Mixture of Granite Waste and LD Steel Slag for use in Cement Production

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**Abstract.** A great amount of granite waste and steel slag is generated daily in Brazil, being those constituted mainly by Si\(_2\)O\(_2\) and CaO, respectively. The objective of this work was to characterize the new material formed after melting and cooling of the mixture of granite waste and LD steel slag, with basicity (CaO/SiO\(_2\)) of 1.0, aiming to evaluate the technical feasibility of this to the Portland cement production. After melting the mixture, one sample was cooled in water and another one in the furnace. The samples characterization was carried out through X-ray diffraction and scanning electron microscopy. The results showed that the new material formed presented amorphous state, to the samples cooled in water and akermanite and gehlenite phases, considered ideals for the hydraulic activity of the slags, in the sample cooled in the furnace. Therefore, the mixture of those two wastes can be a new alternative for the use of both, allied to the decrease of the environmental impact.

**Introduction**

A great amount of wastes is generated daily in Brazil. Among those, the LD steel slag, originating from the steel production and the granite wastes. The LD steel slag is constituted mainly of lime (CaO), while the granite waste is predominantly constituted by silica (SiO\(_2\)). The slag presents high relationship CaO/SiO\(_2\), around of 4, so that there is free CaO [1]. This high relationship represents the main restriction of their use to the production of some products [1,2] as the Portland cement. The steel slag may suffer expansion, due to the free CaO, and its stabilization is slow, which may cause fragmentation in concrete built with this slag [3]. Besides, the free CaO reduces the vitrification of the slag, also damaging the cement properties.

Brazil produced in 2009 approximately 51.5 million tons of cement [4]. To the production of one ton of cement is necessary about 1.6 ton of raw material [5,6]. The Portland cement is constituted mainly by the clinker and a small part of other additions, depending on the cement type. Its production consists basically in the heating of the limestone mixture and clay to the melting, which happens the approximately 1450°C, originating the clinker [7]. The clinker has as main composition: tricalcium silicate (CaO)\(_3\)SiO\(_2\) and dicalcium silicate (CaO)\(_2\)SiO\(_2\), or alite and belite, respectively [4].

Since 1960 is used to the cement production the blast furnace slag, by-product of the pig iron production in the blast furnace, which presents the relationship CaO/SiO\(_2\) between 0.9 and 1.2 [2]. An alternative to the use of the steel slag in the cement production is adjusting its composition so that the relationship CaO/SiO\(_2\) be similar to the one of the blast furnace slag. This correction may be made through the mixture of slag with granite waste [9], since the granite waste has approximately 60% of SiO\(_2\) and 4.6% of CaO [10], while the slag only presents 10% of SiO\(_2\) and 46% of CaO [2].
However, there are some basic requirements which determine the viability of the cement production using slag and waste. One of them is the obtaining of glass slag (amorphous) after the melting and fast cooling of those wastes mixture, which is intending to avoid the alite decomposition \((\text{CaO})_3\text{SiO}_2\) [9], main phase of the Portland cement clinker, and the other, is the presence of the mineralogical phases akermanite \((\text{Ca}_2\text{Al}_2\text{Si}_7\text{O}_{17})\) and gehlenite \((\text{Ca}_2\text{MgSi}_2\text{O}_7)\), considered the mineralogical phases ideals for the hydraulic activity of the slag [11 apud 2].

The objective of the present work was to characterize the new material formed after melting and cooling of the mixture of granite waste and LD steel slag, with basicity \((\text{CaO}/\text{SiO}_2)\) of 1.0, aiming to evaluate its technical feasibility to the Portland cement production. X-ray diffraction (XRD) analysis and scanning electronic microscopy (SEM) were carried out in the new material to analyze if there was the formation of an amorphous product, after cooling in water and the ideal phases for hydraulic activity of the slag, after sample cooling in the furnace.

**Experimental Procedure**

The materials used in this work were samples of LD steel slag and waste from granite cutting using multi-wire technology (granite waste). The sample of steel slag collected was generated in the converters LD (Linz-Danawitz) of a located metallurgical company in Espírito Santo State and the granite waste was collected in a company of dimension stones processing, in the same State.

The chemical composition of the slag [2] and granite waste used in this work is presented in the Tables 1 and 2, respectively.

<table>
<thead>
<tr>
<th>Composition [wt. %]</th>
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<tbody>
<tr>
<td>SiO$_2$ CaO Al$_2$O$_3$ MgO FeO MnO P$_2$O$_5$ S LoI</td>
</tr>
<tr>
<td>10.0 46.0 1.50 7.0 27.0 6.0 2.0 0.04 -</td>
</tr>
</tbody>
</table>

Table 1 - Chemical composition of the LD slag [wt. %] [2].

<table>
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<th>Composition [wt. %]</th>
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<tbody>
<tr>
<td>SiO$_2$ CaO Al$_2$O$_3$ MgO Fe Na$_2$O K$_2$O MnO TiO$_2$ B$_2$O$_3$ LoI</td>
</tr>
<tr>
<td>59.6 4.6 18.1 1.8 1.8 3.1 3.7 0.05 0.93 0.48 5.8</td>
</tr>
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Table 2 - Chemical composition of the granite waste [wt. %] [10].

The necessary amount of each waste, for the preparation of the mixture studied in this work, was determined using the chemical composition of the wastes and intended basicity. To reach the basicity of 1, the amount of each waste used in the mixture was of 65.5 g of granite waste and 100 g of LD steel slag. Two samples were prepared and melted; being one submitted to the fast cooling in water (MW) and another, to the slow cooling, in the furnace (MF).

The mixture MW was melted in the Flyever tubular furnace, model FE50RP controlador. The maximum temperature used in that furnace during the melting process was of 1500°C, for approximately 45 minutes. After that period, the sample was cast quickly in a recipient with water to obtain an amorphous product.

The melting process of the mixture MF was carried out in the furnace to electric resistance, FL 1300, in the approximate temperature of 1350°C, staying in that temperature for approximately 40 minutes. After that period, the furnace was turned off and the mixture stayed in its interior, so that
there was the slow cooling of the same. This procedure intended to verify the akermanite and gehlenite phases formation.

In short, after the melting and solidification, the samples of the new material were dried in a stove at 70°C, submitted to the magnetic separation, milling and sieving to 74 μm (200 mesh). After the preparation, the samples were characterized in terms of X-ray diffraction (XRD), scanning electronic microscopy analyses (SEM) and energy dispersive spectroscopy (EDS). For the analyses of SEM and EDS, the samples were before metalized.

**Results and Discussion**

Table 3 presents the calculated chemical composition of the main oxides of the investigate mixture. In this table, it is observed that with addition of waste in the slag, there is an increase in the percentage of SiO₂ as well as a decrease in the percentage of CaO. It should be noted that the relationship CaO/SiO₂ is approximately 1. The amount of calcium, silicon, magnesium and aluminum oxides, after the adjustment of the slag composition are in the range of values presented for the blast furnace slag [2].

<table>
<thead>
<tr>
<th>Composition [wt. %]</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>FeO</th>
<th>MnO</th>
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<tr>
<td></td>
<td>29.63</td>
<td>29.61</td>
<td>8.07</td>
<td>4.94</td>
<td>16.3</td>
<td>3.64</td>
</tr>
</tbody>
</table>

Fig. 1 shows the XRD pattern of the mixture after melting and cooling in the furnace (MF) with indication of mineralogical phases related to the peaks. In this figure, can be observed that the mineralogical phases akermanite and gehlenite were identified in that new material. Those phases are also found in the blast furnace slag, after his hydration [9]. The presence of those phases is an indicative of the technical feasibility of the use of wastes mixture in the production of the cement. The other phases in the mixture are iron compound.

In study carried out by Polese, Rodrigues and Silva [12] about steel slag characterization was not identified the presence of mineralogical phases akermanite and gehlenite. In the granite waste used in this work were not also identified those phases. Quartz, biotite, microcline and albite were the identified phases in the waste [10].

The XRD pattern of the mixture cooled in water (MW) is shown in the Fig. 2. In this figure, it should be noted that there are not great picks, which characterizes a crystalline product. It is treated, therefore, of a product amorphous or glassy, resulting from a fast cooling in water. This way, it is another indicative of the technical feasibility of the use of the LD steel slag and granite waste mixture in the cement production.
The Figs. 3 and 4 show the SEM photomicrographs of the new formed material (slag). The Fig. 3 shows micrograph of the slag cooled in the furnace and their respective mapping by EDS and the Fig. 4, micrograph of the slag cooled in water. In the Fig. 3a can be observed heterogeneous texture and amorphous areas. The EDS mappings of Si and Ca, Figs. 3b and 3c, main elements in the new material, reveal the presence of these elements distributed evenly in the sample. Through analysis by EDS in the sample (Fig. 3d) was verified the presence of all elements necessary to the formation of the phases akermanite and gehlenite, which were identified by XRD (Fig. 1).

In the material cooled in water (Fig. 4) can be observed a glassy region (amorphous) and the sample presents texture with certain homogeneity. SEM analyses confirm the result of XRD shown in the Fig. 2.
Fig. 3. SEM photomicrograph of the mixture cooled in furnace. (a) SEM photomicrograph (b) mapping of Si (c) mapping of Ca (d) EDS.

Fig. 4. SEM photomicrographs of the slag cooled in water.

Conclusions
For this work, the basicity, relationship CaO/SiO$_2$ of the granite waste and LD steel slag mixture was adjusted for 1. The new formed material presented glassy state (amorphous) to the sample cooled in water, concentration of the main oxides similar to the blast furnace slag and the akermanite and gehlenite phases, considered ideals for the hydraulic activity of the slags, in the sample cooled in the furnace. The results indicate the technical feasibility of the granite waste and
LD steel slag mixture in the cement production. Therefore, the mixture of those two wastes can be an alternative for the use of both, in the cement production and still allied to the environmental preservation.

Acknowledgements

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References


