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Improved clay ceramics incorporated with steelmaking sinter particulates[☆]



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ABSTRACT

Sinter particulates (SPs) retained in the electrostatic precipitator of the sintering stages in a steelmaking plant were incorporated up to 20 wt% into kaolinitic clay to produce improved porous ceramics for building construction. Specimens were prepared by uniaxial press-molding and then fired at 750, 900 and 1050 °C that are typical temperatures for bricks, blocks and tiles production. Ceramic properties and microstructure related to porosity and mechanical strength were evaluated. The results disclosed, for the first time, how porosity might be associated with improved strength in clay ceramics processed at typical temperatures for bricks, blocks and tiles. Owing to the porosity, the ceramic thermal and acoustic insulation were also improved.

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1. Introduction

The sintering stage of a modern integrated steelmaking plant is responsible for production of the sinter used as feedstock in the fabrication of pig iron and steel [1]. During the high temperature sintering, a cloud of particles is generated and should be retained to avoid atmospheric pollution. An electrostatic precipitator collects these sinter particulates (SPs) by means of electrical potential applied between plates that the

cloud is forced to go through [2]. In principle, these SPs could be recycled into the same sintering operation. However, this is technically inconvenient due to the possibility of recirculation of alkaline compounds that are prejudicial to the process and might result in a decrease in productivity. The existing alkaline substances, concentrating in the SPs, will attack the alumina refractory blocks and thus decrease the operational life of the sintering furnace lining [3].

Industrial residues with relatively high amount of iron oxides, such as SPs collected in the sintering stage of a

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steelmaking industry, are being investigated to be used in cement [4] and agricultural soils [5]. Another possibility for application of iron oxide-containing residues is their incorporation into clay ceramics for building construction products, such as bricks, structural blocks and tiles [6–9]. In this regard, clay ceramics present the favorable condition of tolerating the incorporation of materials with distinct compositions. In some cases, the incorporation may contribute to improve the ceramic properties [6–9]. Furthermore, it provides an economy for saving the amount of clay, which is a non-renewable natural resource [7]. Depending on the particle size of the incorporated material, after firing the ceramic acquires a porous microstructure, which might enhance its thermal and acoustic insulation.

Based on these introductory facts, the objectives of the present work were both to characterize the sinter particulates collect in the sintering stage of a Brazilian integrated steel-making plant and to evaluate the effect of incorporation into clay ceramics with advanced properties.

2. Experimental

The materials used in this work were: flying particles collected at the sintering stage of an integrated steel-making plant, Arcelor Mittal Tubarão, Brazil, here denoted as sinter particulates, SP, and a kaolinitic clayey body, CB, used to fabricate bricks in a ceramic industry located in the city of Campos dos Goytacazes, State of Rio de Janeiro, Brazil. The characteristics of this CB are given elsewhere [10]. In short, it is composed of kaolinite, muscovite mica, quartz and gibbsite, presenting high amount of Al_2O_3 and low fluxes, typical of kaolinitic-based clays.

The SP was initially characterized in terms of mineralogical, chemical and physical composition. The qualitative mineralogical phase identification was performed in powder sample by X-ray diffraction (XRD) using a Bruker-D4 Endeavor diffractometer operating with $Co-K_{\alpha}$ radiation (35 kV/40 mA) and a scanning 2θ angle from 5 to 80° . The chemical composition was determined by X-ray fluorescence (XRF) in a Philips PW 2400 equipment. The particle size distribution was determined by both, sieving and sedimentation methods, following the standard [11].

Incorporations of up to 20wt% of SP into the clayey body were performed in a pan mill during 30 min. Prismatic $114.5 \times 2.54 \times 10 \text{ mm}^3$ specimens were obtained by uniaxial pressing at 18 MPa, dried at 110°C for 24 h and then fired at 750, 900 and 1050°C in a laboratory furnace. These temperatures are typically used in Brazil for fabrication of construction bricks, structural blocks and roofing tiles. The heating rate was $3^{\circ}\text{C}/\text{min}$ with one hour soaking at the maximum temperature. Cooling occurred by natural convection inside the furnace after it was turned off. These specimens were tested for the amount of porosity as well as three points bending flexural strength. The porosity percentage was determined by Hg pycnometry, according to a standard procedure [12]. The three-points flexural rupture strength was determined in an Instron 5582 universal testing machine, using a cross head speed of 0.5 mm/min. Scanning electron microscopy (SEM) analyses were performed in a model SSX-550 Shimadzu system.

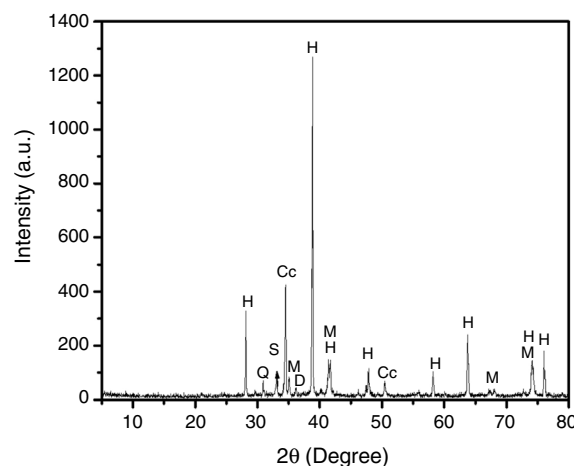


Fig. 1 – XRD pattern of the SPs: Cc = calcite; D = dolomite; H = hematite; M = magnetite; Q = quartz; and S = silvite.

3. Results and discussion

Fig. 1 shows the XRD pattern for the SP, which presents a complex and wide mineralogical composition range owing to the different raw materials involved in the sintering stage of a steel-making plant [3]. The major crystalline phases identified in this figure are: hematite (Fe_2O_3), magnetite (Fe_3O_4), calcite ($CaCO_3$), quartz (SiO_2), dolomite ($Mg.Ca.(CO_3)_2$), and silvite (KCl).

Table 1 shows the chemical composition of the SP, which is predominantly formed by iron compounds such as hematite and magnetite, also detected by XRD in Fig. 1. CaO and SiO_2 occurred with relatively high amounts. The loss on ignition, LoI, is predominantly associated with the combustion of amorphous coke fines, C, that were not identified by X-ray diffraction, as well as with the decomposition of both calcite and dolomite. The small amount of 2.28% of SO_3 suggests the presence of sulfates, possibly of Ca, such as gypsum, which was also not identified by X-ray diffraction.

Fig. 2 shows the SP size distribution and its relevance for the production of different ceramic materials. According to Fig. 2a, the SP have approximately 80% of their particle size concentrated in the range of 20 to $0.300 \mu\text{m}$, which is suitable for applying in clay ceramics. This fine particle size impairs the sintering process in the steel-making process and is another reason to avoid recycling the SP. In Fig. 2b the Winkler diagram [13] with the location of the raw materials as well as some compositions investigated in this work is presented. This diagram is an important tool used to predict the extrusion stage of clay ceramics based on the particle size distribution of the precursor materials. The numerated regions are associated with different products. According to Fig. 2b, the clay body is located in region (3), appropriated for roofing tiles fabrication. The SP is located in the bottom of the diagram near the corner associated with particle sizes higher than $20 \mu\text{m}$ at a region of no practical interest for ceramic production. The incorporation of SP tends to displace the clayey body, CB, to other regions, decreasing its plasticity. This is due to the decrease in the amount of particles with size less than $2 \mu\text{m}$

Table 1 – Chemical Composition of the SP (wt%).

Total Fe	SiO ₂	MnO	SO ₃	Al ₂ O ₃	K ₂ O	MgO	CaO	ZnO	C	LoI ^a
70.70	6.82	0.82	2.28	1.20	1.81	10.33	9.70	0.72	3.3	10.70

^a LoI: loss on ignition.

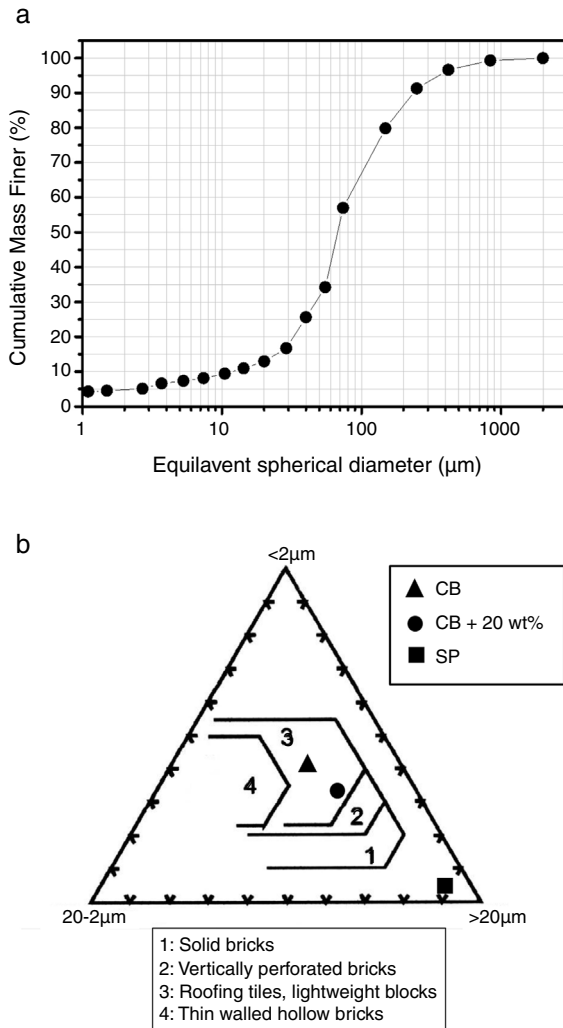


Fig. 2 – Particle size distribution of SP (a) and Winkler diagram showing regions of ceramic application in building construction (b).

that are associated with the clay minerals responsible for clay body plasticity [14]. One should observe in Fig. 2b that the maximum investigated amount of SP, 20 wt%, did not change the relative location of the clay body, which still remains in region (3). This result indicates that the investigated SP can be incorporated in relatively high amounts that will not significantly change the workability of the investigated CB before firing to a final ceramic.

Fig. 3 shows the results of the technological properties after firing. These results indicate that the temperature

causes important physical and mechanical changes on the compositions investigated. Both porosity, Fig. 3a, and flexural rupture strength, Fig. 3b, increase, mainly, at 1050 °C. These results are associated with the ceramic consolidating processes as well as the physical and chemical transformations of the precursor materials during the firing stages [14]. The mineralogical composition of the SP suggests an inert behavior during the firing stage at the investigated temperatures. The incorporation of the SP tends to increase the porosity, Fig. 3a, of the CB at all investigated temperature, mainly at 1050 °C. This augment in porosity contributes to increase the ceramic water absorption, which is an important property, mainly for roofing tiles.

Fig. 3b shows that the flexural rupture strength of the clay ceramic is increased with the incorporation of any amount of the SP at 900 and 1050 °C. At 1050 °C, the clay ceramic presents a significant increase in the mechanical strength only until 10 wt% of incorporation, followed by a moderate decrease. With respect to the linear shrinkage, Fig. 3c, it was observed that the incorporation of the SP practically does not change the value obtained by the clayey ceramic at all temperatures. An exception is that of the composition with 20 wt% SP fired at 1050 °C, in which a beneficial decrease occurs in the linear shrinkage.

The mineralogical constitution of the SP, associated with high amount of iron compounds, suggests an inert behavior during the firing stage of the ceramics. Then, the question is: how could, after firing, the porosity of the clay ceramic change with the incorporation of the SP? The answer to this question is probably related to the packing of the samples during the forming stage. It is suggested that the coarser particle size of the SP in comparison with that of the clay body, not only increases the porosity, but also affects the contact area of the particles. A higher contact area facilitates the sintering mechanisms, both by solid state diffusion and liquid phase formation, which improves the ceramic strength [14].

Fig. 4 illustrates a typical SEM micrograph of the 10 wt% SP incorporated clay ceramic fired at 1050 °C. This was the condition of the highest flexural strength (18 MPa) and porosity around 16%. It reveals, for the first time, evidence of porosity being beneficial to the mechanical properties of incorporated clay ceramics.

Finally, preliminary acoustic tests and thermal conductivity results around 0.9 W/mK, indicated that the SP incorporated clay ceramics display improved thermal and acoustic insulations that are relevant characteristics for materials used in building construction.

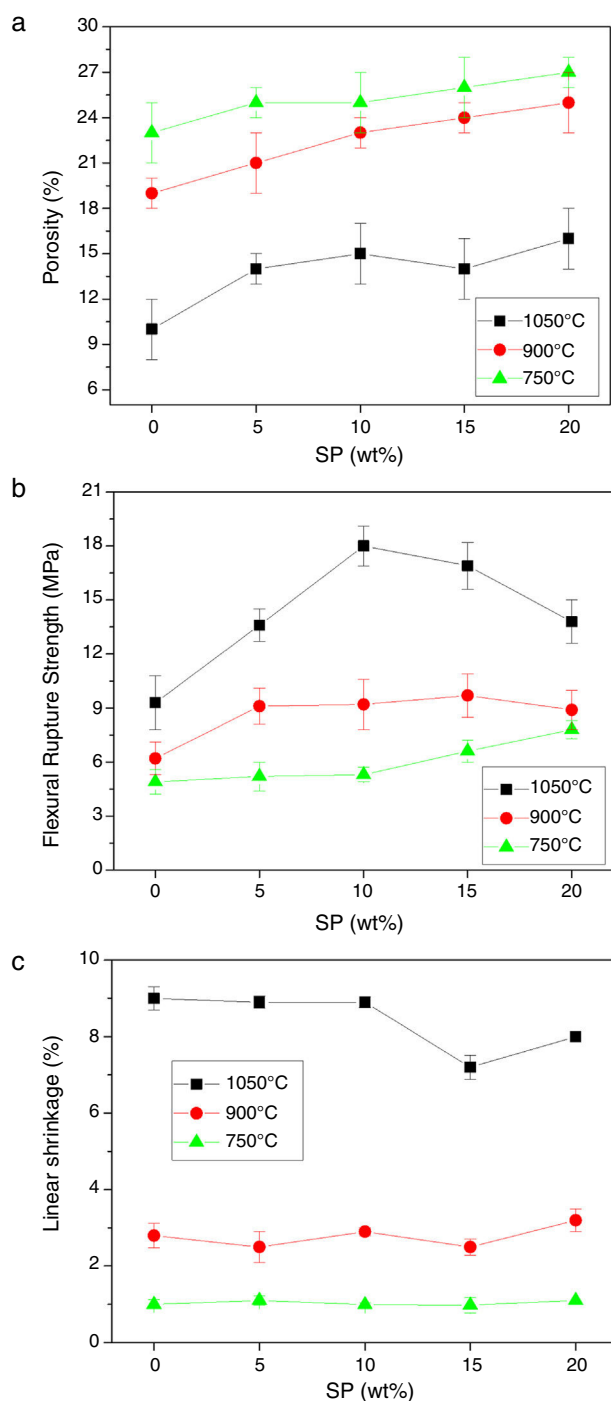


Fig. 3 – Porosity (a), flexural rupture strength (b) and linear shrinkage (c) of the clay ceramic as a function of the amount of the incorporated SP.

4. Conclusions

- Collected particles from the sintering stage of an integrated steel-making plant, has an elevated amount of Fe and Ca compounds. The major crystalline phases were hematite, magnetite, and calcite. The particle size is adequate for its

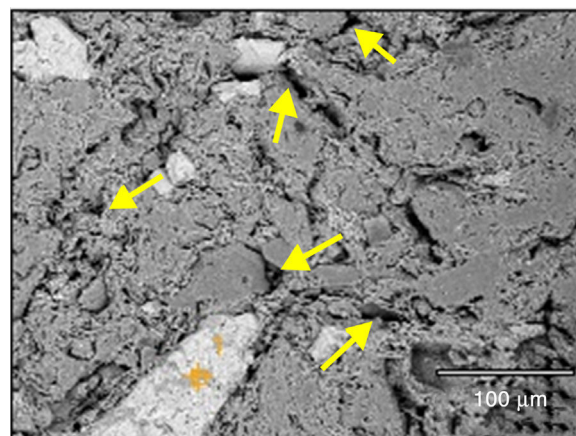


Fig. 4 – SEM micrograph of 20 wt% SP incorporated clay ceramic fired at 750 °C (pores indicated by arrows).

direct incorporation into clay ceramic fabrication, producing porous microstructure.

- The incorporation of these sinter particulates (SPs), in amounts of up to 20 wt%, into a clay body did not change its workability and enhanced the evaluated physical and mechanical properties of the fired clay ceramics. Moreover, the ceramic porous microstructure contributes to improve the thermal and acoustic insulation that are valuable characteristics for building construction.
- The results indicated that SPs have a potential to be used into clay ceramics. The increase in porosity is associated with real benefits both in the processing as well as in the quality of the products.

Conflicts of interest

The authors declare no conflicts of interest.

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REFERENCES

- Wakelin DH, Fruehan RJ. *Making, shaping and treating of steel – iron making*. 11th ed. Warrendale, PA: AIST Steel Foundation; 1999.
- Sun W, Zhao L, Li X, Zhao Y. In: Cavaliere P, editor. *Ironmaking and steelmaking process: greenhouse emissions, control and reduction*. Switzerland: Springer; 2016. p. 355–72.
- Vieira CMF, Ribeiro MM, Monteiro SN. *Microstructural evaluation of clayey ceramic incorporated with powder waste from the sintering plant of a steel-making industry*. *Mater Sci Forum* 2012;727–728:951–8.

- [4] Ciccu R, Ghiani M, Serci A, Fadda S, Peretti R, Zucca A. Heavy metal immobilization in the mining-contaminated soils using various industrial wastes. *Minerals Eng* 2003;16:187–92.
- [5] Tsakirids PE, Agatzini-Leonardou S, Oustadakis P. Red mud addition in the raw meal for the production of Portland cement clinker. *J Hazard Mater* 2004;116:103–10.
- [6] Zhang I. Production of bricks from waste materials – a review. *Constr Build Mater* 2013;47:643–55.
- [7] Monteiro SN, Vieira CMF. On the production of fired clay bricks from waste materials: a critical update. *Constr Build Mater* 2014;68:599–610.
- [8] Velasco PM, Ortiz MPM, Giro MAM, Velasco LM. Fired clay bricks manufactured by adding wastes as sustainable construction material – a review. *Constr Build Mater* 2014;63:97–107.
- [9] Quijorna N, de Pedro M, Romero M, Andrés A. Characterization of the sintering behaviour of Waelz slag from electric arc furnace (EAF) dust recycling for use in the clay ceramics industry. *J Environ Manag* 2014;132: 278–86.
- [10] Monteiro SN, Vieira CMF. Characterization of clays from Campos dos Goytacazes, north Rio de Janeiro State (Brazil). *Tile Brick Intl* 2002;18:152–7.
- [11] Brazilian Association for Technical Norms - NBR 7181/84, Determination of soils granulometric analysis. Rio de Janeiro, RJ, Brazil: ABNT; 1984 [in Portuguese].
- [12] American Society for Testing and Materials – C 373-72, water absorption, bulk density, apparent porosity and apparent specific gravity of fired whiteware products. West Conshohocken, PA: ASTM; 1972.
- [13] Winkler HGF. Importance of the grain size distribution and the mineral composition for coarse ceramic products (in German). *Keramischen Gesellschaft* 1954;31: 337–43.
- [14] Monteiro SN, Vieira CMF. Solid state sintering of red ceramics at lower temperatures. *Ceram Intl* 2004;30:381–7.