Incorporation of mold flux waste in red ceramic

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ABSTRACT

This work has as its objective to evaluate the effect of mold flux waste incorporation in a red ceramic body. The mold flux waste came from an industry of additives for continuous casting of steel, in the municipal area of Guaratinguetá, State of São Paulo, Brazil. Initially, the mold flux waste was characterized in terms of chemical composition, particles size distribution, X-ray diffraction, specific surface area and scanning electron microscopy. Clay mixtures were prepared with additions of 0, 5, 10 and 20 wt.% of mold flux waste. Red ceramic specimens were produced by extrusion and then fired in an industrial furnace at 750, 850, 950 and 1050°C. Some physical and mechanical properties were evaluated. The results indicated that mold flux waste addition optimized the plasticity of the clayey body, increased the flexural and compressive strength and reduced the values for water absorption. The specimens with 5 wt.% of mold flux waste, at 1050°C firing temperature, presented the best results for the properties evaluated, indicating a higher packing for this composition. The incorporation of mold flux waste allowed improvements in the clayey body, producing better quality materials and being an appropriate way of disposal.

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1. Introduction

Mold flux plays important functions in continuous casting of steel. Basically, this synthetic slag must provide thermal insulation, prevention of steel reoxidation and inclusions absorption when applied on the surface of molten steel. In addition, mold flux lubricates and controls the heat transfer in the gap between the mold of copper and the solidifying steel shell [1–8].

The mold flux is composed by various combinations of raw materials. Frequently used raw materials are quartz, feldspar, fluorite, wollastonite and free carbon [9,10]. The fabrication process of the mold flux implies in the generation of a waste that consists in wet and coarse particles. Those particles cannot be applied in the process of continuous casting once they do not have the recommended granulometry, which is usually 200 mesh. Since the mold flux production occurs in a large scale to attend the continuous casting process, the generation of the mold flux waste occurs in an extensive quantity [11].

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It is important to recycle the wastes in different areas such as building materials. The use of wastes as substitutes for clay in the production of red ceramics has been widely studied [12,13]. This environmental correct solutions for the disposal of a large range of solid wastes is possible by the natural variability on the characteristics of clays, the use of simple processing techniques besides relatively low technical performance requisite for the products [14-16].

The incorporation of waste in ceramic makes possible the development of an eco-friendly building material with innumerable advantages like diminish the amount of generated wastes, protect the raw materials from depletion and reduce the environmental pollution. In some cases, the addition of certain residues into a clay matrix enhances the technical performance of the ceramic [17].

The interest in using mold flux waste in red ceramic is mainly due it characteristic that can include biodegradability, combustibility or water solubility [18]. Another concern is the fact that the mold flux waste is usually disposal in industrial landfills. This event promotes negatives environmental impacts that includes a significant source of gases, particulate matter, leachate and very capital intensive [19,20]. The mold flux waste represents an environmental impasse due not only it characteristics but also the costs involved in it correct destination. A huge environment damages can be caused by the inappropriate disposal of this waste, such as the rivers and streams contamination and human health impact by inhalation [21].

This incorporation can improve physical and mechanical properties of ceramic, which can be an economic advantage to the red ceramic [22]. Therefore, this work aimed to incorporate and evaluate the effect of the incorporation of mold flux waste in the physical and mechanical properties of red ceramics.

### 2. Materials and methods

#### 2.1. Raw materials preparation

A clayey body composed by a mixture of a kaolinite clay, red clay and sand, typically used in the fabrication of bricks and roofing tiles in Campos dos Goytacazes, state of Rio de Janeiro (RJ), Brazil, was incorporated with mold flux waste from the fabrication process of mold flux.

#### 2.2. Raw materials characterization

The mold flux and the ceramic mass were initially characterized in terms of their mineralogical, chemical and physical composition as well as firing behavior, by thermo analysis, and morphological aspects. The chemical composition was determined by X-ray fluorescence (XRF) using a PANalytical XRF equipment, model Axios Max. The qualitative mineralogical phase identification were performed by X-ray diffraction (XRD) in powder samples using a PANalytical XRD, model Empyrean, operating with Cu Kα radiation (λ = 0.15418 nm). The particle size distribution were determined by both, sieving and sedimentation methods, according to the norm [23]. The real density of the raw materials was measured by pycnometry. Specific surface areas of the raw materials were analyzed using the multi-point BET method. The raw materials microstructure was determined by scanning electronic microscopic (SEM) in a Shimadzu model Superscan SSX500-50. The plasticity of the specimens was evaluated by the Atterberg limits. The liquidity limit was determined in accordance with ABNT NBR 6459 [24], while the plasticity limit determination was performed following to the standard ABNT NBR 7180 [25].

#### 2.3. Composition preparation

The elaborated mixtures were made with additions of 0, 5, 10 and 20 wt.% of waste in the ceramic mass. Those are shown in Table 1.

![Fig. 1 - Samples of the developed red ceramic prototype, before firing stage (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Raw materials (wt.%)</th>
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<tbody>
<tr>
<td></td>
<td>Ceramic mass</td>
</tr>
<tr>
<td>C0MFW</td>
<td>100</td>
</tr>
<tr>
<td>C5MFW</td>
<td>95</td>
</tr>
<tr>
<td>C10MFW</td>
<td>90</td>
</tr>
<tr>
<td>C20MFW</td>
<td>80</td>
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</table>

#### 2.4. Properties evaluation

After sintering and cooling, the specimens were submitted to water absorption, relative density, linear shrinkage and flexural strength. The water absorption (W.A.) was determined
following to ASTM standard procedure [26], according to Eq. (1).

\[ W.A. = \frac{(\text{Weight humid} - \text{Weight dry})}{\text{Weight dry}} \times 100 \] (1)

The relative density (R.D.) were measured by dividing the dry bulk density by the real density of the composition, following designation ABNT NBR NM52 [27], according to Eq (2).

\[ \text{R.D.} = \frac{\text{Dry bulk density (g/cm}^3\text{)}}{\text{Real density (g/cm}^3\text{)}} \] (2)

The linear shrinkage (L.S.) was obtained by measuring the length of the specimens, using a Mitutoyo caliper with \( \pm 0.01 \text{ mm} \) precision, before and after the firing stage, following to the standard ASTM [28], according to Eq. (3).

\[ \text{L.S.} = \frac{(\text{Length after sintering} - \text{Length before sintering})}{\text{Length before sintering}} \] (3)

The originals specimens were used for flexural test, while to evaluate the compressive strength, a new samples were obtained by cutting the originals specimens with dimensions of 50 mm \( \times \) 25 mm. In both tests, flexural strength and compressive resistance, the same machine (Instron 5582 universal test machine with 100 kN capacity) was utilized. The flexural strength (F.S.) test was carried out following designation ASTM [29] and was realized by loading three points with the load putted by the upper cleat at a speed of 0.5 mm/min until the rupture of the specimen. The results was determined according to Eq. (4).

\[ \text{F.S.} = \frac{3PL}{2bd^2} \] (4)

Where \( P \) = rupture strength (N); \( L \) = Support span (mm); \( b \) = Width of test beam (mm); \( d \) = height (mm).

The compressive strength (C.S.) was evaluated by using two parallel protection plates, with cross bar moving at 0.1 mm/min. Fig. 2 shows some specimens prepared for this test.

The results about compressive strength were determined following to ASTM standard procedure [29], according to Eq. (5).

\[ \text{C.S.} = \frac{\text{Total maximum load (N)}}{\text{Area (mm}^2\text{)}} \] (5)

The sintered specimens microstructure was evaluated by scanning electronic microscopic (SEM) in a Shimadzu model Superscan SSX500-50.

3. Results and discussion

Figs. 3 and 4 show the XRD pattern of the raw materials. The major crystalline phases identified in the mold flux waste, Fig. 3, are: quartz (SiO\(_2\)), wollastonite (CaSiO\(_3\)) and calcite (CaCO\(_3\)). Moreover, was identified the presence of albite (NaAlSi\(_2\)O\(_6\)), anatase (TiO\(_2\)) and cryolite (Na\(_3\)(AlF\(_6\)). In Fig. 4, the diffractogram indicates that the major crystalline phases

Fig. 2 – Specimens prepared for compressive strength test.

Fig. 3 – X-ray pattern of the mold flux waste. a: albite; A: anatase; c: calcite; Q: quartz; r: cryolite; w: wollastonite.
in the clay are: muscovite (K\textsubscript{Al}(Si\textsubscript{2}Al\textsubscript{2})(OH,F)\textsubscript{2}), quartz (SiO\textsubscript{2}) and kaolinite (Al\textsubscript{2}O\textsubscript{3}2SiO\textsubscript{2}2H\textsubscript{2}O). Furthermore, was detected the presence of gibbsite minerals (Al\textsubscript{2}OH\textsubscript{3}) and orthoclase (KAlSi\textsubscript{3}O\textsubscript{8}).

Table 2 presents the chemical composition and the loss on ignition (LoI) of the raw materials. The mold flux waste is basically composed of high amount of quartz (SiO\textsubscript{2}) which is associated with the minerals: quartz (SiO\textsubscript{2}), wollastonite (CaSiO\textsubscript{3}) and albite (NaAlSi\textsubscript{3}O\textsubscript{8}), according to the XRD pattern in Fig. 3. The second major chemical constituent of the mold flux waste is Al\textsubscript{2}O\textsubscript{3} that is probably due to the albite (NaAlSi\textsubscript{3}O\textsubscript{8}) and cryolite (Na\textsubscript{3}AlF\textsubscript{6}) phases. The CaO is mainly due to the calcite (CaCO\textsubscript{3}) phase. The chemical composition of the clay is based on high amount of SiO\textsubscript{2}, relative quantity of Al\textsubscript{2}O\textsubscript{3} and low amounts of alkaline oxides. The high percentage of LoI suggests an elevated fraction of clay minerals. The meaningful amount of Fe\textsubscript{2}O\textsubscript{3} in both raw materials gives to the specimens the reddish colour after firing.

Fig. 5 shows the particle size distribution of the clay and mold flux waste. The coarser fraction of the clay, that includes particle size above 20 \(\mu\text{m}\), is 45%. The percentage of clay minerals, the one who has particle size below 2 \(\mu\text{m}\), is 39%. The clay minerals are responsible for the plasticity of the ceramic mass [30]. The mold flux waste has a high percentage of coarser particle size, when compared to that of the clay. These coarser particles, usually, are associated with quartz. This result corroborates to the raw materials mineralogical analysis, Fig. 3. The real density of the mold flux waste, measured by picnom-

<table>
<thead>
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<th>Raw materials</th>
<th>Oxide compositions</th>
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<tr>
<td></td>
<td>SiO\textsubscript{2}</td>
</tr>
<tr>
<td>Clay</td>
<td>49.66</td>
</tr>
<tr>
<td>Mold flux waste</td>
<td>53.08</td>
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* Loss on ignition.
the progressive incorporation of mold flux waste has a very significant effect on the extrusion behavior. It is associated to the mold flux waste mineralogical composition that is predominantly composed by quartz, Fig. 3. This mineral acts as a plasticity reducer of the ceramic mass.

With respect to the relative density, it is an important data once only by this analysis is possible to check the mold flux waste effect in the clay compaction behavior [33]. Fig. 9 presents the relative density of the elaborated compositions. One should notice that 10 wt.% and 20 wt.% tend to decrease the relative density. On the other hand, the 5 wt.% addition tend to increase the relative density, as compared to all other compositions. This increase is related to the more efficient particles compaction [34].

According to Fig. 10, the linear shrinkage almost does not have significantly variation, for all of compositions in 750 °C and 850 °C, considering the statistical error. This effect can be related to a low sinterability of the bodies. At 950 °C, it can be observed an increase in the linear shrinkage to all composition with addition of mold flux waste, as compared to 0 wt.%. This increase becomes more significant at 1050 °C. This event is mainly due the vitrification process, which is capable of fill, partially, the open porosity between the particles and provides the shrinkage and densification of the ceramic bodies [35].

By contrast, Fig. 11 shows that the mold flux waste addition decreases the water absorption with the temperature incre-

<table>
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<th>Table 3 – Specific surface area of the raw materials.</th>
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<tr>
<td>Raw materials</td>
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<td>Clay</td>
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<tr>
<td>Mold flux waste</td>
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Fig. 6 – SEM photomicrographs of the mold flux waste. (a) 200x; (b) 1000x.

Fig. 7 – SEM photomicrographs of the clay. (a) 200x; (b) 500x.

Fig. 8 – Extrusion prognostic through Atterberg limits. (●) Locations of the compositions.

Fig. 9 – Relative density of the elaborated compositions.

Fig. 10 – Linear shrinkage according to the content of mold flux waste incorporated in specimens sintered at 750, 850, 950 and 1050 °C.

Fig. 11 – Water absorption according to the content of mold flux waste incorporated in specimens sintered at 750, 850, 950 and 1050 °C.

Fig. 12 – Flexural strength according to the content of mold flux waste incorporated in specimens sintered at 750, 850, 950 and 1050 °C.

This decrease is more significant for 5 wt.% addition. This result can be related to the more efficient compaction behavior in this specimen, Fig. 9. The increase in linear shrinkage and the decrease in water absorption with mold flux waste addition are consequences of the higher fluxes content, Table 2, as compared to that of the clay. At higher temperatures the fluxes (K₂O and Na₂O) cause an increase in the liquid phase promoting densification and improving the sintering process.

Figs. 12 and 13 show the results of flexural rupture strength and compressive strength, respectively. The flexural strength is a property tightly dependent on the porosity and microstructural defects of the bodies. One should observe that the mold flux waste addition increases the flexural strength with the temperature increment, specially at 1050 °C. It is
already expected, due the densification. It is relevant to notice that the addition of 5 wt.% get the higher values of flexural strength for all temperatures analyzed, Fig. 12. A reduction in flexural strength is observed with the 10 and 20 wt.% addition of mold flux waste, when compared to 5 wt.%. One should wonder why the improved densification obtained by the flux action of the mold flux waste does not result into a better flexural strength for all compositions. Even though the mold flux waste incorporation contributes to diminish the open porosity, the median pore diameter increases sharply. This event, together with the higher amount of quartz in the 10 and 20 wt.% compositions, may introduce large enough pores and micro-cracks to implicate in a drop of the flexural strength [36].

The compressive strength, similar as flexural strength, presented higher values for specimens with mold flux waste addition, which reaches 27% at 1050 °C, when comparing the compositions containing 20 and 0 wt.% of waste. The increase in temperatures, in consortium with the incorporation of mold flux waste, contributed positively to the mechanical resistance.

Scanning electron micrographs of the fracture surface of bodies without addition, C0MFW, and with 20 wt.% of mold flux waste, C20MFW, fired at 750 °C and 1050 °C, are shown in Figs. 14 and 15, respectively. It can be notice that both bodies present a rough fracture surface. The micrographs of C0MFW show a comparatively larger quantity of defects such as cracks and voids. On the other hand, C20MFW shows a better-sintered microstructure with smoother areas e fewer
defects as compared to COMFW, specially at 1050 °C which the higher temperature makes possible a more efficient vitrification process, Fig. 15. This may be due to the flux action of the mold flux waste, that improves the sintering process.

4. Conclusions

In this work, the characterization and evaluation of the effect of a industrial waste, mold flux waste, generated during the production of mold flux into red ceramic led to the following conclusions:

- The mold flux waste can improve the extrusion process, optimizing the plasticity.
- The mold flux waste incorporation decreases the open porosity of the fired clay. Consequently, the water absorption decreased with the mold flux waste content and, by contrast, the flexural strength and compressive strength increased.
- The use of mold flux waste is viable for some types of ceramic pavers. The results of water absorption and compressive strength indicated that the specimens with 5 wt.% of mold flux waste, with a firing temperature of 1050 °C, can be produced for implementation systems hard (type R) and implementation systems flexible (type F) according to ASTM [37]. Furthermore, this same composition at 1050 °C, can be produced for floors where the pavers may be frozen while saturated with water (SX) according to ASTM [38].
- The SEM microstructural analysis showed that the composition with 20 wt.% of mold flux waste has a finer fracture surface with less defects as compared to the clay without mold flux waste incorporation.
- The use of mold flux waste in red ceramic can be a technological solution to the problems caused by the indiscriminate disposal into the environment.

Conflicts of interest

The authors declare no conflicts of interest.

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REFERENCES