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Potential for reuse of tungsten mining waste-rock in technical-artistic value added products

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ABSTRACT

Mining and quarrying activities in Europe generate approximately 55% of total industrial wastes, according to a recent Eurostat report. Most of these wastes are directly dumped on land or deposited in landfill sites. The first solution may lead to negative environmental impacts on land (removal of vegetation, deforestation, land slope changes and increased risk of erosion), water (pollutant transport through surface runoff, soil infiltration and contamination of water resources), may lead to the contamination of agricultural goods and may impose risks on human health. In Portugal, about 20% of industrial waste produced originates from mines and quarries, particularly from Panasqueira mining, one of the largest tungsten mines in the world. Currently, Panasqueira mining generates almost 100 tonnes of waste-rock, per day. Such waste-rock have accumulated over a number of years into very large heaps and it is desirable to seek new economic solutions that can contribute towards their reuse. In this context, this work discusses the potential for reuse of waste-rock piles of Panasqueira tungsten mine, which may be a case statement to be followed. The proposed solution described in this paper consists in developing innovative polymer-based composite materials, obtained from non-contaminated waste-rock tailings. Such materials must have suitable properties for technical-artistic value added applications, such as conservation, restoration and/or rehabilitation of historic monuments, sculptures, decorative and architectural intervention, or simply as materials for building revetments.

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1. Introduction

In most European countries (EU27), according to the Eurostat, industry is the main waste generating economic sector, followed by construction, services and agriculture. Both industry and construction generate the highest volume of waste, together accounting for about 83% (Eurostat, 2009). Within the industrial sector, in 2006 in the EU27, about 55% of industrial waste was a by-product of mining and quarrying. In this period, in one third of the countries, the mining and quarrying industry accounted for 40% or more of industrial waste, on the other hand about half of the countries did not have a significant mining industry. Romania and Bulgaria reported most of their waste from mining and quarrying (approximately 90% and 65%, respectively) while at the other end of the spectrum, Luxemburg and Malta reported less than 10% of mining and quarrying waste production. In Portugal, during the

same period, mining and quarrying waste accounted for almost 20% of the total industrial waste accumulated (Eurostat, 2009). Thus, mining, and as a consequence mining waste, is unevenly spread over the European countries (EU27).

The accumulation of waste from mining and quarry industry, over the years, has lead to the formation of large deposits. These deposits present a potential risk of environmental pollution and cause serious landscape impacts, thus affecting the quality of life of local populations. The storage of these wastes directly on land may lead to negative environmental impacts, since they include some harmful pollutants (e.g. heavy metals). Dumping wastes on land normally contributes to disfiguring the natural landscape, removal of vegetation and deforestation, release of green house emissions (Bandara and Hettiaratchi, 2010), loss of biodiversity, loss of aesthetic value to the local landscape, loss of land productivity, changes to landscape, slope stability and, consequently increases the risk of soil erosion under action of wind and storm runoff (Zoran et al., 2010; Kabas et al., 2011). The water surface runoff may transport pollutants from wastes to land, groundwater and surface water, which may accumulate in agricultural lands and water

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sources for public supply and, therefore, become a risk to public health (Kreith and Tchobanoglous, 2002; Sahu, 2007). These environmental and public health problems also contribute towards rising social and economic problems such as the depreciation of land value, dereliction of land uses and depopulation (Kreith and Tchobanoglous, 2002; Bandara and Hettiaratchi, 2010).

The use of earth/rock dams or lagoons to store the wastes seem to be a safer option. However, the collapse of such structures may also have serious impacts on the environment and human health and safety, notable examples in 1998 include; Aznalcóllar, Spain (Galán et al., 2002) and Baia Mare and Baia Borsa, Romania (Lucas, 2001).

Currently, member states of the European union must has adopt measures to prevent or minimise any adverse effects on the environment and consequent risks to health resulting from the management of waste from the extractive industries, such as tailings and displaced material. A comprehensive framework for the safe management of waste from extractive industries has been set in the following documents: Directive 2006/21/EC of 15 March 2006 (Management of waste from the extractive industries – the Mining Waste Directive) and The Reference Document on Best Available Techniques for the Management of Tailings and Wasterock in Mining Activities (EC, 2004).

Regarding the reuse of waste, a number of studies (Tiruta-Barna et al., 2007) show the important potential of its reuse and lack of regulation in this field. The main issues concerning mineral reuse are the local impacts and the saving of natural resources. In a comprehensive review of recycling and reuse routes of mineral waste and relative legislation, the authors propose that the choice and evaluation of solid mineral wastes recycling and reuse strategies could be based on ecological risk assessment (EcoRA) and life cycle assessment (LCA), and should serve as a basis for further research (Tiruta-Barna et al., 2007).

2. Reuse of mining and quarrying waste

Most mining and quarrying wastes obtained from grinding of rocks, placed in deposits in specific locations/regions, can be reused in earthworks and construction, in particular the coarser fractions. Typical applications include use in asphalt pavements (Akbulut and Gürer, 2007); (Castro-Gomes et al., 2006) and concrete (Hebhoud et al., 2011); (Yellishetty et al., 2008). However, the potential for reuse on a national scale is primarily constrained by transport and consequently by economic aspects. As a result it is desirable to seek added value solutions that can contribute to the recovery and reuse of such waste materials.

Waste from mines and quarries are likely to become raw material for industrial applications where the high value of the product does not prejudice its reuse due transport costs, which includes, as an example, processing of calcium carbonate waste for Portland cement production in the specific case of marble industry (Raupp-Pereira et al., 2008), or the reuse of fine tailings from abandoned mine in polyester mortars (Mun et al., 2007). Other studies, concerning the reuse of fine tailings as a raw material in the construction industry are being conducted and are considered to be most promising, both from an environmental and economic point of view. Notable examples include research on the development of alkaline activated binders (geopolymers) using alumina-silica based waste mud from mining and quarrying industry (Torgal et al., 2008); (Torgal et al., 2009); (Zhang et al., 2011).

Although geopolymers are presented as a solution for concrete production, some studies have quantified the environmental impact of such production using fly ash, blast furnace slag and metakaolin as precursors (Habert et al., 2011). Another aspect to be studied in the future is the environmental impact based on the Life Cycle Assessment (LCA) method as suggested by Huijbregts et al. (2003). This evaluation may be carried out on impact categories such as global warming, energy demand and resource depletion. Habert et al. (2011) show that the production of different types of geopolymer concrete had a slightly lower impact on global warming than standard Ordinary Portland Cement (OPC) concrete. Geopolymer made from fly ashes or granulated blast furnace slags requires less sodium silicate solution for activation and, therefore, has a lower environmental impact than geopolymer made from pure metakaolin. In order to reduce carbon emissions, geopolymer production should use waste-based precursors with low sodium silicate solution. Therefore, manipulating the technology of geopolymer production it might be possible reduce some process energy, making the geopolymer greenhouse emissions several times lower than the values obtained with cement production. There is great potential for geopolymers to reduce the climate change impacts of cement production with 44%-64% improvement in greenhouse gas emissions over OPC, while the cost of these geopolymers can be up to twice as high as OPC McLellana et al. (2011); Gäbel and Tillman, 2005 also showed that an increase in the use of recovered material and alternative fuel for cement production may reduce the emissions of CO₂, NOX, SO₂, CO, VOC, CH₄ and dust can be dropped between 30% and 80%.

Other added value applications for reusing mining and quarrying wastes are the production of compact composites, particularly, from marble or quartz wastes. Compact composite materials are constituted by several sizes of particles/aggregates linked by a polymeric resin matrix, where the aggregate/polyester matrix is optimised for best performance of mechanical and durability related properties. The economic value of such composites depends primarily on its aesthetic appeal, which is imparted primarily by the unique textures and colour scales of the wastes.

The authors believe this to be an innovative approach for reusing mining waste materials, as was proposed in a recent study carried on by the Department of Sculpture at the University of Granada, aimed at developing new applications for architectural, technical-sculptural and restoration process, by reusing wastes of quarrying industry of Macael region, Spain. The research included an experimental phase on the characterisation of the waste composites as well a discussion of innovative approaches to reuse. The study considered different types of polymer-based mortars incorporating different fine waste materials, from dust to sand sized particles, as illustrated in Fig. 1. The study concluded that mortar properties and potential for industrial applications



Fig. 1. Visual aspect of polymer-based mortars of different particles sizes obtained by reusing wastes from quarrying industry of Macael region, Spain (Peralbo Cano, 2007).

depended on the texture and white colour scale of the particular waste (Peralbo Cano, 2007).

Well-known company brands, such us, Silestone, Technistone, Compac, Zodiaq, Corian and Caeserstone, are polymer-based composite materials that can be used in many areas of the building and furniture industry, containing around 93-94% of selected natural materials, primarily quartz or granite, resin and colour pigments and selected additional ingredients that confer it high durability, resistance, consistency, and the required design. From countertops, to floor and walls or furniture, this technology makes it possible to modify the original colours of natural quartz, to achieve a large variety of designs, formats and finishes, combining science, technology and art. Such advanced composite materials are compacted under intense vibration, vacuum, and pressure, resulting in dense, non-porous slabs. Its properties differ according to the raw materials used and hence appearance, in addition to a number of other properties. Besides quartz or granite, marble is also used in such composites, which, obviously, can also incorporate wastes from mining and quarrying industries.

In this context, an interdisciplinary research work has been carried out regarding the study and reuse of coarse wastes of Panasqueira mine, one of the most important and largest tungsten mines in the world. The primary motivation for the development of this study was that the waste-rock Panasqueira tailings had endured substantial natural ageing over many years resulting in specific colours and textures that impart highly aesthetic properties to these stones.

3. Tungsten mine coarse tailings

3.1. Mining activity

Panasqueira is an underground mine situated in central Portugal on the southern edge of the Sierra of Estrela mountain range, a natural park, near the Sierra of Açor, a protected landscape, and also near the Zezere river. Tungsten and tin have been mined in the Panasqueira area since the 1890s. The mine has been in production for over 120 years and is one of the largest economic vein deposits in the world. During the period 1947–2001, over 27 million tonnes of rock were mined, from which approximately 92,800 t of tungsten concentrate, 4,800 t of tin concentrate, and 28,600 t of copper concentrate were produced (Smith, 2006). Mineral extraction and processing produce, primarily, two main types of mine tailings, accordingly to its grain size: coarse waste-rock tailings (sterile material) derived from rock blasting and waste-mud tailings (crushed and milled waste-rock) conveyed by pipelines into lagoons (mud dams), amounting to several million tons. In the 1980's Panasqueira mining was generating of about 300 tons of waste-rock tailings per day; currently, it is still generating almost 100 tons per day. Panasqueira heaps already assume enormous proportions (see Fig. 2); the Rio tailings (aprox. 1,200,000 m³) has one mud dam $(a prox. 731,034 m^3)$ and the Barroca Grande $(a prox. 7,000,000 m^3)$ has two mud dams (aprox. 1,193,885 m³) (Ávila et al., 2008).

In Panasqueira, the ore treatment process begins with heavy media separation for the coarse fractions of material. In a second phase, cyclones are used to produce ore concentrates with high metal content, and tables are used to treat the sands. These preconcentrates contain all the existing heavy minerals, such as wolframite, cassiterite, sulphides, and siderite. It should be noted that arsenopyrite (the main sulphide present) is rejected with the tailings, which contains about 30% of arsenic (Ávila et al., 2008). The potential leaching of heavy metals, especially arsenic, from tungsten waste muds it could perform a risk of toxicity for humans and the environment. Therefore, the safely reuse of this type of waste can contribute to minimise both public health problems and



Fig. 2. Partial view of Barroca Grande tailings (waste-rock and mud lagoon), in Panasqueira.

environmental impacts. Solidification/stabilization is an established technique utilised in the treatment of hazardous materials such as waste or contaminated soil in developed countries, which uses cement, lime, or other agents to get a solid material that encapsulates the harmful compounds.

Results of tests carried out by Pacheco-Torgal (2007) pointed out that heavy metals concentrations leached from alkali-activated tungsten waste mud were low (the leached arsenic concentration was under 0.002 mg L^{-1}) and therefore this process seems to provide a safely encapsulation for metals. Leaching experiments conducted over a range of pH conditions revealed that total arsenic leaching varied among different materials (fly ash, leachants, including HNO₃, H₂SO₄, sodium citrate, geopolymer, and EDTA) and its encapsulation is pH dependent (Wang et al., 2008), ranging from less than 5% in ashes tested at pH from 5 to 9, to more than 30% in very acid or very alkaline conditions (US EPA, 2006). Recent investigations carried out by Silva et al. (2010a, 2010b) have concluded that tungsten waste mud alkali-activated binders take up to 2 weeks to stabilised the pH around 7 after immersion in water. This pH value is within the range (2-8.5) where arsenic leaching is very low (Wang et al., 2005) Therefore, under typical environmental conditions (pH from 6 to 8), low arsenic leaching is expected when binders are in contact with water. Ho et al. (2011) have evaluated the potential for leaching of metals from kaolin activation admixed with cement as the binder and rubber chips as an additive, having concluded that arsenic maximum leaching concentration (0.0045 mg L^{-1}) was not harmful to the environment or public health (the limit set up for drinking water is 0.05 mg L^{-1}).

Until 1996, the pre-concentrates were transported to the Rio plant, but today, the final separation procedures are carried out exclusively in Barroca Grande. A huge tailings pile and two mud dams exist at this site (see Fig. 2). One of the dams is still being fed with steriles (sand, mud and slush) obtained from the ore dressing operations (some rich in sulphides) (Ávila et al., 2008). Coarse sterile material from the mine and coarse tailings (sterile material) from heavy media separation, are being deposit in the surrounding huge tailing piles. It is now clear that oxidation of sulphides tailings and flow from open impoundments are the main source of pollution in the surrounding area and is responsible for the mobilisation and migration of metals from the mine wastes into the environment (Ávila et al., 2008); (Godinho et al., 2010).

3.2. Mineralogy, geochemistry and texture

The Panasqueira deposit consists of a series of stacked, subhorizontal, hydrothermal quartz veins intruding into the Beira schists and shales. Thus, the mineralogy of these tailings, accordingly to the local geology was found to be mainly quartz and muscovite, determined by XRD diffraction. Kaolinite, illitemontmorilonite, montmorilo- nite-vermiculite, and chlorite, and also arsenopyrite, wolframite, and natrojarosite are also present in the mineralogy of this tailings (Ávila et al., 2008); (Cavey and Gunning, 2006).

Waste-rock tailings in Barroca Grande have the size like coarse aggregates (on average, diameter size of 5 mm–25 mm) and mud containing very fine particles (diameter size of less than 2 mm). Coarse steriles are constituted by a major percentage of greywacke schist and about 10% of white quartz (Antunes, 2009); (Castro-Gomes et al., 2011).

Typical chemical composition of waste-rock is presented in Table 1. Composition was determined by energy dispersive spectrometry (SEM/EDS) at Optical Centre of University of Beira Interior. Analysis was carried on milled samples of coarse materials. The results show it consists mainly of silica and alumina with smaller percentage of iron and potassium, and minor constituents.

However, it is known that part of Panasqueira tailings (particularly waste-mud) contain high sulphide (As) concentrations and sulphide-related heavy metals (Cu, Pb, Zn, and Cd). Concentrations of different chemical elements in tailings and dams from the Barroca Grande were carried on by INETI in the scope of e-Ecorisk project in 2005. Median concentrations were found to be as follows: Ag(40), As(4,715), B(3,312), Ba(182), Cd(79), Co(5), Cu(3,548), Mn(641), Ni(34), P(1,880), Pb(171), Sb(39), Sn(702), V(81), W(2,434), Y(168), Zn(460) expressed in mg kg⁻¹, and Fe(7,3) expressed in percentage (Ávila et al., 2008).

Table 2 presents physical and mechanical properties of wasterock materials. Particle shapes were characterised on the basis of EN933-3 and EN933-4 standards for concrete aggregates. Particles maximum and minimum dimensions were determined accordingly to EN933-1 and EN12620. Mechanical and physical properties were determined by EN1097-2, EN1097-3, EN1097-6 and BS812-110. From the results obtained it is evident that waste coarse particles present good properties, equivalent to those found in good quality granite aggregates (Pereira et al., 2009).

Immediately after being extracted and deposited, coarse steriles present a light grey colour, typical of schist rocks. However, due its mineralogy and composition and exposure to natural environmental conditions along time, its colour gradually changes to ochre, an iron colour tone.

4. Technical-artistically value added products

Since Panasqueira most waste-rock tailings have been exposed to weathering for many years it has suffered natural ageing, thus transforming into a specific colour and texture that gives it high aesthetic value. In this context, an interdisciplinary research work has been carried out focused on the study and reuse of coarse wastes of Panasqueira mine, with an objective of developing technical-artistic value added products. The experimental study consisted in developing polymer-based composite materials incorporating tungsten mining coarse wastes, as sourced directly from one of the several heaps of Panasqueira mine.

Table 1				
Element chemical	composition	of coarse	wastes	(wt.%).

Table 1

0	Na	Al	Si	К	Ti	Fe	Mg	Ca
57.53	1.81	7.70	23.47	2.73	0.62	3.09	0.88	2.16

Table 2

Physical and mechanical properties of waste coarse particles versus good quality granite aggregates.

Designation	Waste coarse particles	Granite aggregates
Flakiness index (FI)	27.7	14.0
Shape index (SI)	53.2	5.0
Maximum dimension [mm]	25.4	25.4
Minimum dimension [mm]	1.19	9.52
Loose bulk density [g/cm ³]	2.79	2.66
Water absorption [%]	0.2	0.2
Resistance to fragmentation	19.2	20.0
(Los Angeles) [%]		
Aggregate crushing value [%]	16.5	21.5

4.1. Mixture formulation

Composites were produced using a polyester resin (Crystic 199 from Scott Bader, Barcelona, Spain) considering its low cost and ease of use at ambient temperatures. Polyester resin presents ideal properties for most industrial and technical-artistic applications. Polyester has good surface hardness and stiffness, good compressive, tensile and shear strength, withstanding relatively well high and low temperatures. It suffers slight deterioration when submitted to atmospheric agents and additionally it presents low density (Peralbo Cano, 2007).

Initially, as part of this investigation, different formulations of composite wastes were studied in laboratory. Thus, several mixtures compositions having different sizes of coarse wastes, resulting in various prototypes were evaluated (Antunes, 2009). Later, was decided to use the wastes in its natural state, as found in heaps, although its particle size distribution presents discontinuity. Optimal resin content was based on a balance between the physical and mechanical properties of composites, i.e. resin content required for a good coverage of all particles and to provide good mechanical properties, like stiffness.

Moreover, a technological method was developed for the production of a terrazzo tile prototype with tungsten waste materials. It consists in a relatively simple and low cost process of two main stages, mixing and compacting in moulds. The process requires low energy and does not use water, thus being environmentally friendly.

4.2. Study of waste-rock chromatic properties

One of the most relevant aspects of the final appearance of these polymer composites has to do with the colour of waste that constitute it and the possibility of its modification. A number of earlier studies focused on examining and measuring colour using a number of techniques and instruments are documented in the literature. Of particular relevance to this investigation is earlier research work conducted on various polymer composites (mortar and concrete) for technical and artistic applications (Durán Suárez, 1996) (Corpas Iglesias et al., 2002). According to these studies, the use of colorimetric measurement instruments taking into account the existing standards, facilitate determination of the characteristic parameters for the manipulation and colour correction of the various materials composing the mixture.

In this investigation, colour measurements were made on the surface of the waste particles in its original state, i.e. as obtained after rock blasting, and in its aged state, i.e. as found in heaps. Colour measurements were also conducted on particle surfaces following exposure for a period of 2 h at conditioning temperatures of 800 °C and 1000 °C. Fig. 3 shows the original aspect of coarse wastes (A), the aged state (due to weathering) (B) and both states



Fig. 3. Visual aspect of rock-wastes, (A) original state, (B) aged state, (C) submitted to 800 °C, (D) submitted to 1000 °C.

after being submitted to 800 °C (C) and to 1000 °C (D). A general darkening, resulting from iron oxide reactions, was observed in the wastes following exposure to 1000 °C accompanied by volumetric expansion.

With respect to colorimetric values, the chromaticity diagram shown in Fig. 4 presents the colour values corresponding to the different states of wastes as shown in Fig. 3. This diagram was obtained by using a Konica Minolta model CM-2500c colour spectrophotometer. By analysis of results, it appears that the chromaticity values increase considerably when waste particles are conditioned at 800 °C. In this case, there is a significant increase of red and yellow colours. By contrast, when wastes are subjected to a temperature of 1000 °C, a decrease in the saturation of these two colours is observed. In any case, brightness of waste particles



Fig. 4. Chromaticity diagrams of rock-waste.

decreases as it suffers ageing or when subjected to high temperatures, when compared to its natural state, as shown in Fig. 5.

Thus, it can be concluded that despite of the visually pleasing characteristic colour (ochre) of aged wastes as found in the Panasqueira heaps, the waste may be heat-treated to change its colour, further widening the scope and opportunities for use in technical artistic applications, such as mortars for intervention in historic heritage and many architectural applications.

4.3. Value added prototypes

Taking into account its colour characteristics, and the good physical and mechanical properties of coarse wastes, the development of terrazzo tiles for external use in architectural applications may be a viable opportunity for immediate application of these composites (Peralbo Cano et al., 2010). Thus, in this study, unit prototypes of 30×30 cm size and 3 cm thickness were produced. Mix compositions were determined using optimal resin percentages whilst minimising final cost. In view of its technical feasibility, selected physical and mechanical characteristics were studied to obtain CE marking taking into account requirements of EN13748-2



Fig. 5. Brightness diagrams of rock-waste.

Table 3

Results obtained	of CE m	arking req	uirement t	ests, for t	errazzo tile	prototypes.

Test	Mean values	Class	CE marking
Breaking strength:			
Flexural strength	$f_{\rm cf}=3.0~{ m MPa}$	1	ST
Compressive strength (unnecessary test)	$f_{\rm c}=7.5~{ m MPa}$	Not applicable	Not required
Abrasion resistance:			
Abrasion wheel test	$V_{\rm AD} = 24.8 \ { m mm}$	2	G
Method of Böhme	$\Delta V = 3.90 \text{ cm}^3/50 \text{ cm}^2$	4	Ι
Slip/skid resistance (unnecessary test)	USVR = 45	Not applicable	Satisfactory
Weathering resistance:			
Water absorption	$W_{\rm ma}=1\%$	2	В
Freeze/thawing resistance	No weight loss	3	D
Reaction to fire (unnecessary test)	Quality evaluation	Alfl	Not required
Thermal conductivity (unnecessary test)	$k = 0.479 \text{ W mK}^{-1}$	Not applicable	Not required

standard for terrazzo tiles, specifically for outdoor use. According to EN13748-2 the following experimental tests were carried out: flexural strength, compressive strength, abrasion resistance, slip/ skid resistance, weathering resistance, reaction to fire and thermal conductivity (Antunes et al., 2010), (Castro-Gomes et al., 2011).

Table 3 presents the average results obtained of CE marking test requirements for terrazzo tile prototypes. It can be seen in Table 3 that some tests are not required for CE marking for terrazzo tiles for external use. In the list of required tests, namely flexural strength (breaking strength), wheel abrasion and Böhme abrasion tests, water absorption and freeze/thawing resistance, the results obtained correspond to different CE marking labels.

Prototypes from this investigation have shown a very good flexural strength as well excellent freeze/thawing behaviour. Flexural test was carried on a ZWICK universal testing machine having a 5 kN load cell and applying a 3 mm min⁻¹ rate test. Test were done by following the methodology presented in EN12390-5 with some adaptations, using testing specimens of $4 \times 4 \times 16$ cm size, as illustrated in Fig. 6. The results obtained in this test were between 2.8 and 3.5 MPa which correspond to "Class 1"accordingly to EN13748-2 and "ST" as CE marking.

Compressive strength testing is considered unnecessary for CE marking, according to the EN13748-2 standard, since flexure strength represents more accurately tile breaking resistance.

Abrasion resistance was determined by both wide abrasion wheel test and method of Bhöme. Results of groove obtained in wide abrasion wheel test, vary from 21.5 to 24.8 mm, showing relatively good behaviour, while in Bhöme test very good results were obtained.

Unpolished slip resistance values (slip/skip resistance) were determined by pendulum friction test, as show in Fig. 7. Since waste terrazo tiles present ridges and grooves on outer surface, such a test is also considered unnecessary accordingly to EN13748-2 and CE marking should indicate "satisfactory".

The water absorption average value obtained was of $W_{h,24} = 0.12 \text{ g cm}^{-2}$, and the value of absorption capacity obtained was of $W_{m,a} = 1\%$ (wt.). This is a very low value which is justified by the fact that wastes are coated with polyester resin, which prevents it from absorbing water.

Freeze/thaw testing was carried on accordingly to EN13748-2, using a freeze/thawing prototype equipment, consisting of submitting prototype specimens to 28 freeze/thaw cycles whilst immersed in a water solution containing 3% NaCl, with each cycle lasting 24 h and ranging from $-20 \,^{\circ}$ C to $20 \,^{\circ}$ C. Prototypes resisted without any deterioration to a sequence of 28 freeze/thaw cycles.

Regarding fire resistance, terrazo tiles for external use are considered to be reaction to fire class "A1fl" without the need for testing according to EC Decision 96/603/EEC, as amended. However, by carrying on a non-standard test it was found out that as expected, polyester resin easily incinerated when submitted to fire.

Thus, the global results presented in Table 3, clearly show that tungsten waste composites developed in this study, fulfil CE requirements in the frame of a possible industrial production.

An added value for the reuse of waste (aggregates) as a raw material is the development of new polymer composite products which make the transition between the technological and



Fig. 6. Three point bending test carried on in tungsten mining waste composites.



Fig. 7. Prototype of urban furniture (outdoor bench) framed in a historical centre of a Portuguese city.

functional character. Furthermore, the new product can form the basis of a number of artistic concepts having different aesthetic qualities such as texture, colour and shape. Last but not least, the proposed product can be manufactured using low-tech principles and is sourced directly from industrial waste heaps. An example of an artistic application that highlights the sensorial properties of the proposed product is the design of an urban furniture product line that can be framed and showcased in an aesthetically appealing setting of historical or environmental significance as shown in Fig. 7.

Using moulds the prototypes were built at a half scale with a percentage of resin of 4% by mass. In spite the constraints imposed by the geometric moulds associated with the manufacturing process, the proposed product line were specifically designed to be functional products, with non-rectilinear shapes for applications as diverse as; security barriers on roads, flower boxes, garbage cans, park benches, balusters, among others. The products obtained show the validity of reusing wastes (aggregate) to build more complex parts, often requiring the use of metal armour and framed through virtual photogram's, in ranges of products for granite environmental contexts of historic centres of some Portuguese cities.

5. Conclusions

This paper discusses the potential for reuse of rock-waste tailings, a by-product from Panasqueira mining operations in Central Portugal, one of the largest tungsten mines in the world. It is estimated that mining and ore processing at Panasqueira mining site have produced approximately 10 million m³ of mine wastes, including vast quantities of waste-rock tailings, over a period of more than 120 years, which clearly justifies the interest in their reuse.

This paper presents experimental and prototype work that have resulted in polymer-based composites incorporating the aforementioned waste-rock tailings. The composites are capable of utilising the natural characteristics of the rock-wastes, particularly with respect to their finished appearance and visual impact.

A major outcome of this study is a methodology for incorporating recovered and waste-rock mine tailings into value-added products and applications. The trials discussed in this paper were restricted to materials sourced from Panasqueira mine, but the proposed methodology is equally applicable to other mining and guarry wastes and by-products.

It can be concluded from this work that aided by their colour and texture, coarse waste fractions from Panasqueira mining are highly suited for reuse in technical and artistic applications, namely sculpture and architecture, with no requirements for any special pre-treatment (e.g. grinding or heat-treatment). Furthermore, the colour of the wastes can be modified by heat-treatment and possibly via other process, e.g. chemically based, not described in this paper.

Taking into account their mechanical and physical characteristics, it is believed that there is a potential for the reuse of Panasqueira aged rock-wastes as new polymer-based construction materials in technical-artistic applications, particularly as terrazzo tiles for outdoor use, fulfilling CE marking requirements and in development of new polymer composites products make from the interception between the technological and artistic concept.

Finally, a key objective of this study was to offer a contribution towards environmental protection, particularly with respect to recovery and reuse of mining waste tailings in a context of a global concern to achieve sustainable development. It must be mentioned at this point that a fraction of the Panasqueira wastes, as might be the case of other mining wastes, contains high sulphide

concentrations and sulphide-related heavy metals. The current findings of this project, at this stage of time, cannot recommend the reuse of such contaminated fractions.

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