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Characterisation of Sand Casting and Oyster Shells as Potential Sources of Raw Material for the Production of Soda-Lime Glasses

Bianca G. de Oliveira Maia[a], Sabrina Arcaro[a], Marcelo T. Souza[a], Antonio P. Novaes de Oliveira*[a], T.M. Novais de Oliveira[b], João B. Rodrigues Neto[a]

[a]Graduate Program in Materials Science and Engineering – PGMAT, Laboratory of Glass-Ceramic Materials – VITROCER, Federal University of Santa Catarina - UFSC, 88040- 900 Florianópolis - SC, Brazil
[b]University of Joinville Region – UNIVILLE, 89219-710 Joinville - SC, Brazil
antonio.pedro@ufsc.br

In this work, foundry sands (silica source) from metal casting and oyster shells (source of calcium carbonate) wastes were collected and characterized for use as raw materials for the production of soda-lime glasses. The wastes were characterized and classified according to their physical, chemical and mineralogical natures. The sands and crushed oyster shell samples had a particle size distribution suitable for the production of glasses (up to 200 µm). Chemical analysis confirmed the high silica content of sand samples (~ 96 %) and calcium oxide in oyster shells (~ 54 %). The results showed that the foundry sands and oyster shells are potential candidates to be used for the production of soda-lime glasses allowing thus the recovery of these wastes.

1. Introduction

The majority (99 %) of the commercial glasses consists of oxides and most of them are based on silica and divided into five main groups according to their major components: soda-lime glasses; silica glasses; lead glasses; borosilicate glasses and boroaluminosilicate glasses (Varshneya, 1994).
The soda-lime glasses are probably the most common and oldest commercial glasses. These glasses contain about 15 % of alkali oxides (Na_2O + K_2O), 13 - 16 % alkaline earth oxides (CaO + MgO), and about 70 % SiO_2 (Fernandes, 1999). One way to get part of the raw materials (Si and Ca) necessary for the production of soda-lime glasses is through the reuse of wastes.
In the state of Santa Catarina (Brazil), two sources of waste rich in calcium and silica are related to the cultivation of oysters (ostreiculture) and metal casting, respectively. The ostreiculture is an activity directly related to the industrial production of food and pearls being one of the fastest growing sectors in the global scenario. In 2013, according to data from Epagri (2014) the state of Santa Catarina, which is also the largest producer of oysters in Brazil, commercialized about 3 t of shellfish, providing a financial turnover of about US$ 7.8 M.
To a sustainable ostreiculture is of prime importance a correct waste disposal, consisting mainly of shells. The current options adopted in the final waste disposal are not compatible with environmental preservation, considering that more than half of the shells are discarded and/or deposited in landfills and beaches (Alvarenga et al., 2012).
The oyster shell is composed mainly of calcium carbonate ($CaCO_3$), about 96 %, as crystals of calcite and aragonite. For this reason, this residue has been the subject of research relating to its use mainly in building materials such as aggregate in concrete (Yang et al., 2005), among other applications (Chong et al., 2006), and in wastewater treatment (Luo et al., 2013) for example.

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The metal casting industry is closely related to the level of industrial development of a country. According to the American Foundry Society (2014), Brazil ranks seventh in the ranking of countries producing castings indicating its importance in the global context and consolidating the progress of this industry.
The sand is the main waste generated in foundry industries in the manufacture of moulds and cores. It is estimated that for each 1 ton of produced part 1 t of sand are used (Siddique et al., 2010). The moulding sands are composed of quartz sand, bentonite and coal powder. On the other hand, the sands core are composed of binders based on phenolic resins that have toxicity and can affect the quality of the soil and underground water, depending on the quantities involved, and can be leached out when disposed in the environment (Winkler and Bol'shakov, 2000).
According to Siddique et al. (2010), classification of foundry sands depends up on the type of binder systems used in metal casting: clay-bondedsand (green sand) and chemically bonded sand.
Clay-bonded (Green) sand is composed of naturally occurring materials, which are blended together such as high-quality silica sand (85 – 95 %), bentonite clay (4 – 10 %) as a binder, a carbonaceous additive (2 – 10 %) to improve the casting surface finish and water (2 – 5 %). It is black in colour due to carbon content. Green sand also contains trace chemicals such as MgO, K_2O, and TiO_2.
Chemically-bonded sand involve the use of one or more organic binders. Consists of 93 – 99 % silica and 1 – 3 % chemical binder. Chemically bonded sands are generally light in colour and in texture than clay-bonded sands.
Beneficial reuses of foundry sands span a variety of applications related to infrastructure engineering and rehabilitation works. These alternate applications offer cost savings for both foundries and user industries, and an environmental benefit at the local and national level (Koff et al., 2010).
Due to the importance of these two economic sectors, and the opportunity of recovering the waste generated, the objective of this work was to characterize oyster shells and foundry sands as potential substitutes of raw materials for the manufacture of glasses.

2. Materials and methods

The wastes used in this work and employed as raw materials for the production of glasses were foundry sands (FS) and oyster shells (OS). Two samples of foundry sands were collected: Sand A (chemically bonded sand) from the aluminium casting process and sand B from the sand moulding of casting iron process (green sand), collected in the container of recycled sands. The supplier of the samples is a company located on the north coast of Santa Catarina state (SC).
The sand A was deagglomerated in a fast mill (SERVITECH, CT-242) with porcelain jars containing alumina balls for 5 min. The sand wastes were classified according to the collection of ABNT (Brazilian Association of Technical Standards): NBR 10004; NBR 10005; NBR 10006 and NBR 10007/2004.
The oyster shells of the species *Crassostrea gigas* (Figure 1) were obtained from cultivations of local mariculturists in Enseada de Brito Beach located in the Palhoça City (SC).

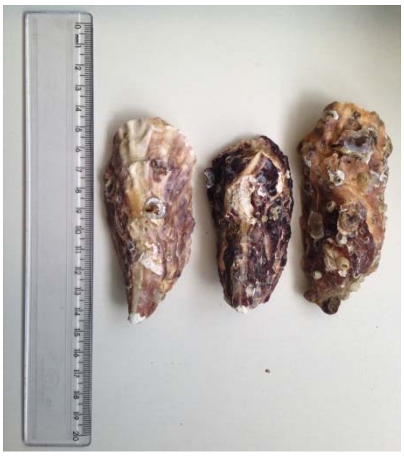

Figure 1: Photography of oyster shells samples

The oysters were removed from the sea, washed and steamed for the softening the flesh. Subsequently, the organic part of the oysters (flesh) was removed and the shells were then dried in the sun for removing the remaining organic material. After this procedure, the shells were placed in a muffle at 110 °C for 2 h and then ground on a crusher (SERVITECH, CT-058).

The distributions of particle sizes and their average sizes, samples of FS and crushed OS, were determined using a laser scattering particle size analyser (CILAS 990). The chemical composition of the studied wastes was determined by X-ray fluorescence (XRF) on a Bruker equipment (S2 Ranger) with palladium tube and power of 50 W. To determine the crystalline phases of the foundry sands and oyster shell, powdered samples were analysed using computer assisted X-ray diffractometry, XRD (Philips X'Pert) with CuKα radiation. To identify the crystalline phases in the wastes the JCPDS data base was used. The phenomena associated with the physical-chemical reactions in the wastes as well as the mass loss on the decomposition of organic matter of the samples were identified by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) on a TA instrument (SDT – 600) at 10 °C/min in an oxidizing atmosphere.

3. Results

The sands were classified according to ABNT as residue class II A - "No hazardous and not inert". Waste foundry sand consists primarily of silica sand, coated with a thin film of burned carbon, residual binder (bentonite, sea coal, resins/chemicals) and dust (Siddique et al., 2010). Table 1 shows the chemical composition of the foundry sands (FS) and oyster shell (OS) obtained by FRX. It can be verified the predominant presence of SiO_2 in the sands from the two casting processes and also the similarity of the chemical compositions of the two samples. The great difference in loss on ignition (LOI) between the foundry sands (FS) and the oyster shell (OS) is related to large amount of $CaCO_3$ contained in the OS that, at high temperature, decomposes forming CaO and CO_2.

Table 1: Chemical composition of FS (Sand A and Sand B) and OS. LOI.: Loss on Ignition

Waste/Oxides (wt%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	MnO	P_2O_5	TiO_2	LOI
Sand A	96.5	1.20	0.13	0.06	0.03	-	-	-	0.03	0.05	2.02
Sand B	96.9	1.21	0.14	0.05	0.03	-	-	-	0.03	0.05	2.07
OS	0.64	0.05	0.03	53.7	0.04	0.94	-	-	0.03	-	44.6

In fact, the residue/waste OS stands out by the large amount (53.7 %) of CaO, a source of calcium for the production of glasses. The average particle size of the FS samples was 150 μm for sand A and 180 μm for Sand B. The OS crushed particles had an average diameter of 166 μm. These results are indicative of fine industrial sands (particles with sizes between 60 and 200 μm), according to the classification of NBR 6502/93 and typically used for glass production according to Navarro (1991) and Varshneya (1994). In this case, the use of foundry sands (FS) and oyster shell (OS) as raw materials does not require some kind of particle size correction. Figure 2 shows X-ray diffraction patterns of samples of oyster shell (OS) and foundry sands (FS).

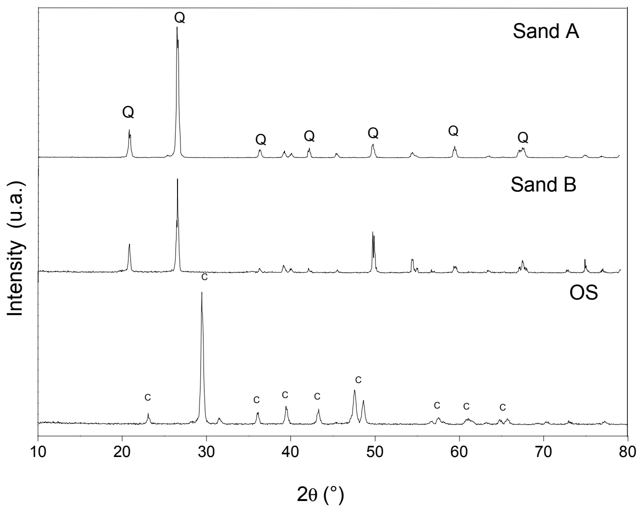

Figure 2: X-ray diffraction patterns of sand A, sand B and OS. C: Calcium carbonate; Q: Quartz

The first two diffractograms, referring to the foundry sand samples, indicates the presence of SiO_2 in the form of quartz (JCPDS File No. 33-1161). The third XRD pattern of OS sample showed peaks relating to calcium carbonate, $CaCO_3$ (JCPDS File No. 05-0586).
Figures 3 and 4 show thermograms (DTA/TGA) related to sand A and sand B.

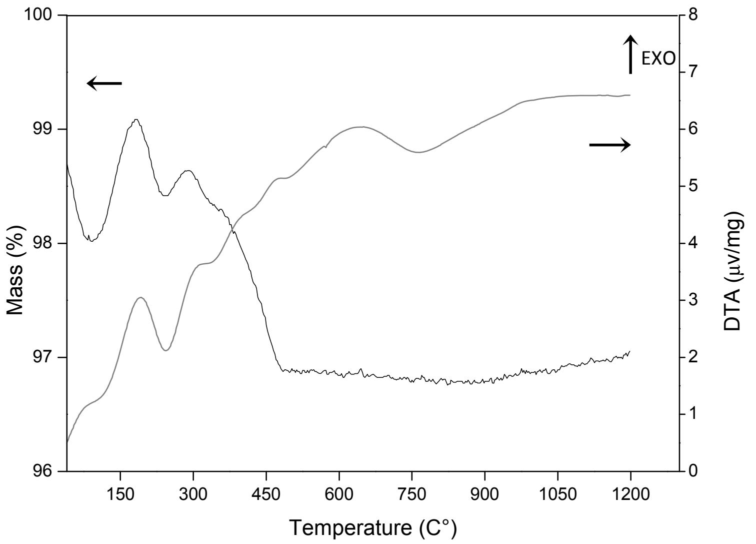

Figure 3: DTA/TGA curves of sand A

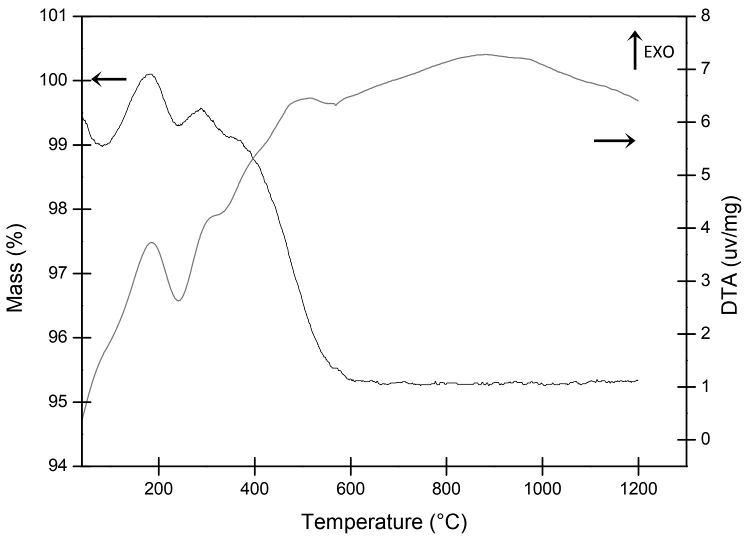

Figure 4: DTA/TGA curves of sand B

In the same way, Figure 5 shows DTA/TGA curves of an oyster shell (OS) sample in an oxidizing atmosphere.

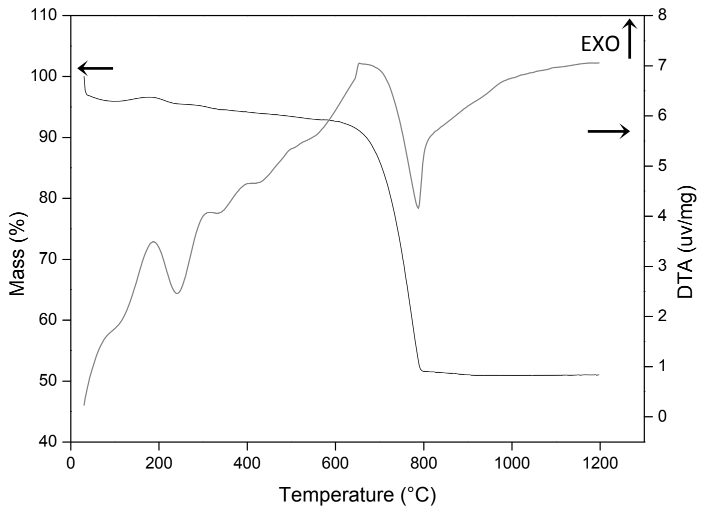

Figure 5: DTA/TGA curves of an oyster shell (OS) sample

From Figures 3 and 4 it is concluded that the smaller mass loss of the foundry sand samples are related to moisture loss and the decomposition of bentonite in the sand B as well as the decomposition of organic compounds from the phenolic resins used in the core sands (sand A).

In the sand B, even if it is predominantly from moulding process where resin is not used, there may be traces of organic compounds since the collected sample was recycled sand which may have been mixture of sands from different moulding processes.

The sample of oyster shells (Figure 5) shows up to 600 °C an initial mass loss of 2 % which is related to the elimination of the organic fraction. In a second step, between 650 and 800 °C, there was a mass loss of approximately 45 % which is related to the decomposition of calcium carbonate ($CaCO_3$), forming calcium oxide and releasing CO_2 (Yang et al., 2005). For temperatures above 800 °C, until the measurement limit, there was no mass change, indicating that the remaining material is in the form of oxide.

4. Conclusions

The investigated foundry sands were classified according to ABNT (Brazilian Association of Technical Standards) as residue class II A - "No hazardous and not inert" containing relatively high silica contents (> 96 %) and with crystal structures corresponding to quartz.

The oyster shell samples analysed are constituted by calcite with high calcium oxide contents (~53 %).

The studied wastes showed particle sizes adequate for glass melting (particle sizes between 60 and 200 μm).

Based on the objectives proposed in this work, it is concluded that the foundry sands and the oyster shells wastes are potential candidates as raw materials for the manufacture of soda-lime glasses allowing thus the valuation of these materials and minimizing the environmental impacts caused by their disposal in the environment.

Acknowledgements

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