Characterization of mineral wools obtained from ornamental rock wastes

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Abstract

The study aimed to characterize the mineral wools obtained from wastes of the cutting step of marble and granite, in order to evaluate the possibility of their use on an industrial scale. Mixtures of marble and/or granite wastes were prepared in order to reach the chemical composition of rock and glass wools. The batches were melted in an electric arc furnace in laboratory scale at 1450°C and casted with water, in order to obtain a higher cooling rate. Characterization work was performed in batches that formed vitreous material, and with superior incorporation of the residues: 11.7% and 14.6% of marble waste with glass wool and rock wool, respectively; 78.3% and 91.6% of an association of marble and granite wastes with glass wool and rock wool, respectively. Computational thermodynamics was used in order to obtain the main phases at 800°C and determine the liquid and solid content at 1400, 1450 and 1500°C. In addition, the materials obtained were characterized via chemical analysis using X-ray fluorescence, DTA, X-ray diffraction and SEM. The results indicate that the marble and granite waste are composed mainly of CaO (34.7 wt.%) and SiO_2 (66.3 wt.%), respectively. An amorphous crystalline structure was obtained in all tests, indicating that this material can be used as an insulation material. The crystallization temperatures were determined around 800°C.

Keywords: marble, granite, recycling, mineral wool, glass characterization.

1. Introduction

The Brazilian production of ornamental rock was 9.5 Millions of tons in 2015, in which 52.58% was finished product, i.e. polished plates or other finishing. During the step of the block´s sawing to obtain the plates, it is estimated that there is a loss in the range of 20-30% of the blocks. This suggests a waste production in the range of 1.0-1.5 millions of tons per year (Mashaly *et al*., 2016). In most cases, this waste is deposited in a tailings dam close to the companies, which causes serious environmental problems (Junca *et al*., 2015).

The waste generated by the ornamental rock sector is mainly composed of oxides, where the marble waste is composed mainly of CaO and MgO, and the granite waste is composed mainly of SiO_2 and Al_2O_3.

Mineral wools are inorganic fibers, typically made of high amounts of silica.

In addition, these materials also contain calcium, magnesium and iron oxides. These materials are sometime known as alkaline earth silicate glass, and due to the high concentration of alumina, they are also called aluminosilicate glasses (Müller *et al*., 2009). Due to its physical properties, such as thermal and acoustic insulation, fire protection, chemically neutral and water resistant, it is an important input in the construction and automotive sector (Väntsi and Kärki, 2014).

In this way, the marble and granite waste can be used as a source of CaO and SiO_2, respectively. Thus, the aim of this article is to study the use of marble and granite waste as raw material to produce rock and glass wools.

2. Experimental

2.1. Raw material

Ornamental rock wastes (marble and granite waste) from the cutting stage were obtained from a company in the Espírito Santo State, Brazil. Pure chemical reagents were also used, such as silicon oxide (SiO_2), aluminum oxide (Al_2O_3), magnesium oxide (MgO), iron oxide (Fe_2O_3) and Borax (16.25% Na_2O, 36.51% B_2O_3 and 47.24% H_2O).

The marble and granite wastes were dried in a muffle furnace at 90°C for 24 hours. Then, two aliquots were obtained to perform the chemical and morphological (Scanning electrons microscopy-SEM) characterization. This step was necessary to determine the chemical balance of the batches to produce the glass and rock wools.

The objective of the full project was to 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 by mass of such batches were:

- M-GW: 11.7% of marble waste on the raw material of glass wool;
- M-RW: 14.6% of marble waste on the raw material of rock wool;
- MG-GW: 78.3% of an association of marble and granite wastes on the raw material of glass wool;
- MG-RW: 91.6% of an association of marble and granite wastes on the raw material of rock wool.

Table 1 shows the chemical composition of the furnace loads obtained from the mixtures of marble and/or granite wastes, in association with chemical additives. This composition was also used to perform the thermodynamic simulation via FACTSAGE software.

Element	M-GW	M-RW	MG-GW	MG-RW
SiO_2	76.3	46.1	63.6	52.5
CaO	4.4	15.9	4.0	13.4
MgO	6.2	8.0	8.4	6.5
Al_2O_3	5.1	13.2	17.5	15.1
Fe_2O_3	0.9	1.62	6.5	10.3
Na_2O	2.2	5.0	-	1.0
K_2O	-	0.4	-	0.4
TiO_2	-	0.2	-	0.2
B_2O_3	5.0	9.5	0.3	0.6

Table 1
Chemical composition of the batches that were characterized (in wt. %).

2.2 Melting tests

The batches were heated in a laboratory-scale electric furnace with no controlled gas atmosphere during 50 min. Melted samples were quenched in a water bath at room temperature in order to rapidly cool the materials. Resulting products were dried in a muffle furnace at 90°C for 24 hours before performing the characterization.

2.3 Product characterization

The cooled materials were characterized by chemical analysis using X-ray fluorescence technique, Differential Thermal Analysis (DTA), X-ray diffraction and Scanning electrons microscopy (SEM). The DTA was performed in a Netzsch 409C equipment with alumina crucibles, air atmosphere, and heating rate of 15 °C/min in the range of 25-1480 °C. X-ray diffraction was accomplished in a Philips equipment, model MPD 1880, with copper radiation of Kα (λ=1.5418 Å), 40 kV tension and 40 mA, scan range of 10-70º with step width of 2º, during 1 s. A Philips XL-30 SEM was used to investigate the product's morphology. In addition, computational thermodynamic was used in order to obtain the phases at 800°C. In this way, the phases present in the glass temperature can be determined. The simulation was performed via software FactSage 7.0, database FToxid and sub-database Slag A.

3. Results and discussion

3.1 Raw material characterization

Table 2 shows the chemical composition from marble and granite wastes. The marble waste is composed mainly of CaO (34.7%) and MgO (18.6%). A loss on ignition (LOI) of 40.2% was recorded, mainly due to calcium and magnesium carbonates of the marble waste. The granite waste is composed mainly of SiO_2 (66.3%), and Al_2O_3 (19.3%). CaO, MgO, Fe_2O_3, Na_2O, B_2O_3, and K_2O were also detected.

Table 2
Chemical composition of marble and granite waste.

Compound, %	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	B_2O_3	K_2O	Other	LOI*
Marble waste	34.7	18.6	2.1	0.2	0.1	0.3	---	---	3.8	40.2
Granite waste	4.5	1.6	66.3	19.3	2.3	1.3	0.8	0.6	0.6	2.7

* Loss on ignition (1050°C).

3.2 Characterization of glass and rock wools

Table 3 shows the chemical composition of the glass and rock wools produced. It was noted that SiO_2 and CaO are the main components present in the wools, which it is also mentioned by several authors (Marabini *et al*, 1998; Gualtieri *et al.*, 2009).

Table 3
Chemical composition of glass and rock wools produced with marble and granite waste (in wt. %).

	SiO_2	CaO	MgO	Al_2O_3	MnO	Fe_2O_3	Na_2O	K_2O	TiO_2	B_2O_3
M-GW	67.0	6.8	2.2	4.1	---	0.5	12.3	1.1	0.001	5.0
M-RW	53.0	17.2	13.1	7.3	0.2	7.0	1.6	0.6	0.001	---
MG-GW	67.4	6.0	5.2	2.0	---	0.6	12.7	1.9	0.001	4.2
MG-RW	52.0	15.0	10.0	11.6	0.1	6.2	3.2	1.7	0.001	---

Glass viscosity is directly affected by the function of oxides present in the chemical composition (glass former, glass modifier, or intermediary). Alumina does not form glass under normal conditions, however when added to an alkali-silicate glass, it may assume a tetrahedral coordination similar to silica, i.e. becomes a glass former (Alves *et al.*, 2015; Bansal e Doremus, 1986). Considering the alumina as a glass former (i.e. associating with SiO_2, B_2O_3, P_2O_5), the material produced contains around 60-76% of glass forming elements.

The X-ray patterns (Figure 1) indicate that the glass and rock wools presented an amorphous structure in all mixtures, without crystalline peaks. Several authors have mentioned that glass and rock wools are inorganic and vitreous materials that present an amorphous structure (Luoto, *et al.*, 1998; Alves *et al.*, 2015). Therefore, the glass and rock wools produced with marble and granite wastes presented the same structural characteristic from the conventional glass and rock wools.

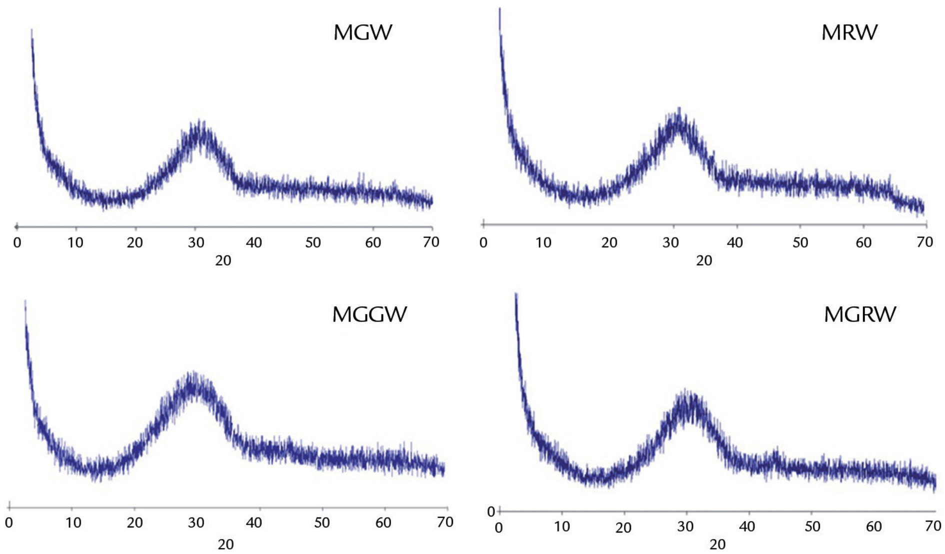

Figure 1
X-ray patterns of the minerals rock wools produced with marble and granite waste.

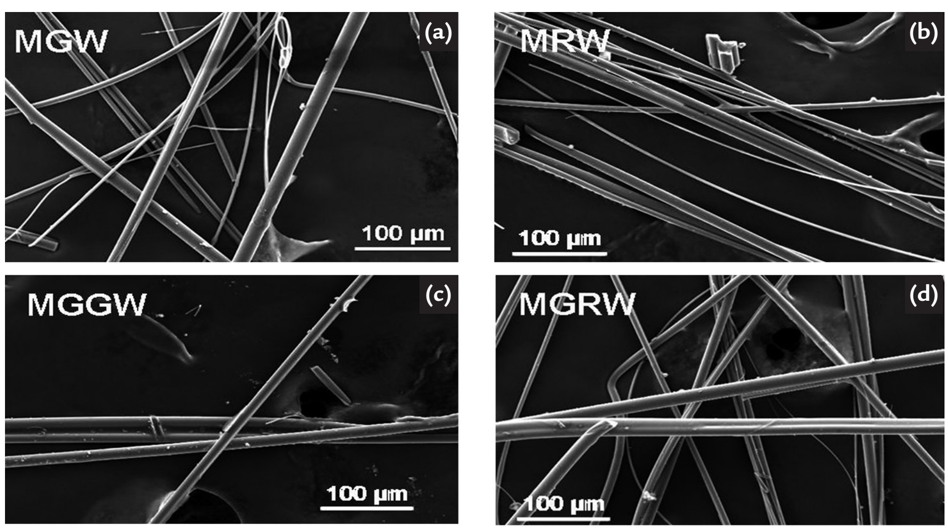

Figure 2
Images of scanning electron microscopy obtained via back-scattered electrons detector from glass and rock wools: (a) M-GW, (b) M-RW, (c) MG-GW and (d) MG-RW.

Images of secondary electrons obtained via SEM (Figure 2) show the morphological aspect of the glass and rock wools. It was noted that all fibers presented a diameter around 10 µm, which is mentioned as the conventional diameter for mineral wools (Talbot et al., 2000). In addition, the images also suggest a formation of homogeneous structures.

Figure 3 shows the DTA curves obtained from the produced materials. The crystallization temperature can be noted by the exothermic peaks at 800, 809, 820 and 796°C to the mixtures M-GW, M-RW, MG-GW and MG-RW, respectively. Table 4 shows a stipulation of phases present at 800°C, obtained via FACTSAGE software, which were performed in order to obtain information close to the crystallization temperature.

The main phases present in the mixtures at 800°C were silicates, a similar result was also found by Hunger *et al.* (2010). Quartz was identified as the main phase in the mixtures to produce glass wool (M-GW 81.8% and MG-GW 40.51%), and the anorthite was detected as a main component in the mixtures to produce rock wools (M-RW 28.93% and MG-RW 39.32%). Furthermore, the mixtures M-RW, MG-GW and MG-RW contain higher content of Al_2O_3, propitiating the formation of $Mg_2Al_4Si_5O_{18}$ and $CaAl_2Si_2O_8$. In addition, the mixtures M-GW and MG-RW presents the diopside phase ($MgOCaOSi_2O_4$), which is one of the expected phases of traditional batches to produce mineral wools at 800°C (Siligardi *et al.*, 2017).

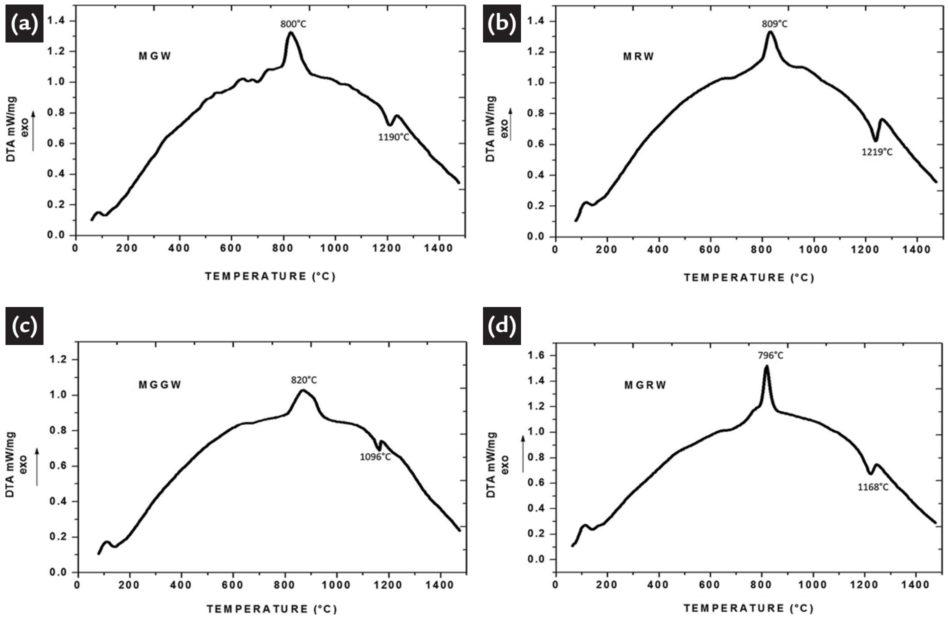

Figure 3
Differential thermal analysis from mineral wool produced with marble and granite waste: a) M-GW, b) M-RW, c) MG-GW and d) MG-RW.

Phase	M-GW	M-RW	MG-GW	MG-RW
SiO_2	81.80	4.87	40.51	17.87
Mg_3B_2O6	9.37	-	-	-
$MgOCaOSi_2O_4$	8.82	-	-	23.35
$Mg_2Al_4Si_5O_{18}$	-	-	25.01	-
$CaAl_2Si_2O_8$	-	28.93	19.45	39.32
$Mg_2B_2O_5$	-	13.73	8.20	-
Fe_2O_3	-	-	5.88	11.67
$(Al_2O_3)_9(B_2O_3)_2$	-	-	0.94	-
$Na_2Ca_3Si_6O_{16}$	-	22.28	-	-
$NaAlSi_3O_8$	-	15.85	-	-
$CaB_2Si_2O_8$	-	10.98	-	-
$Ca_3Fe_2Si_3O_{12}$	-	3.35	-	-
$MgSiO_3$	-	-	-	7.79

Table 4
Stipulation of phases present in the mixtures at 800°C obtained via Factsage (in % of solid phases).

Mineral wools typically present devitrification temperatures of about 725-900°C, then form a polycrystalline material that is thermally and essentially dimensionally stable. Such proprieties are enough to contain a structural fire for several hours (Alves *et al.*, 2015). The produced materials devitrified at temperatures of 796-820 °C, therefore these are within the recommended devitrification temperature range.

The materials produced registered endothermic peaks of 1096°C (MG-GW), 1168°C (MG-RW), 1190°C (M-GW) and 1219°C (M-RW), which measurements may be associated with the melting temperature. Gualtieri *et al.* (2009) investigated the melting temperature of several mineral wools whose results indicated a maximum firing temperature of 1100°C. Therefore, mineral wools produced in this study presented melting temperatures in the range of 1096-1219°C, which is in compliance with the results of the standard material.

4. Conclusion

Vitreous materials were formed using residues from the ornamental rock cutting step in the proportion of: 11.7% and 14.6% of marble waste with glass wool and rock wool, respectively; 78.3% and 91.6% of an association of marble and granite wastes with glass wool and rock wool, respectively. The material produced presented chemical compositions of around 60-76% of glass forming elements, including alumina. Produced materials assumed the fiber form with diameters around 10 µm, which is according to the conventional mineral wools. The characterization process for the materials produced showed that an amorphous crystalline structure was obtained in all tests, and the crystallization temperatures were determined around 800 °C, which may indicate the possibility of use as a thermal insulator. Computational thermodynamic simulation showed that the main phases at 800 °C were silicates, in which quartz and anorthite were the major elements in the mixtures to produce glass and rock wools, respectively. The production of mineral wools may be an opportunity for large scale recovery of residues from granite/marble cutting, mainly due to the process capacity to absorb discrepancies in the chemical composition of the charges.

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