Use of ornamental rock residues for mould flux development

Abstract

Ornamental rock production, such as marble and granite plates, have great importance in the southeastern region of Brazil. Its residues are composed of some compounds used in continuous casting as mould fluxes. Therefore, the aim of this article was to study these residues to formulate mould fluxes. First, the raw materials were chemically characterized by energy dispersive X-ray spectroscopy (EDS) and two new fluxes were developed based on two different commercial fluxes used for peritectic and low carbon steels. All fluxes were analyzed for their ability to form crystalline phases, by performing the modified Stollberg test. The slag formed was analyzed by X-ray diffraction (XRD), thin section microscopy (TSM) technique, and a mathematical model for comparison. Also, sample fluidity was measured using the known “boat test” and viscosities were predicted by FactSage® software. Crystallinity and fluidity of new fluxes were compatible with those observed for the commercial fluxes. The FactSage® simulations identified crystalline phases, such as cuspidine (Ca$_3$Si$_2$O$_7$F$_2$), for all fluxes. In commercial low carbon flux (CLC) and new low carbon flux (NLC), X-ray results have shown that non-crystalline phases are formed. And in commercial peritectic flux (CP) and new peritectic flux (NP), X-ray results have shown crystalline phases. The results showed similar characteristics between the new fluxes and the commercial ones; however, further tests in an industrial setting are required to obtain additional information and confirm equivalent behavior during their industrial use.

Keywords: continuous casting; steels; peritectic steel; mould fluxes.

1. Introduction

For a well-controlled solidification with high productivity in continuous casting, a mould flux powder that allows obtaining the fastest casting speed as possible while at the same time keeping an excellent quality of the solidified product is required. The solidification conditions in the mould are fundamental and mould fluxes mainly influence following aspects: i) lubrication between the mould and solidified shell; ii) heat transfer between mould and slab; iii) thermal insulation at the top of the mould; iv) protection against oxidation; and v) inclusion absorption at surface (Mills et al., 2004). These effects have a decisive influence on quality and productivity. Overall, mould fluxes are constituted of a mixture of minerals based on the CaO-SiO$_2$-Al$_2$O$_3$-Na$_2$O-CaF$_2$ system and when in contact with liquid steel melt and generate a liquid slag with specific characteristics for each casting condition (Li et al., 2004). Among the various types of steel produced, peritectic steels have a higher incidence of longitudinal cracks formation due to the contraction of the alloy when steel is solidifying. The contraction occurs due to the different types of packing factor of ferrite (δ) and austenite (γ) for alloys containing 0.06–0.18% of carbon (Mills et al., 2004). In this case, fluxes with lower heat transfer coefficient by radiation are required. This specific characteristic can be obtained by using fluxes with high crystallinity, which may be increased by adding lime and fluorite. Another important type of steel is steel of low carbon content; in this case, casting speed is higher when compared with peritectic steels, and fluxes are produced with lower binary basicity and lower amount of fluorite. However, these rules can be changed if other oxides are present, such as high percentage of MgO. If the mould flux has a MgO content higher than 7 %wt, then some fluorite and other oxides must be added to ensure the formation of crystalline phases. However, it is difficult to predict and to adapt the composition because a new complex system of slag is formed.

Usually, raw material used in flux production comes from limestone and other materials found in nature. In this work, granite and marble residues were chosen to produce fluxes due to their chemical similarity and their great availability in Brazil. In 2014, production of these rocks was about 7 million tons (ABIROCHAS, 2014) and residues result from extraction.
cutting and polishing of the blocks. During the sawing stage, about 25–30% of the block is transformed into powder, which is then disposed in landfills (Moura et al., 2002). Therefore, besides the economic advantage that can be attained, the use of these residues may increase sustainability of the industrial process of ornamental rock production.

2. Materials and method

2.1 Raw material

The raw materials used in this work were analyzed by scanning electron microscopy (SEM – Zeiss Model EVO 10) with energy dispersive X-ray spectroscopy (EDS-Oxford). Table 1 shows the results obtained, and the chemical composition was

<table>
<thead>
<tr>
<th>Components</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
<th>CaF₂</th>
<th>C</th>
<th>lbc (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marble residue</td>
<td>35.4</td>
<td>2.1</td>
<td>0</td>
<td>16.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>45.9</td>
</tr>
<tr>
<td>Granite residue</td>
<td>2</td>
<td>66.4</td>
<td>15.3</td>
<td>1.1</td>
<td>2.9</td>
<td>4.6</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>2.7</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>58.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>41.5</td>
</tr>
<tr>
<td>Fluorite</td>
<td>0</td>
<td>4.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>95.5</td>
</tr>
<tr>
<td>Graphite</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Lime</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

(*lbc) loss by calcination

Table 1
Chemical composition of the raw materials.

2.2 Formulation of new mould fluxes

The NP and NLC fluxes were developed with the aim of comparing new fluxes with commercial ones, two fluxes were obtained from a steelmaking company: a peritectic flux (CP) and a low carbon flux (CLC). The raw materials shown in Table 1 were used to produce two new fluxes as follows: the first, similar to CP, was called new peritectic flux (NP) and the second, similar to CLC, was called new low carbon flux (NLC).

The commercial and new fluxes were characterized using techniques that will be described next and each stage is identified in Figure 1.

Table 2
Chemical composition of mould fluxes measured by wet chemistry analysis for CP, CLC, NP, NLC.

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>F-</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>46.1</td>
<td>30.8</td>
<td>7.4</td>
<td>3.3</td>
<td>0.9</td>
<td>4.3</td>
<td>0.5</td>
<td>1.2</td>
<td>5.7</td>
</tr>
<tr>
<td>CLC</td>
<td>34.3</td>
<td>35.8</td>
<td>7.9</td>
<td>2.8</td>
<td>2.8</td>
<td>10.9</td>
<td>0.2</td>
<td>0.5</td>
<td>4.8</td>
</tr>
<tr>
<td>NP</td>
<td>44.5</td>
<td>24.7</td>
<td>10.8</td>
<td>4.6</td>
<td>2.7</td>
<td>4.4</td>
<td>2.1</td>
<td>1.8</td>
<td>4.4</td>
</tr>
<tr>
<td>NLC</td>
<td>34.7</td>
<td>25.5</td>
<td>11.2</td>
<td>4.3</td>
<td>8.0</td>
<td>4.6</td>
<td>2.1</td>
<td>1.8</td>
<td>7.6</td>
</tr>
</tbody>
</table>

The NP and NLC fluxes were developed aiming at the same CaO percentage as the commercial fluxes due to their high influence on crystallinity. The other compounds are quite different mainly due to a higher level of MgO in the marble residue. According to Mills et al. (2004), a high level of MgO leads to a vitreous phase; therefore, more fluorite was added to the peritectic flux and less Na₂O to the low carbon flux. Table 2 shows the chemical composition of the commercial and new fluxes measured by wet chemistry analysis. The new flux compositions used approximately 50 %wt and 74 %wt of residues for NP and NLC, respectively. The composition was adjusted using other raw materials shown in Table 1, such as lime, sodium carbonate, fluorite and carbon.

![Figure 1](https://example.com/figure1.png)

Steps for developing mould fluxes.
2.2.1 Crystallinity analysis

In order to study the susceptibility of the fluxes to form crystalline phases, the modified Stollberg test was used (Li et al., 2004). First, each sample was decarburized by heating it at 650 °C for 16 h; after that, about 23 g of material was placed in an alumina crucible for heating at 1300 °C for 20 min; then, the melted sample was poured into a stainless steel crucible and kept in an oven at 610 °C for 20 min to induce crystallization; finally the crucible was quenched in water. The slag thus formed was analyzed by X-ray diffractometer, and the microstructures of the samples were analyzed using thin section microscopy (TSM). X-ray diffraction patterns were obtained on a Bruker model D8 Advanced based on a Bragg Brentano parafocusing goniometer using Cu-kα radiation with a wavelength of 0.15418 nm. The XRD scans were digitally recorded with a step size of 0.02°, 20 angle ranging from 20 to 100°, reading time of 2 s and a rotation of 10 rpm. Also, thin films were prepared according to ABNT/NBR standards (ABNT, 1992). This method consists of attaching a thin slice of solidified slag on a glass slide with subsequent sanding and polishing until obtaining an approximately 30 μm-thick film. Verification of the thickness and parallelism of the samples on the slide as well as the thin film analysis were carried out in a Leica DM750P petrographic microscope with Laz EZ software.

\[
\frac{NBO}{T} = \frac{2x_{CaO} + 2x_{BeO} + 2x_{FeO} + 2x_{Na}_2O + 2x_{Al}_2O_3 + 6x_{F}_2O_3 + (2x_{MgO} + 2x_{MnO})}{x_{SiO}_2 + 2x_{Al}_2O_3 + x_{Ti}_2O_2 + 2x_{B}_2O_3 + (x_{MgO} + x_{MnO})}
\]

\[
\%C = 141.1 \frac{NBO}{T} - 284.0
\]

where x is the molar fraction of mould flux components and %C is the crystallinity percentage. The parentheses in the denomin- tor/numerator mean that their contents will be included in the denominator, if %MgO > 7 and/or %MnO > 4, otherwise, it will be included in the numerator.

2.2.2 Fluidity Analysis

Control of the melt viscosity at the working temperature is essential to minimize the non-uniformity of the heat flow in the mold, mainly reducing longitudinal cracks (Cruz et al., 2007). An empirical and comparative way of determining which melt is more or less viscous is through the "boat test". In this test, the samples were arranged at the end of the test boats and these were placed on a horizontal refractory brick. The arrangement was placed in an oven at 1300 °C and kept in it for 30 min. After this, the refractory brick, which has a cut that allows the boat to be tilted at 45°, was held in that position for 5 min. The brick was then returned to the horizontal position and the samples were taken out of the oven for photographing and fluidity comparison (Valadares et al., 2014). In addition, the wet chemical analysis results were entered into FactSage® software version 6.4 to predict viscosities.

2.2.3 Phase thermodynamic simulation

According to Castañeda et al. (2011), FactSage® software can be used with a high degree of confidence for determining the main mineralogical phases formed in the mould fluxes. Therefore, it was used to determine likely phases that form during heating/cooling between 800–1500 °C. According to chemical species present in the fluxes, the SiO_{2}-Al_{2}O_{3}-CaO-MgO-CaF_{2}-Na_{2}O system, which includes almost the entire range of chemical composition, was considered the stable phase diagram. In addition, the FToxid, FactPS and FToxid-SLAGH databases were used for predicting compounds more accurately.

2.2.4 Granulometric distribution

The granulometric distribution of marble and granite residues in commercial and new fluxes was measured using a Mastersizer 2000 laser granulometry size analyzer model APA2007 from Malvern Instruments Ltd.

3. Results

Figure 2 shows the results of the granulometric analysis. According to the data obtained from the control software, the grain size range of CP flux, CLC flux, marble and granite residues was 0.240-158 μm, 0.240-158 μm, 0.499-630 μm and 0.363-831 μm, respectively.
After the modified Stollberg test, the slag fluxes looked as shown in Figure 3. Macroscopically, it is possible to confirm two types of fluxes. The first flux is a translucent vitreous flux type, such as the commercial (CLC) and new low carbon (NLC) fluxes, respectively. A crystalline index was assigned to CP and NP fluxes, which have a totally opaque look.

The slag X-ray diffraction obtained after modified Stollberg test is shown in Figure 4. First, measurements were made on the surface in contact with the stainless steel crucible, and crystalline phases were identified in all samples seen in Figure 4-(a). After that, surfaces were sanded and a thin layer of approximately 0.2 mm was removed for new measurements. Figure 4-(b) shows that only peritectic fluxes keep crystalline patterns, which is an evidence that low carbon fluxes have low percentage of crystalline phases.
Table 3 shows the percentage of crystallization using Equations 1 and 2 (Mills, 1993) and their results are consistent with those shown in Figures 3 and 4.

Table 3
Calculation of crystallinity percentage as a function of NBO/T.

<table>
<thead>
<tr>
<th>Mould Fluxes</th>
<th>NBO/T</th>
<th>% Crystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>2.9</td>
<td>100</td>
</tr>
<tr>
<td>CLC</td>
<td>2.1</td>
<td>17</td>
</tr>
<tr>
<td>NP</td>
<td>3.7</td>
<td>100</td>
</tr>
<tr>
<td>NLC</td>
<td>1.9</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 5 shows the microstructure obtained with transmitted-light microscope. The vitreous aspect is evident for CLC and NLC fluxes, which have the same look as a glass microstructure. On the other hand, CP and NP fluxes showed a crystalline aspect with the formation of some grains, which in some cases revealed to be similar to calcite. These results show that the NBO/T ratio is an important parameter that could be calculated when developing new fluxes.

Results of the thermodynamic simulation for CP, CLC, NP and NLC fluxes can be observed in Figure 6. Under equilibrium conditions, all fluxes showed crystalline phases, and cuspidine formation was also predicted.
Regarding fluidity, the appearance of the boats after the corresponding test is shown in Figure 7a. Figure 7b shows the results from FactSage® software, measured slag pool length obtained from the boat test, and viscosity in-

4. Discussion

Figure 2 shows the granulometric distribution of marble and granite residues, which is in accordance to commercial fluxes. The mould flux manufacture involves a pulp production, which generates an agglomerate particle. The mere fact that the granulometry of the material is within the range of use does not indicate that it is suitable for the production of a new flux. Thus, it is still necessary to investigate the rheological properties of the pulp formed. The granulate residue had only 3.4% of grains above the range found for commercial fluxes, while the marble residue had 6.3%. However, this small amount of grain out of the range may impair the spray dryer process, since the granulometry distribution of raw materials affects the sphere forming conditions; therefore, it may be necessary to selectively grind or separate residues.

For low carbon fluxes, the formation of crystalline phases is not required, as in the case of peritectic fluxes; therefore, it was possible to produce the NLC flux using 74% of residue. MgO contents of more than 5-7% favor vitreous phase formation (Li et al., 2004); thus, a smaller amount of marble was used for the NP flux, which was designed for peritectic steels. As explained previously, these types of steel show higher contraction after peritectic transformation. Because of this phenomenon, it is necessary to control heat transfer by radiation and, thus, more crystalline phases are required for these fluxes. The formation of crystalline phases depends directly on the chemical composition. For example, high fluorite content and basicity increase the most abundant phase in flux at higher temperatures, cuspidine (Ca$_3$Si$_2$O$_7$F$_x$).

However, in this type of flux, it is usual to find smaller amounts of pectolite (Na$_2$Ca$_2$Si$_4$O$_8$) and pseudo-wollastonite (CaSiO$_3$) phases. When alumina is added to the powder, anorthite (CaAl$_2$Si$_2$O$_8$), gehlenite (Ca$_2$Al$_2$SiO$_6$) and nepheline (NaAlSiO$_4$) are also formed (Cruz et al., 2007). X-ray diffraction patterns obtained for peritectic fluxes (Figure 4) have identified some of these phases, including cuspidine.

The macroscopic photos in Figure 3 show slags obtained from the modified Stollberg test. The CP and NP fluxes are very similar, as are the CLC and NLC fluxes, since the crystalline phases are more evident when the translucency is reduced. The formation of crystalline phases for all the fluxes in Figure 4-(a) is evident, but in the case of CLC and NLC fluxes, these phases appear due to the formation of a thin crystalline layer in the slag in contact with the crucible during heating. The X-ray diffraction patterns obtained after removal of this thin layer did not show any crystalline phases for CLC and NLC fluxes (Figure 4-b). The vitreous phase formation in NLC is attributed to the large amount of magnesium oxide (MgO) used in this flux (see Table 2).

In addition, Figure 4 shows that the X-ray diffraction patterns of slags have a great similarity between commercial and new fluxes. When comparing results of diffractometry, it was observed that the main phases were cuspidine and nepheline. Fluxes with fluorine contents above 12% tend to form compounds such as cuspidine (Cruz et al., 2007). Nepheline is present in higher amounts in CLC and NLC, which is favorable for the casting of low carbon steels, where the optimal solidification temperature should be between 1040-1060 °C. The formation of other phases is related to Na$_2$O, MgO and Al$_2$O$_3$ contents and, therefore, some variations among the fluxes were observed. Some of these phases, such as akermanite and gehlenite, were also found by other authors (Susa et al., 2011). Similarly as in X-ray diffraction, cuspidine and nepheline formation was observed in the thermodynamic simulation (Figure 6). The formation of these compounds was also observed by Seo et al. (2014). However, many phases obtained in X-ray diffraction results are not in accordance with FactSage® preview.

The microstructures shown in Figures 5-(d) and 5-(e) for CLC and NLC fluxes are very similar to Figure 5-(f), which was obtained for common glass. These materials do not present grains but show a continuous region characteristic of materials that do not form crystalline or amorphized phases. The thin layers were analyzed in the center of the samples and this explains why no crystalline phase appears, differently from what is seen in the X-ray in Figure 4-(a). It is believed that the vitreous phase shows up in CLC due to higher Na$_2$O and MgO contents and lower basicity compared to CP, and due to higher MgO and lower basicity in NLC compared to NP (Table 2).

Furthermore, in Figure 5, grain formation due to induced crystallinity was observed for CP and NP fluxes. The crystallinity of the NP flux was attributed to the lower MgO content and higher basicity when compared to the NLC flux, since the fluorine content was the same. It is believed that the time and temperature to which they were submitted were not enough for a better formation of miner-
aloids, making it impossible to identify them clearly in the petrographic microscope using transmitted light. However, when mineral identification techniques were applied, similar habits were observed, such as extinction and birefringence. The presence of calcite (CaCO₃) could be confirmed due to its cleavage characteristic, as seen in Figure 5-(c). For CP and NP fluxes, this same cleavage could be seen in Figures 5-(a) and 5-(b) in the circled areas. In addition, a carbonate localization test was performed, in which 25% hydrochloric acid was added to the samples and the boiling of material was observed. Moreover, when comparing Figures 5-(a) and 5-(b), it was found that CP has larger grain sizes than NP. According to Susa et al. (2011), bigger grain size may decrease heat transfer by radiation.

5. Conclusion

Ornamental stone residues consist of some compounds which are similar to those used for the production of commercial mold fluxes. Therefore, it was possible to obtain two types of fluxes with the phases, fluidity and crystallinity, compatible with commercial fluxes. Of course, there are some clear differences; however, the results showed that it is possible to produce two extreme types of fluxes with high crystallinity (peritectic fluxes - CP and NP) and others with a vitreous tendency (low carbon fluxes – CLC and NLC). Thus, the use of these residues for manufacturing mould fluxes is possible. However, to develop a new flux it is necessary to examine other characteristics during their use in an industrial plant, and the procedures applied in this work can be used to avoid industrial tests with compositions which will undoubtedly produce an undesired result. Also, the use of residues in mould flux production can increase sustainability in the continuous casting process.

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