Recovery of Steelmaking Slag and Granite Waste in the Production of Rock Wool

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Steelmaking slag and residues from granite cuttings are industrial wastes with considerable production, however limited applications. This work studied an inertization and recovery process of such wastes as raw materials into production of rock wool (i.e. a thermo-acoustic insulator with growing market). Several batches were produced aiming the chemical proprieties of a currently marketed rock wool. Mixtures were casted at temperatures of 1400-1500 °C, then quenched in water and also poured into a Herty Viscosimeter. Produced materials with thickness smaller than 500µm were characterized by chemical analyses, XRD, SEM, EDS and DTA. ThermoCalc software was used to simulate the cooling curves of rock wools. Results showed that incorporation of wastes does not affect the main qualities of rock wool, the thermal insulation and prevention of fire spread. Raw material batches of rock wools may assimilate up to 66% of granite waste, or 53% steelmaking slag, or 70% combining both materials.

Keywords: steelmaking slag, granite waste, rock wool, thermal insulator

1. Introduction

Recycling of solid wastes has been growing steadily in recent years, along with rising industrial production. The waste generation increase presents a serious problem of environment and costly disposal. Recovery of industrial wastes into useful subproducts might be economically viable, and it is desirable since the disposal involves expensive transportation, as well as the monitoring of deposit areas. Vitrification process has been widely used as final destination for hazardous materials due to the inertization capability of organic toxics, heavy metals, fly ashes and nuclear wastes.

The world production of crude steel in 2010 reached about 1.4 billion tons, registering a new record of production. Considering that for each ton of steel produced are generated 150 kg of steelmaking slag, approximately 210 million tons of such waste were produced in 2010. The production of steel from electric arc furnaces has expanded due to the higher availability of steel scrap, which is the main component of the production charge. Steelmaking slag is the result of an aggregation of several elements which the presence is not important on steel making process. Among different wastes from the steel process, steelmaking slag represents one of most hazardous since it may contains heavy metals such as chromium, manganese and iron. About 20% of the world’s production of steelmaking slag is not reused due the characteristics of this waste, mainly the expansibility problem. A large portion of industrial parks are occupied for this waste, which raises the disposal costs. Therefore, recycling and reusing slag is a technical, economic and environmental solution for steel companies.

Another industrial sector with high production of waste is the industry of granite cutting. Approximately 30% of powdered wastes are generated during the granite extraction process, specifically on the rock cutting. Such values represents that a single company may produce up to 35 tons of this residue per month. The granite waste need be appropriately managed, since the discharge in rivers, lakes or watersheds can cause siltation. Also, this residue may cause serious human health problems, such as silicosis. Currently, the granite waste is mainly used in civil construction to produce materials in the form of mortar, bricks and tiles. New applications for this waste are necessary due to the high produced volumes and the average growth of world production estimated at 6% per year.

Rock wools are man-made mineral fibers (MMMF) fabricated with the melting of basalt or other natural rocks at temperatures above 1400 °C. The thermo-acoustic characteristics of fire resistance, and not rendering toxic smoke ensure to rock wools a broad consumer market in the industries of construction, automotive, and electric-electronics, among others. Rock wools are usually produced with melting spinning process, in which a thin stream of material is dripped onto a wheel internally cooled with water or liquid nitrogen that causes a fast solidification.

This study aims to recovery steelmaking slag and granite cutting waste as feedstock of rock wools by the replacement of traditional raw materials, reducing the costs and impact of disposal of such residues. In addition, the use of recycled materials decreases extraction of non-renewable resources necessary to produce the rock wool.
2. Experimental Methods

2.1. Materials

The raw materials used in this study were steelmaking slag from an Electric Arc Furnace (EAF), granite cutting residue from an industry on Espírito Santo State - Brazil, and chemical reagents (i.e. silica, alumina, magnesium oxide, iron oxide, calcium carbonate, and borax). Steelmaking slag was received in blocks, thus the material was cracked into pieces smaller than 4.76 mm. Granite waste was received in a fine powder form, thus these were dried at 90 °C for 24 hours before use.

2.2. Sample preparation

Several mixtures were prepared using the residues and chemical additives. The batches were based on the chemical composition of a currently marketed rock wool provided by a thermo-acoustic company, and the range of composition recommended in the literature. Three cases were prepared: a) using only granite waste; b) using only steelmaking slag; and c) using both residues. The mixtures were homogenized during 10 minutes in a laboratory scale agitator.

The main objective of the work was maximize the amount of residues in the batches, however some tests presented melting points above the furnace capacity or insufficient fluidity to allow pouring, thus these materials were discarded from the investigation. In this aspect, the characterization work was performed in the materials from batches with efficient and superior incorporation of the residues. The mixing compositions of such batches were:

a) Using only granite waste - 66% granite waste and 34% chemical reagents (22.7% calcium carbonate, 6.6% magnesium oxide and 4.7% iron oxide);
b) Using only steelmaking slag - 53% steelmaking slag and 47% chemical reagents (30.3% silica, 6.1% alumina, 6.1% magnesium oxide and 4.5% Borax);
c) Using both residues: 46% granite waste, 23% steelmaking slag and 31% chemical reagents (21.9% calcium carbonate, 6.4% magnesium oxide and 2.7% iron oxide).

The batches were heated in a laboratory-scale electric furnace with no controlled gas atmosphere during 50 min. The equipment operates open, the system pressure is constant, and a variation on oxygen pressure does not affect the equilibrium of phases. Melted samples were quenched in a water bath at room temperature in order to rapidly cool the melted material is poured. Thus, the distance travelled by the material before solidification is measured, and an approximation of viscosity value is obtained\textsuperscript{19,20}. A laboratory-scale Herty viscosimeter was applied in this work to measure variations on viscosity according to different batches compositions and casting temperatures.

ThermoCalc software version “n” running SLAG3 databases was used to perform thermodynamic and phase diagram calculations for multi-component systems of practical importance. In this work, the numerical code was used to simulate the cooling curves of an industrial rock wool and of the produced materials in order to compare the primary solid phases. Chemical compositions of the materials, previously determined, were used for the ThermoCalc simulations.

3. Results and Discussion

3.1. Chemical analysis of wastes

Results of the chemical analysis of steelmaking slag (see Table 1) shown that the main component of this residue is calcium oxide (46.9 wt. %). The recovery of steelmaking slag has restricted applications due to the volume instability, in which the main cause is the phenomenon of hydration of free lime, although hydration of free magnesia may

<table>
<thead>
<tr>
<th>Elements</th>
<th>Steelmaking slag</th>
<th>Granite waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>16.9</td>
<td>66.3</td>
</tr>
<tr>
<td>CaO</td>
<td>46.9</td>
<td>4.5</td>
</tr>
<tr>
<td>MgO</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>5.4</td>
<td>19.3</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>16.2</td>
<td>2.3</td>
</tr>
<tr>
<td>MnO</td>
<td>5.5</td>
<td>---</td>
</tr>
<tr>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
<td>2.1</td>
<td>---</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>---</td>
<td>1.3</td>
</tr>
<tr>
<td>B\textsubscript{2}O\textsubscript{3}</td>
<td>---</td>
<td>0.8</td>
</tr>
<tr>
<td>Other</td>
<td>4.4</td>
<td>3.9</td>
</tr>
</tbody>
</table>

produced materials, therefore only the characterization results of samples poured at 1450 °C were selected to present in this work.

Produced materials were characterized by chemical analysis, X-ray diffraction (XRD) and Differential Thermal Analysis (DTA). Scanning Electronic Microscopy (SEM) was used to verify formation of secondary phases in the produced materials, and Energy Dispersive Spectroscopy (EDS) was applied to establish the phase compositions. XRD analysis was carried out using a Philips MPD 1880 40 mA Diffractometer adjusted with copper Kα radiation (\(\lambda = 1.5418 \text{ Å}\)) and voltage of 40 kV. The DTA was performed in a Netzsch 409C equipment with alumina crucibles, air atmosphere, and heating rate of 15 °C/min. SEM/EDS analyses were conducted with a Philips XL-30 instrument using 3 kV voltage and working distance of 8.2 mm.

The Herty Viscosity Test is frequently used in industry to provide quick and approximate values for comparative purposes. A Herty viscometer is composed of two steel blocks with a groove in the middle interface in which the melted material is poured. Thus, the distance travelled by the material before solidification is measured, and an approximation of viscosity value is obtained\textsuperscript{19,20}. A laboratory-scale Herty viscosimeter was applied in this work to measure variations on viscosity according to different batches compositions and casting temperatures.

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also contribute. The volume instability can be solved by submitting the steelmaking slag to a vitrification process.

Table 1 also provides the chemical analysis of the waste from granite cuttings. The main components of this residue are silica and alumina, together such oxides are responsible for almost 86% of the chemical composition. Therefore, granite waste was used as a source of these components in the production of vitreous materials.

3.2. Physical characteristics of formed materials

Produced materials showed proprieties similar to glass: translucent, fragile and brittle at room temperature. The materials displayed a green color, which is reasonably due to the content of Fe₂O₃ (7.6-11.1% by wt.). Different sizes and formats of materials were produced: pieces about 10 mm, fibres with thickness about 500 µm, and thin powder.

3.3. Chemical analysis of formed materials

Table 2 provides the results of the chemical analyses of the rock wools produced in this study, sorted by each residue. This table also shows the chemical analyses of an industrial rock wool and the chemical composition range of rock wools cited in the literature.

Produced materials showed high silica content (43.2-47.7% by wt.), which is the most common glass forming oxide. Responsible for about 30% of the chemical composition (43.2-47.7% by wt.), which is the most common glass forming oxide. Therefore, the use of steelmaking slag and granite waste as raw material should also contribute. The volume instability can be solved by submitting the steelmaking slag to a vitrification process.

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<table>
<thead>
<tr>
<th>Elements</th>
<th>Reference Values</th>
<th>Produced Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Industrial sample</td>
<td>Literature range*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Granite waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Steel. slag</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Both residues</td>
</tr>
<tr>
<td>SiO₂</td>
<td>44.9</td>
<td>41.0 - 53.0</td>
</tr>
<tr>
<td>CaO</td>
<td>17.8</td>
<td>10.0 - 25.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.1</td>
<td>6.0 - 14.0</td>
</tr>
<tr>
<td>MgO</td>
<td>8.5</td>
<td>6.0 - 16.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.8</td>
<td>3.0 - 11.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.9</td>
<td>0.8 - 3.5</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.2</td>
<td>0.5 - 2.0</td>
</tr>
<tr>
<td>MnO</td>
<td>0.3</td>
<td>0.0 - 0.3</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.9</td>
<td>0.9 - 3.5</td>
</tr>
<tr>
<td>Others</td>
<td>1.6</td>
<td>0.0 - 0.6</td>
</tr>
</tbody>
</table>

* Values cited in the literature by several authors: Buck; Liddell & Miller; Luoto et al.; TIMA.
Recovery of Steelmaking Slag and Granite Waste in the Production of Rock Wool

Figure 1. Cooling curves of rock wools fabricated using only granite waste (a), only steelmaking slag (b), both residues (c), and from an industrial sample (d).

Figure 2. X-ray diffraction spectra of rock wools fabricated using only granite waste (a), only steelmaking slag (b), both residues (c), and from an industrial sample (d).
confirms the homogeneous curve and serves as reference to compare with the produced materials.

The material obtained using only granite waste presented a spectrum with some crystalline peaks (see Figure 2a). Such peaks are characteristic of spinel, the first solid phase formed during the cooling, which is in accordance with the thermodynamic computational simulation of rock wools (Figure 1). The spinel formation indicates that the fast cooling process was not successfully performed, in other words, the process established enough time to form the first crystalline phase previously the occurrence of the vitrification.

Figures 2b and 2c respectively shown the X-ray diffraction spectra of materials produced using only steelmaking slag and both residues. Absence of notable crystalline peaks indicates that the materials are amorphous. Therefore, the fast cooling processes were successfully performed.

3.6. Scanning Electronic Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analyses of materials

Images obtained by SEM analysis of the formed materials are shown in Figure 3. The image of a current marketed rock wool is shown in Figure 3d. The homogeneous appearance of such image serves as reference to compare with the produced materials.

The image of rock wools produced using only granite waste is shown in Figure 3a, in which the formation of a secondary phase was presented. Thus, EDS analysis was used to identify this region, the obtained spectrum is shown on Figure 4. The result is characteristic of the spinel phase, such fact is consistent with the spinel peaks shown in the XRD image of this material (Figure 2a).

The homogeneous appearances shown in Figures 3b and 3c indicate that secondary phases were not formed on materials produced using only steelmaking slag or both residues. Such results are in accordance with the amorphous curves in the XRD spectra obtained for these materials (Figures 2b and 2c).

3.7. Differential Thermal Analysis (DTA)

Figure 5 shows the results of DTA testing, where the graphics express the thermal behavior of the produced materials. Exothermic peaks correspond to the crystallization temperatures of the materials, while endothermic peaks represent the melting temperatures.

Differential thermal analysis of material produced using only granite waste is shown in Figure 5a. Results indicate a crystallization temperature of 780 °C and a

![Figure 3. SEM images of rock wools fabricated using only granite waste (a), only steelmaking slag (b), both residues (c), and from a industrial sample (d).](image-url)
melting temperature of approximately 1200 °C. Figure 5b shows that the material produced using only steelmaking slag presented a crystallization temperature of 840 °C and melting temperature of 1150 °C. The association of both residues generated a material with crystallization temperature of 850 °C and melting temperature of 1220 °C, as presented in Figure 5c. Images obtained by SEM analysis of the formed materials are shown in Figure 3. Results of all produced materials are in an accordance with the DTA obtained from a current marketed rock wool (Figure 5d), since the crystallization temperature of 830 °C and melting temperature of 1160 °C are close to the range obtained.
Rock wool is employed for the manufacture of products designed to prevent fire spread. According to the Thermal Insulation Manufacturers’ Association, the temperatures reached in a typical building fire are approximately 925 °C and 1030 °C after 1 and 2 hours, respectively. The rock wool reached in a typical building fire are approximately 925 °C designed to prevent fire spread. According to the Thermal Insulation Manufacturers’ Association, the temperatures reached in a typical building fire are approximately 925 °C and 1030 °C after 1 and 2 hours, respectively. Considering the alumina as a glass former, a tetrahedral coordination similar to silica, i.e. becomes a glass former when added to an alkali-silicate glass it assumes a structural material that is thermally and essentially dimensionally stable, which is high enough to contain a structural fire for several hours. The produced materials devitrified at temperatures of 780, 840 and 850 °C, therefore these are within the recommended devitrification temperature range. Gualtieri et al. investigated several mineral wools and concluded that rock wool can be melted with a maximum firing temperature of 1100 °C. Produced materials in this work presented melting temperatures in the range of 1150-1220 °C, complying with the standard established for rock wools. Therefore, the above discussed thermal behavior of produced materials qualifies them as appropriate for use as fire inhibitors.

3.8. Herty Viscosity Test

Results of the Herty viscosity test are shown in Table 3. The measures indicate the distance traveled by the materials prior to solidify, therefore the highest fluidity values correspond to the lowest viscosities.

<table>
<thead>
<tr>
<th>Casting temperature</th>
<th>Granite waste</th>
<th>Steel slag</th>
<th>Both residues</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400 °C</td>
<td>40 mm</td>
<td>120 mm</td>
<td>110 mm</td>
</tr>
<tr>
<td>1450 °C</td>
<td>50 mm</td>
<td>150 mm</td>
<td>130 mm</td>
</tr>
<tr>
<td>1500 °C</td>
<td>70 mm</td>
<td>180 mm</td>
<td>160 mm</td>
</tr>
</tbody>
</table>

Table 3. Herty Viscosity Tests: results of the distance traveled by each batch prior to solidify.

The viscosity decreased, i.e. fluidity increases, proportionally with growth of casting temperature for all the batches composition. Such phenomena is in accordance with the normal glass making behaviour, in which viscosity decreases logarithmically with the increase in temperature. The increase on casting temperature from 1400 °C to 1500 °C resulted in fluidity alterations of 30 mm (only granite waste), 60 mm (only steelmaking slag) and 50 mm (both residues).

4. Conclusions

Tests performed using only granite waste showed that a maximum amount of 66% of this residue may be used in substitution to traditional raw materials during the manufacture of rock wool. The use of higher amounts of granite waste increases the viscosity, which causes difficulties in the quenching process. The high content of silica and alumina present in the granite waste establishes this material as a potential substituent for the glass formers in rock wool production. Steelmaking slag may assume up to 53% of raw materials in rock wool production, mainly substituting the calcium carbonate and iron oxide. Batches with only steelmaking slag presented the higher fluidity and lower melting temperature. The use of steelmaking slag combined with granite waste as raw materials for rock wool production proved to be efficient, and provides a substitution rate up to around 70% of the total mixture, with a 1:2 slag/granite waste weight ratio. Thermal analysis also showed that steelmaking slag and granite waste may be used as partial substitutes of raw materials in rock wool production, since the addition of such wastes does not affect the overall quality of the material produced in terms of thermal insulation and prevention of fire spread.

The recovery of steelmaking slag from EAF and residue from granite cuttings as raw materials in the production of rock wool is recommended due to the reduction in extraction of non-renewable resources necessary to produce such material. Furthermore, the technique may also contribute to reduce the costs and hazard of waste storage by steelmaking and granite extraction companies, since these are residues with considerable production and limited applications.

References


