

Tailings from Zn ore processing as raw-material for glass-ceramic coating

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ABSTRACT

Immobilization and transformation of mining tailings have been considered an alternative aligned with the ESG strategy for producing glass-ceramic coating. In this regard, the route of controlled crystallization of glasses derived from these tailings is the key to absorb the large volume mined and cost reduction on dams and its decommissioning. In addition, the need to stimulate employment and income for mine-side communities can be satisfied by introducing glass-ceramic coating production after depletion of mines. For example, recovery of tailings from NEXA Resources' Unit in Três Marias – Minas Gerais, Brazil –, where Zn ores are processed and can generate 550,000 m² of high-quality glass-ceramic coating, can provide revenue from a by-product usually classified as cost. Production of glass-ceramic coatings using only mining tailings is displayed throughout this work. Methodology includes homogenization, melting, grinding, particle size distribution, forming and heat treatment operations. The properties of the resulting material are exhibited in order to prove its quality. This technology is based on the dynamics of mineral exploitation, change of mining fronts, and the variability of what has already been disposed in dams for years. This approach, developed both technically and economically, ensures a new vision on managing waste and innovation in contrast to traditional solutions. The next step is to apply this approach to other mining tailings and evaluate this technology in metal recovery processes.



INTRODUCTION

Responsible supply chains are considered a key subject on Environmental, Social and Governance (ESG) assessment in modern global companies. For instance, World Economic Forum defines their impact on the environment and their ability to improve local economic activity based on a set of 31 proven supply chain practices from leading companies (World Economic Forum, 2015). Therefore, decision-makers may have a guidance for their businesses in order to lead them to the achievement of sustainable development goals (SDG).

Regarding to the decision framework from the Landscape of Supply Chain Practices (World Economic Forum, 2015), the feasibility of introducing circularity based on immobilization and transformation of mining tailings for production of glass-ceramic coating had been evaluated in previous work (Fonseca et al., 2019). Technical principles are based on the presence of metals in tailings composition which enables nucleation in a glass matrix and results in a glass-ceramic material. Furthermore, its technological process is well known by glass and ceramic industries, and it is based on grinding, melting, and forming, followed by heat treatment for crystallization.

Although chemical composition changes from different tailings, the process to immobilize and turn it into glass or glass-ceramic is feasible if it presents glass-forming substances in its composition. Glass-ceramic is an inorganic and non-metallic material, produced from controlled crystallization of glasses by different methods. These materials exhibit crystal functional phase and a residual glass phase (Deubener *et al.*, 2018). Controlled crystallization consists of inducing crystal phase from the glass matrix by submitting it to thermal treatment in order to achieve a critical number of nuclei and followed by crystal growth.

This solution, though, is energy-intensive which may be considered a drawback. Even so, the benefits from glass-ceramic materials derived from tailings are considerable. For example, construction may be the only feasible activity capable of absorbing the amount of tailing generated from mining. Thus, application of glass-ceramics as tiles and coatings for construction is consistent in terms of competitiveness, both technical and economically. Besides, market is wide and diffusive which favourites new entrances and costumer approval based on price and quality.

The technology developed in this work is an alternative to disposal in dams or dry stacking. And from now on, we will call this technology for immobilization and useful use of tailings as nextone. Besides, it is a sustainable approach for the following reasons. First, several studies indicate that all elements, which include metals, are transformed into a safe, solid, and inert material (Gillian & Wiles, 1992). Second, it stimulates employment and income for mine-side communities by introducing glass-ceramic coating production, even after mining depletion. Finally, it provides new, sustainable, and high-quality products to a broad range of customers at affordable prices which leads to continuous absorption of large quantities of material.

As circular economy is based on mass and energy restorative flow (Weetman, 2016), it matches with the introduction of tailings as circular input to downstream processes. It is also aligned with

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responsible supply chain practices of seeking for more sustainable sources, designing for maximum recyclability and circularity, considering sustainability criteria in location decision, reducing energy, water use and emissions and centralizing and optimizing waste management, only to name a few (World Economic Forum, 2015). It is also worth mention that glass-ceramic coatings produced from mining tailings are cost and quality competitive in comparison to traditional ceramic coatings.

Thus, the objective of this work is to expose the technological route to produce glass-ceramic material using tailings from Zn ore, starting with the generation of glass frits resulted from quenching technique – i.e., pouring the hot molten glass into a metal container filled with water at room temperature. Then grinding it and defining a particle size distribution to the ground frit. Finally, forming the ground frit by pressing and in sequence, submitting it to heat treatment for crystallization, resulting in the glass-ceramic material. Results from conventional essays are then displayed and verification of its properties is aimed. Finally, economic feasibility is described and suitability of this proposal to produce glass-ceramic coating from tailings by frit route is discussed.

METHODOLOGY

Leaching and solubilization tests

Crude tailings and treated samples were analysed according to ABNT NBR 10,004 standard (2004) for leaching and solubilization as a mean to evaluate heavy metal content and efficiency of vitrification.

Homogenization, melting and quenching

Tailings sample was homogenized and then melted under 1,400°C. Quenching technique was adopted next to produce vitreous material by transferring the melt into a metal container filled with water under room temperature – i.e., 25°C. The result was the production of frit sample which was then sent to grinding stage.

Grinding and particle size distribution

Grinding was designed for returning a particle size distribution below 75 μ m after classification. Sieving was defined as the technique to classify the ground frit. The result was an amount of 50 kg of ground frit with particle size distribution below 75 μ m.

Forming and heat treatment

The amount of 50 kg of ground frit was collected and the following essays were considered before and after forming the sample and also after heat treatment (Table 1). These essays are usual references for evaluating suitability of ceramic coating material for application in construction.



Essay	Method
Sieve residue	Wet sieving essay
Moisture content	Humidity detector set in 130°C
Apparent density	Mercury-displacement method
Retraction after burning	Registration of dimension change between dried and sintered samples
Water absorption	Porosimetry test
Flexural strength	Three-point flexural test

Table 1. Essays considered for evaluating ceramic coating material suitability

Forming consisted in uniaxial compaction designed in 100 mm x 100 mm plates and 50 mmdiameter discs while heat treatment was conducted in a roller hearth kiln where sintering was defined on maximum densification condition.

RESULTS AND DISCUSSION

Evaluation of metal immobilization from current tailings was based on a national standard (ABNT NBR, 2004) while its characterization and transformation into value added products as well as its use as raw-material for glass-ceramic production have been considered in previous work (Fonseca et al., 2019). Results from the production of glass-ceramic plates and discs by frit route using only mining tailings are displayed and economic feasibility is discussed as the following.

Evaluation of metal immobilization

Leaching of crude tailings sample revealed concentrations of lead (Pb) and other metals over the maximum allowed value (MAV) by the national standard (ABNT NBR, 2004b) in contrast to the values revealed in the treated sample which on the other hand resulted in appropriated values.

Similarly, solubilization test of the crude tailings sample revealed concentration of lead (Pb), iron (Fe), and zinc (Zn) over their respective MAV (ABNT NBR, 2004c). Not only metals, but sulphate (SO_4^{-2}) was also over its corresponding MAV. After treatment, however, all elements exhibited concentration values lower to their respective MAV.

From leaching and solubilization results, it was recognized that vitrification of tailings was successful in immobilizing heavy metal elements. It meant that the proposed solution meets with technical and safe requirements. The next step was the evaluation of its suitability to produce glassceramic coating for construction based on typical essays for ceramic coating materials.

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Glass-ceramic suitability as coating material

The crude residue from the sieve residue test performed $0.11_{\text{WW/W}}$ which indicated accomplishment of particle size distribution below 75 µm during the grinding stage. Similarly, moisture content performed $0.34_{\text{WW/W}}$ which agrees to correct drying procedures before grinding stage. Therefore, these essays confirmed the quality of grinding and drying stages respectively.

Also, values of water absorption (%) and retraction after heat treatment (%) were obtained due to change in temperature from 1,020°C and 1,070°C while their behaviour was tracked by plotting the gresification curve, including apparent density change (Figure 1).

It was possible to identify a range of temperature where maximum densification occurs at the cost of maximum linear retraction and the benefit of minimum water absorption. This range was determined between 1,050°C and 1,060°C which is significantly lower compared to sintering values of temperature usually observed in ceramic industry. Figure 2 exhibits a sintered 50 mm-diameter disc used in this essay.

Finally, flexural strength essay was designed under maximum densification condition after heat treatment– i.e., 3.149 g/cm3 – and indicated the value of 98.3 MPa. This result is suitable for production of glass-ceramic coating based on the flexural strength indicated for traditional ceramic coating using in construction. The resulted sintered plates with dimensions of 100 mm x 100 mm were gathered in Figure 3.



Figure 1. Gresification curve indicating water absorption (%) and linear retraction (%) of 50-mm sintered disc





Figure 2. Sintered 50 mm-disc produced by compaction pressure of 39.2 MPa and 10% w/w starch-based ligant due to temperature change



Figure 3. Sintered plates of 100 mm length x 100 mm width after polishing are displayed

Economics behind technical feasibility

After technical feasibility of the route was confirmed from the results of the essays above mentioned, a study of economic feasibility of this technology was made, using as references the parameters of the ceramic coating industry in Brazil, third largest in the world regarding production volume (Junior et al., 2010).

Although we have developed a complete economic study, in summary, as the production method is the same for producing ceramic coating, with no need to develop new equipment or processes, the economic feasibility of the new material is easy to verify by making simple comparisons as follows.

Of all production cost items, in high quality ceramic tile production plants, thermal energy (23%), porcelain enamel (23%) and raw material (5,8%), generally represent more than 50% of the total production cost (Junior et al., 2010).

In the case of glass-ceramic production technology, the cost-saving benefits arising from a lower temperature used in the heat treatment - 1,100°C - compared to conventional ceramics coating -1,350°C – can be offset by the extra energy required to produce glass frits at 1,400°C.

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On the other hand, there is no cost to purchase raw material – using tailings currently disposed in dams – and there is also no need for special enamels in the process, as the product, as we can see in Figure 3, has an excellent presentation after polishing, with its natural color and tonal variation as found in natural decorative stones.

Also, we would like to emphasize that in the economic study, we did not consider the elimination of the costly process of disposing of tailings and the maintenance of dams and dry stacking, which will certainly have a positive impact on the profitability of the mining operation.

CONCLUSION

Immobilization of metals was confirmed from leaching and solubilization tests based on national standard which indicated safety for its technical application. Furthermore, usual essays for evaluation of ceramic coating materials attested suitability of the glass-ceramic material produced from the thermal treatment of the ground frit for coating application. Finally, cost-saving benefits were mentioned and compared based on typical processes from the ceramic industry, exhibiting the advantage of using tailings as raw-material for coating production.

This work had displayed a technical, innovative, and sustainable alternative for tailings, avoiding disposal in dams or dry stacking. Besides, mine-side communities may benefit from this initiative even after mining depletion. Furthermore, production line for tiles and coatings are well-known by glass and ceramic industry which favours implementation. Thus, development of glass-ceramic coating from tailings aims to reinforce environmental, social, and economic values which sustain an ESG approach by embodying circular economy concepts – e.g., circular input, upcycling and industrial symbiosis.

Next step is to evaluate tailings from different sources and their ability to produce glass-ceramic materials based on the concepts of glass-ceramic technology. Still, metal recovery must be considered in future studies as it is of great interest for industry.

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NOMENCLATURE

ESG	environmental, social and governance
SDG	sustainable development goals
Fe	iron
Pb	lead
Zn	zinc



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