Minimizing environmental impacts through the elimination of tailings from mining operations

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ABSTRACT

The proposed solution aims to eliminate 15000 t/month of tailings generated at Três Marias smelter unit, transforming it into value added products through glass ceramic technology, avoiding disposal in dams. After immobilization/transformation (I/T) into glass ceramic, tailings will be conformed as floors and coverings replacing ceramic and granite in the construction industry. The current methods of tailings disposal, such as dams and dry stacking, generate maintenance costs, environmental impacts and unpredictable liability. The goal is to minimize tailings disposal through its use as raw material, demonstrating that circular economy is technically and economically viable.

The technical principles of convert tailings into glass ceramic materials are based on the use of metals contained in tailings to enable the nucleation of the glass. Undergoing tests are evaluating the need of using structural additions in the glass network. Although glass ceramic technology is well known, it was never applied before in large scale or with the objectives of this present study. The challenge of this innovative approach is to adapt a known technologic process to offer new, ecological and high-quality products to a large base of customers at affordable prices.

Technical feasibility is being evaluated through chemical, mineralogical, differential thermal and thermal microscopy analyses to model and control the fusibility/crystallization of the tailing. The technological route contemplates the generation of glass frits (molten glass coming into contact with water in room temperature), followed by the adequacy of the grain-size distribution through milling, casting and heat treatment for sintering/crystallization into plates.

INTRODUCTION

Environmental impact from mining and smelter operations lately has become a key subject for all companies, wherever operating worldwide. In fact, in few more years, this is going to be the key subject for the future survival of all these companies.

Aware of this very important subject, NEXA decided to invest in researches for innovative approach on this field after verifying that, most of the alternative solutions to disposal in dams or piles are the use of tailings to produce bricks, small blocks for paving streets and sidewalks, and as aggregate for concrete or base for roads, with limited uses and results. None of these proposed solutions is capable to really immobilize metals on tailings, as NEXA desires to achieve in Três Marias – Zinc Smelter Unit.

Starting from the simple observation that Três Marias tailing, subject of this study, is basically formed by minerals containing metallic elements commonly used in glass-ceramic production to enable nucleation processes (Navarro, 1985), the researches were oriented to study the transformation of tailings into glass-ceramic materials.

The transformation of tailings into glass-ceramic materials is a known process using a sequence of grinding, melting at high temperatures and casting, followed by heat treatment for crystallization of new phases into the vitreous matrix (Fonseca et al., 1993; Fonseca et al., 1995; Fonseca et al., 1996; Fonseca et al., 2004a; Fonseca et al., 2004b). Several studies indicate that, after gone through this process, all elements including metals, are transformed into a solid and inert material, forever immobilized (Gillian & Wiles, 1992).

Technical feasibility was evaluated through chemical, mineralogical, differential thermal and thermal microscopy analysis to model and control the fusibility and crystallization of the tailings, showing positive results so far.

The remaining challenge of this innovative approach is to adapt a known technologic process to offer new, ecological and high-quality products to a broad base of customers at affordable prices, providing the continuous absorption of large quantities.

The glass-ceramic material is extremely hard, having high mechanical resistance and low water absorption (Davies et al., 1970), specifications that meet and even surpass highest standards for marble, granite and stoneware, demonstrating the potentiality application of this material as a substitute of these products in civil construction industry.

Since this new material can be produced in the same production lines of ceramic floors and coverings, with similar operational parameters, its production costs can be compared to stoneware products, indicating that it can be offered to the market at competitive prices, with the additional benefit of being an environmental friendly material.

In a short summary, this technology aims to minimize the disposal of tailings in dams, bringing an additional source of revenue to NEXA through sales of the glass-ceramic material.

METHODOLOGY

Material

The material - tailing – investigated in this study was the "Cake of the Belt Filters", that constitutes a metallurgical residue from the sulfide and silicate circuit of the Production Unit of Metallic Zinc, located in Três Marias, MG, Brazil, belonging to NEXA Resources.

Method

Starting with 20 kg of tailings dried at room temperature, sieved through a 1 mm mesh, crushing the coarse fraction in impact crusher and sieved one more time (until no residue remained in the 1 mm sieve), homogenized in piles, quartered, bagged and stored in 200 liters drums.

The tailing was characterized by chemical analysis - gravimetry, Inductively Coupled Plasma (ICP), atomic absorption, volumetry and potentiometry, and by X-ray diffractometry (XRD).

Heating microscopy (MwH) was used (from 800 °C) to evaluate the fusibility of the tailing, allowing characteristic temperatures to be determined and the definition of melting temperature to be used to melt the tailings.

The tailing was fused for six hours in an electric furnace (silicon carbide elements) using ZAS – zirconia, alumina, silica – crucibles, with a capacity of 60 g, resistant to severe melt corrosion. The vitreous pieces were obtained by pouring the molten glass into a metallic mold, and in sequence were annealed in an electric furnace for two hours.

The typical temperatures of the glass obtained from the melting of the tailings - glass transition temperature (Tg) and crystallization temperature (Tc) - were determined by Differential Thermal Analysis (DTA) of the ground glass, using a heating rate of 10 °C/min from room temperature up to 1000 °C.

The loss of mass in the tailings melt was determined by Thermal-Gravimetric Analysis (TGA/TGD) performed between room temperature and 1500 °C with a heating rate of 10° C/min.

The characterization of the crystallized material - glass-ceramic - obtained from the controlled devitrification of the glass was done by X-ray Diffraction.

RESULTS AND DISCUSSION

To investigate the possibility of using the tailing as raw material for the production of glass-ceramics, the existence of vitreous network forming elements is one of the factors to be considered. From the literature (Navarro, 1985), some oxides have the function of being glass-forming compounds for the vitreous network, this is the case for SiO_2.

Based on the results of the chemical and mineralogical (FIGURE 1) characterization, the content of SiO_2 (27.68 %) in the tailing led, in principle, to the belief that additions could be needed to consolidate a glass structure after melting. However, as shown in the results of the MwH analysis discussed below, the fusibility demonstrated by the tailing is consistent with its industrial processing as it generates a glass mass in temperatures compatible with the economy of the process. This lead to the supposition that the contents of Fe (8.96%), Ca (8.48 %), Zn and Pb, when oxidized as vitreous network modifiers (Navarro, 1985), contributed to the glass formation.

Other elements, when oxidized and depending on the type of atomic coordination developed when forming the glass net, certainly also favored the good fusibility of the tailing.

The identified crystal phases (FIGURE 1) - gypsum [$Ca(SO_4).2H_2O$], hematite [Fe_2O_3], jarosite [$K_2Fe_6(OH)_{12}(SO_4)_4$], quartz [SiO_2], anglesite [$PbSO_4$], sphalerite [ZnS] and franklinite [$(Fe,Mn,Zn)^{2+}(Fe,Mn)^{3+}{}_2O_4$] will certainly be destroyed in the melting process. Therefore, these crystal phases will be significantly responsible for the contribution of elements present in the tailing, without disregarding the amorphous phases compatible with the XRD base line profile.

Due to the fast cooling adopted by pouring the molten glass into water, from 1400 °C to room temperature (30 °C), the incorporation of the metals present in the tailing into the glass network generated by melting is very probable and desirable, since these metals will favor the controlled crystallization of the obtained glass and be immobilized in the process.

Additionally, as in the melting process considerable amounts of SO_2 and / or SO_3 will be generated, the use of both in the production of sulfuric acid (H_2SO_4) can present a positive aspect to the circular economy concept of this process.

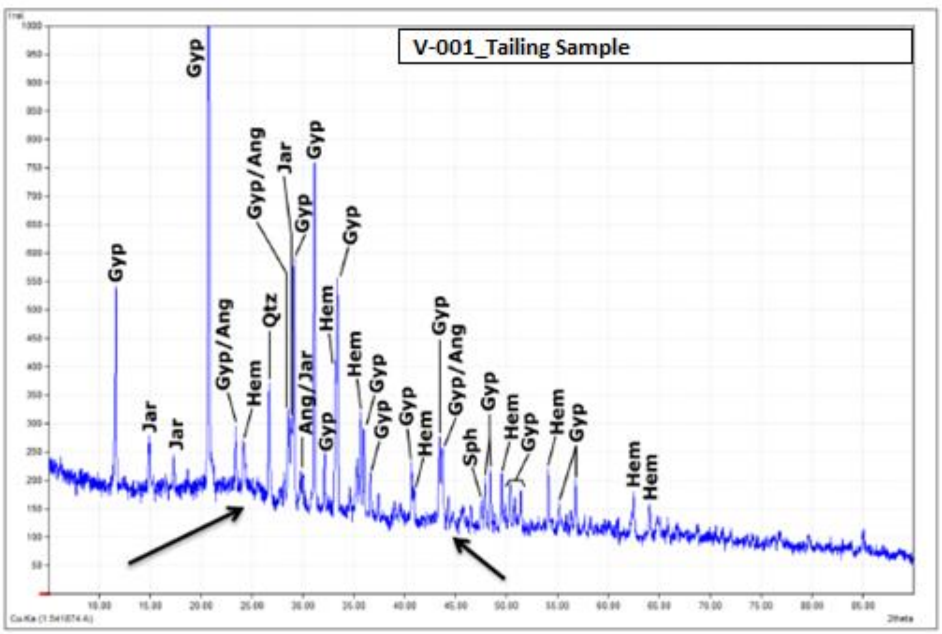

Figure 1 X-ray Diffractogram representative of the tailing

The analysis by MwH (FIGURE 2) revealed characteristic points of relatively low tailings fusibility, which presents a promising result in terms of the economics of a future Industrial Unit, as it will represents a lower energy consumption, compared to the glass industry in general.

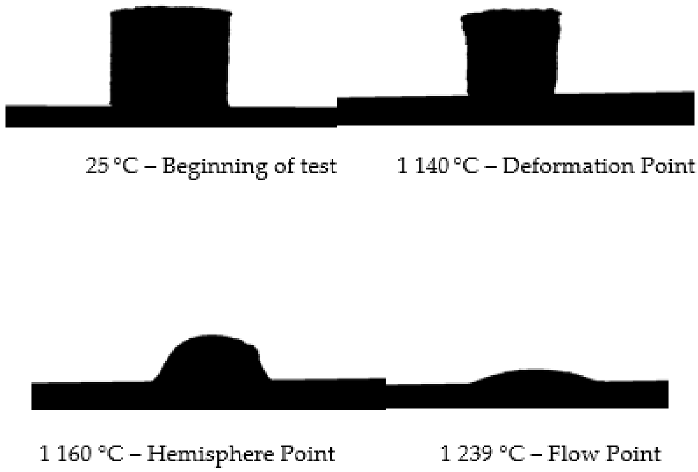

Figure 2 Tests by microscopy with heating

Due to the flow temperature of the glass obtained from the tailing (1239 °C), the fusion tests were initiated, establishing a temperature limit of 1400 °C. The first fusion test aimed to produce a glass frit in order to generate material for the thermal analysis tests (FIGURE 3).

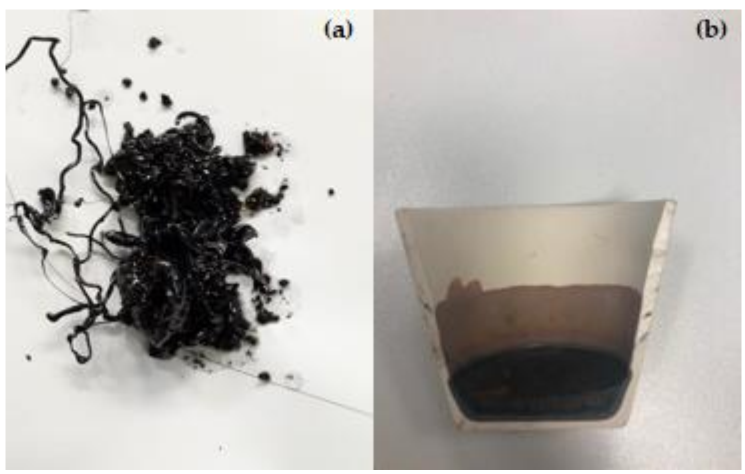

Figure 3 Fusion tests (a) Frit generated by pouring molten glass into water; (b) Half cut of the ZAS crucible

The TGA analysis reveal a water loss (humidity) around 110°C, followed by a set of volatilizations that intensify starting at 1150°C, probably corresponding to the decomposition of the sulfate present, associated to the generation of SO_2 / SO_3. The total mass loss recorded varies between 50% and 60%.

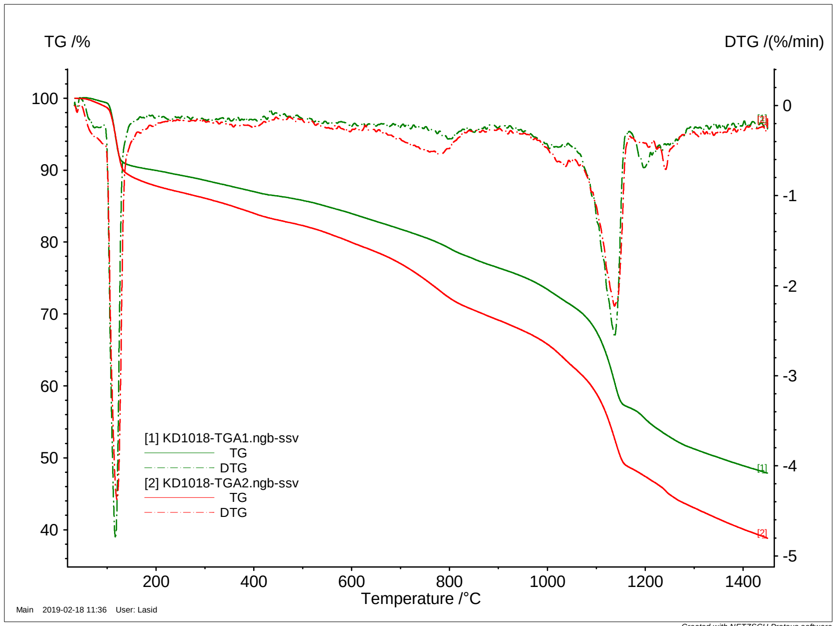

Figure 4 Thermogravimetric analysis (TGA) revealing the heterogeneity of the tailing

From the glass frit, a set of thermo-differential analysis was carried out with different objectives. The first was to determine the characteristic temperatures of the glass, meaning its Tg - glass transition temperature - and Tc - crystallization temperature. The Tg has significant relevance in the process, since it is from this temperature that the atoms in the glass structure acquire mobility to establish stable interactions towards the promotion of chemical bonds with other atoms with which the electronic affinities can favor the nucleation necessary for the crystallization of the glass.

From these results – FIGURE 5 - a new set of fusion tests was carried out in order to obtain crystallized materials (submitted to Tc), starting from molded and annealed glass pieces (submitted to Tg).

Figure 5 Crystalized glass-ceramic pieces at 850 °C obtained from melting (1400 °C) and annealing (675 °C)

A series of tests were carried out to optimize the melting and crystallization conditions of vitreous parts, based on the DTAs, using different heating rates (5 °C/min, 10 °C/min. and 20 °C/min) as well as distinct particle-size fractions of vitreous material (diameter ranges from 425 µm to 300 µm; 149 µm to 125 µm; 44 µm to 37 µm; and less than 37 µm).

These analysis show that the Tc of 850 °C is not affected by the decrease in particle size of the vitreous material, confirming that the phenomenon has, mainly, bulk characteristics - volumetric crystallization, as shown in FIGURE 6. Otherwise, in the occurrence of surface crystallization, the Tc would be significantly reduced, since the driving force of the phenomenon is the surface area.

Figure 6 Glass and glass-ceramic pieces obtained from the tailings

In order to verify the immobilization of metals, the glass-ceramic material was submitted to leaching and solubilization tests according to Brazilian legislation (ABNT NBR 10005, 2004; ABNT NBR 10006, 2004) and the obtained results meet the specifications (ABNT NBR 10004, 2004) to classify the material as non-hazardous.

The monthly production of the glass ceramic material required to absorb 15000 tons of tailings generated in Três Marias is estimated to be 200 thousand m². In Brazilian market – which is the third largest in the world in volume of consumption and production of stoneware, reaching 690 million m² in 2017 – this amount represents less than 0.4% of the total volume (ANFACER, 2017).

The following stage is to evaluate the economic feasibility of the process and sale of this material on the market. Preliminary studies to estimate the production costs of this material, using the ceramic flooring and coating industry as a parameter, indicate that, in the near future, is affordable to offer a product with comparable qualities to porcelain stoneware and granite, at competitive prices.

CONCLUSION

The present study allowed to investigate the typical crystallization temperatures of the glass obtained from the tailing, and to generate vitreous and crystallized units, which indicate the capability of immobilizing and transformation of tailings into value added products.

A series of studies will be performed in the next phase of the project to validate the technical and financial aspects of the technology, in order to consolidate the developed process of immobilization of tailings. This includes the characterization of gas emissions to identify eventual volatilization of metals during melting, also considering SO_2 / SO_3 gases formed in the melting process and its potential use for production of sulfuric acid - input for zinc ore processing. In addition, performance tests of the glass ceramic will be performed according to Brazilian standards for stoneware.

It is worth mentioning that this step is carried out in an oxidizing atmosphere, and therefore the metals present in the tailings are at least in part oxidized and / or incorporated into the glass network. Therefore, phase II of the project contemplates the comparison between the contents of the metals present in the tailings (weight percent) and their corresponding contents incorporated into the developed glass ceramic material. This way, we seek to consolidate the proposed immobilization approach, considering the results obtained in the solubilization and leaching tests performed on the glassceramic samples obtained from the tailings.

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