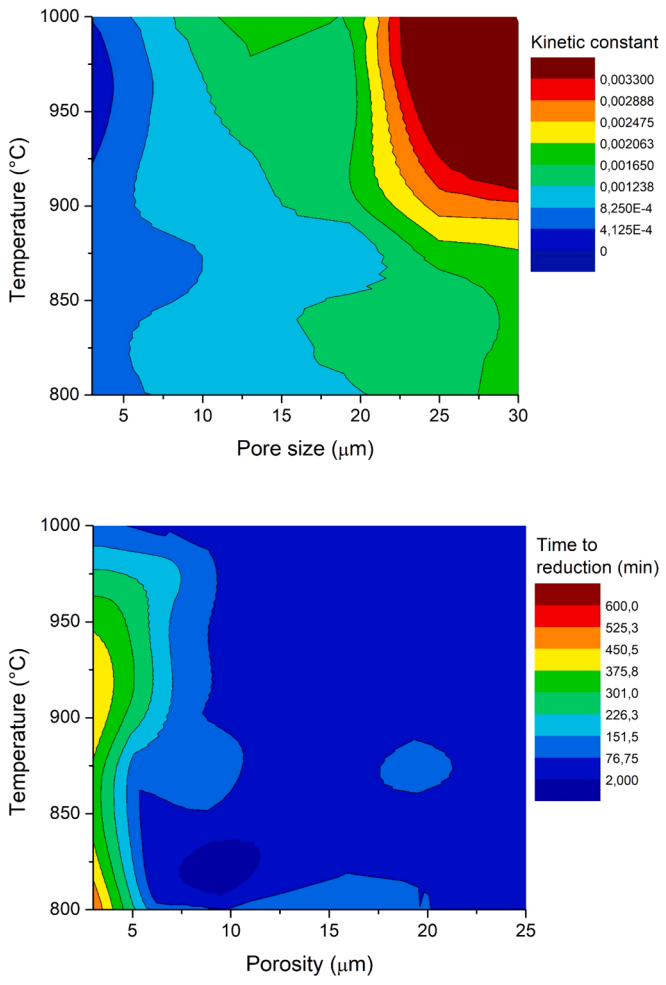

Fig. 10. Kinetic constant and time to reduction as a function of the most influencing parameters.

pore size determine the specific surface area of the pellets, thus defining the available surface for reaction development. This aspect is crucial and needs to be accurately included in a model that can effectively describe how these systems evolve (Lyu et al., 2023).

Entropy generation arises from two main factors: chemical reactions and mass transfer. When we analyze these factors individually, we observe that as the porosity of the pellet decreases, entropy generation caused by heat transfer increases (Bai et al., 2022). In this situation, entropy rapidly increases during the initial stages of reduction because of the temperature difference between the pellet surface and the heated hydrogen. Afterward, entropy decreases and reaches a stable state as the temperature gradient diminishes during the progression of the reduction process (Rukini et al., 2022).

On the other hand, when we consider pellets with increasing porosity, the resistance to gas penetration inside the pellets decreases. Consequently, entropy generation due to gas flow decreases. The second contribution pertains to entropy generation from chemical reactions. In this case, entropy generation tends to rise rapidly during the initial reaction stages but then decreases to zero as the chemical reactions progress (Li et al., 2023). Here as well, an increase in pellet porosity leads to a decrease in entropy generation. It's important to note that entropy generation results in increased energy consumption for the overall reduction process.

An example of the reduction curves in some experimented conditions is shown in Fig. 9.

As a matter of fact, Fig. 10 shows the results of the reduction behaviour as a function of temperature and pores size for the studied high-grade pellets.

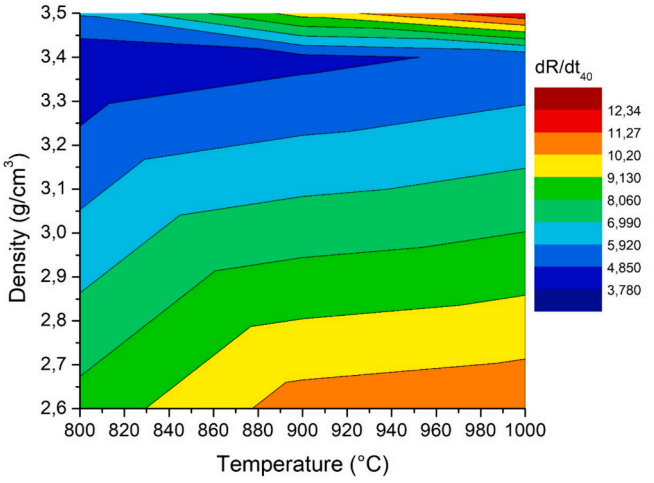

Fig. 11. dR/dt40 index as a function of reduction temperature and pellets density.

The kinetics of reduction are significantly accelerated as the dimensions of the pores increase, regardless of the temperature. In other words, larger pores lead to faster pellet reduction. The reduction reactions of high-density pellets progress stepwise, which can be described using a shrinking core model. On the contrary, for low-density pellets,