



Incorporation of sulphidic mining waste material in ceramic roof tiles and blocks

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ABSTRACT

The demand for building and construction materials increases as the world population keeps growing, thus increasing the need of shelter, as a basic human need. This increasing demand for building and construction materials not only leads to higher demand for primary raw materials, such as clay or sand, but also to higher emissions of carbon dioxide which contribute to the greenhouse effect leading us to the biggest and ongoing threat to life on earth: global warming. The potential use of secondary raw material sources, such as mining waste, in building and construction products not only minimises the ecological footprint of this sector but also minimises the pressure on the primary raw material sector, hence fostering the transition towards a more resource efficient and sustainable world. The goal of this study is to evaluate the potential use of uncleaned sulphidic mining tailing material from two inactive Zn—Pb (Plombières, Belgium) and Cu—Zn—Pb (Freiberg, Germany) mines, and uncleaned sulphidic mining waste rock material from an active Cu—Zn mine (Neves-Corvo, Portugal), in ceramic roof tiles and blocks taking into account production parameters (shaping, drying and firing processes), product quality (technical, aesthetical and chemical properties) and environmental compliance of secondary raw materials for use as building products. After a detailed physical, mineralogical, chemical and thermal characterisation of the materials, blends for ceramic roof tiles and blocks were made by partly or totally replacing some primary raw materials (mainly clay and sand) by 4 different mining waste materials. Roof tile and block blends containing 5 wt% and 10 wt% mining waste materials, respectively, were produced on a lab scale. The required technical, aesthetical and chemical properties for each ceramic product were evaluated. Freiberg tailing and Neves Corvo waste rock materials presented considerable amounts of sulphur and metal(loid)s. Moreover, technical, aesthetical and chemical properties of the blends using these mining waste materials were not satisfying and Neves Corvo waste rock materials have the disadvantage of needing a mechanical treatment (grinding and sieving) before integrating them into the ceramic blends. Therefore, the Freiberg tailing and both Neves Corvo waste rock materials are less suitable to replace primary raw materials in ceramic roof tile and block blends, even in smaller amounts (5 wt% and 10 wt%, respectively). In contrast, Plombières' fine tailing material was characterised by a low sulphur and metal(loid) content as well as satisfying environmental performance. The roof tile and block blends, in which Plombières tailing material was integrated, showed satisfying technical, aesthetical and chemical properties. Consequently, Plombières' tailing material can be considered as the best fit to partly or totally replace some primary raw materials in both ceramic roof tile and block blends.

1. Introduction

After construction and demolition waste (CDW), extractive waste is the largest waste stream in the EU. Extractive waste involves materials that must be removed to gain access to the mineral resource, such as topsoil, overburden and waste rock, and tailings, which are the remaining fraction after minerals have been largely extracted from the ore and processed (European Commission, n.d.) (Fig. 1). In 2016, extractive waste accounted for over a quarter (25.3%) of all the EU waste

streams, equivalent to around 600 Mt. of mining and quarrying waste generated in the EU-28 (Eurostat, n.d.).

Extractive waste, more precisely mining waste, can be divided into 3 different categories according to its risk to environment and health: hazardous, non-hazardous and non-inert, and non-hazardous and inert waste (Ecologic Institute, 2012). Non-hazardous and inert waste materials don't pose a significant threat to the environment and therefore they are used for smothering riverbeds or sold as an aggregate material for building and construction applications. However, hazardous (inert and non-inert) mining waste materials have a strong environmental

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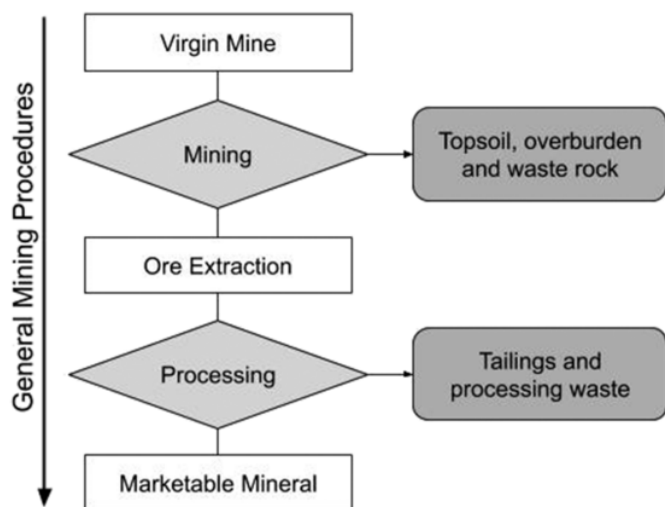


Fig. 1. Types of mining waste generated during mining procedures (adapted from BRGM, 2001)

footprint since they contain harmful substances, such as sulphur (S) and hazardous metal(loid)s (As, Cd, Pb and others). Through the extraction and subsequent mineral processing, metals and metal compounds tend to become chemically more available, which can result in the generation of acid or alkaline mine drainage, posing significant environmental and health hazards (European Commission, n.d.). Mining waste management often involves dealing with residual processing chemicals and elevated levels of metal(loid)s (European Commission, n.d.). In many cases mining waste is stored in large tailing dams and waste rock piles. The poor management of mining waste materials (by lack of waste treatment techniques and sustainable management practices) (Silva et al., 2013 & Candeias et al., 2015), as well as the collapse of dams and/or piles, such as the recent Brumadinho dam disaster in Brazil (Sznellar et al., 2019), can lead to serious environmental, human health and safety hazards (European Commission, n.d.).

Sulphidic Cu—Zn, Pb—Zn and Cu—Zn—Pb mining waste residues pose one of the largest challenges, as they can lead to acid mine drainage. Acid mine drainage takes place when sulphide-rich waste composed of sulphide minerals, such as pyrite (FeS_2), chalcopyrite (CuFeS_2), galena (PbS), sphalerite (ZnS) and arsenopyrite (FeAsS), is exposed to oxygen, water and micro-organisms (Park et al., 2019 & Rodríguez-Gálan et al., 2019), and oxidised through chemical, electrochemical and biological reactions, forming Fe(hydr)oxides and sulphuric acid (Candeias et al., 2014). Hazardous metal(loid)s and sulphates, which are leached at low pH, end up in soil and aquatic environments (Rodríguez-Gálan et al., 2019 & Candeias et al., 2014). Moreover, fine-grained mining waste materials, such as tailings, can lead to serious environmental and health hazards, not only because of their chemical content but also because of their physical properties. With strong winds, small tailings' particles can be transported, affecting the areas around the tailings (Salinas-Rodríguez et al., 2017).

Apart from the hazardous metal(loid)s, mining waste residues also can contain valuable base, precious and critical metals which can be used in different applications of emergent technologies, thus helping to close the materials loop. Nevertheless, the technological and economic limitations on the recovery of these secondary raw materials are, besides regulatory limitations, the major cause for the accumulation of these potential resources in tailing dams and waste rock piles over decades. In addition, a fraction of the mineral residue of these mining waste materials can contain considerable amounts of silicates and aluminosilicates, which can potentially be used in the ceramic industry and/or other industries. Using secondary raw material sources, not only minimises the pressure on the exhaustive primary raw material sector,

but also contributes to the sustainable supply of raw materials within the EU, and to a more resource efficient economy (European Commission, 2013).

Furthermore, the recycling and use of mining waste in raw-material-intensive applications is an interesting alternative for the expensive mine waste management and associated restoration efforts (Kinnunen et al., 2018). In sum, secondary sources like mining waste can supply not only the demand for metals but also boost recycling while minimising harmful waste, dissipation and associated hazards (Chung et al., 2019).

Regarding mining waste applications in traditional ceramic roof tiles, only a few studies were published. One of these studies, dealing with the use of hard rock dust from blasting and crushing processes (Maddhapara Hard Rock Mine), showed that the hard rock dust could be used as an alternative raw material (up to 40 wt%) in ceramic roof tiles without further need of glazing (Sultana et al., 2015). Other studies investigated the combination of kaolin processing waste and granite sawing waste (up to 50 wt%) in ceramic roof tiles. This combination gave better mechanical properties (rupture modulus) at lower sintering temperatures, compared to the use of kaolin processing waste only (Menezes et al., 2007).

Other published studies on mining waste applications in traditional ceramic inner wall blocks focus on the use of kaolin processing waste and granite sawing dust, which allowed to maximize the content of waste materials in ceramic blocks, while maintaining technical and mechanical properties (adequate water absorption and rupture modulus) (Menezes et al., 2007; Campos et al., 2007). Furthermore, ornamental rock waste mixed with clay showed satisfying physical and chemical results for the manufacturing of ceramic blocks (Cerqueira et al., 2016); while waste clay from coal preparation tailings showed acceptable mechanical and chemical properties at low additive ratios at higher sintering temperatures (Abi et al., 2011).

Several studies have also been performed concerning the use of mining waste in other ceramic applications, mainly in traditional ceramic bricks (Monteiro and Vieira, 2014; Boltakova et al., 2017). In fact, according to Wiegers and Sijbers-Wismans (1999), a case study in the Netherlands showed that it was possible to replace 30 wt% of clay by (washed and sieved) mining waste to produce an insulation brick. In this case study, the consumption of primary raw materials (clay) was reduced and the energy consumption during firing decreased due to the lower lime content of the mining waste. Moreover, mining waste (spodumene, $\text{LiAlSi}_2\text{O}_6$, ore tailings) integration in low-temperature ceramic bricks have shown compliance with product specifications (Lemougna et al., 2019a), promising sintering results as well as compliance with environmental regulations (Lemougna et al., 2019b). Mining tailings from Ag—Au exploitation have been used as feldspar substitutes to manufacture ceramic bricks, giving similar or better technical properties to that of a conventional brick (Salinas-Rodríguez et al., 2017).

Concerning traditional fine ceramics, the integration of boron-bearing sludge into ceramic (wall and floor) tiles showed the necessity to also integrate feldspathic rocks in order to minimise technical deficiencies (Zanelli et al., 2019); another study dealing with the integration of boron mining waste in ceramic (wall and floor) tiles has shown acceptable industrial standards (Cicek et al., 2018). Integration of tungsten tailings in ceramic (wall and floor) tiles at low sintering temperature has shown to be a cost-effective solution for producing high-strength ceramics (Wu et al., 2016). Analogously, silica-rich tailings from iron ore extraction can be incorporated for up to 40 wt% in ceramic (wall and floor) tiles (Das et al., 2000).

Besides the studies on traditional ceramic roof tiles, blocks, bricks and fine ceramics, the replacement of primary raw materials by mining waste has also been investigated for glass ceramics, by using silica-rich tailings (Kim and Park, 2020; Park and Park, 2017; Cetin et al., 2015; Arancibia et al., 2013); or Mg-rich tailings (Marabini et al.,

1998). Moreover, this proved to be a suitable solution to immobilise heavy metals in crystalline phases (Marabini et al., 1998).

The use of mining waste materials (spodumene, $\text{LiAlSi}_2\text{O}_6$, ore tailings) was also studied in high-performance ceramics, also called technical ceramics, and they have shown to achieve high mechanical performances and compliance with product specifications (Lemougna et al., 2020). Moreover, the use of spodumene tailings in porcelain ware, showed promising sintering results always comparable to the reference (Lemougna et al., 2019b).

The goal of the present study is to evaluate the potential use of uncleaned sulphidic mining tailing materials from two inactive Zn—Pb (Plombières, Belgium) and Cu-Zn-Pb (Freiberg, Germany) mines, and uncleaned sulphidic mining waste rock materials (fresh and stored) from an active Cu—Zn mine (Neves-Corvo, Portugal), in two different ceramic products (roof tiles and blocks), taking into account production parameters (shaping, drying and firing processes), product quality (technical, aesthetical, and chemical properties) and environmental compliance of secondary raw materials for use as building products. The use of mining waste materials (tailings and waste rock), without any pre-treatment (cleaning), in ceramics (roof tiles and blocks) has not been investigated before, and could offer an alternative to the use of primary raw materials in this sector.

2. Materials and methods

The materials used in this study consist of 4 different mining waste materials (2 tailing and 2 waste rock materials) and the raw materials used in the production of two different ceramic products: roof tiles (4 different raw materials) and blocks (6 different raw materials).

A detailed physical (moisture content, grain size distribution and specific surface), chemical (lime content, elemental composition, total carbon and sulphur, loss on ignition and soluble ions) and thermal (thermogravimetry and differential scanning calorimetry) characterisation was performed on all the materials. Moreover, a mineralogical characterisation by X-ray diffraction (qualitative XRD) and environmental compliance tests (total concentrations of metal(loid)s and organic compounds as well as column leaching tests) as described in the Flemish regulations on the sustainable management of material cycles and waste (VLAREMA, 2012), were performed on the four mining waste materials. These environmental compliance tests were performed in order to evaluate the potential use of the mining waste materials as raw material as building products.

After the full characterisation of the materials, 5 different ceramic mixtures were prepared for each ceramic product type:

- Ceramic roof tiles: 1 standard mixture (reference) and 4 mixtures using 5 wt% of mining waste.
- Ceramic blocks: 1 standard mixture (reference) and 4 mixtures using 10 wt% of mining waste.

The technical, aesthetical and chemical properties were assessed for all of the unfired and fired blends and compared to the standard.

2.1. Materials

2.1.1. Mining waste materials

The mining waste materials were sampled at two inactive Pb—Zn (Plombières, Belgium) and Cu-Zn-Pb (Freiberg, Germany) mines and one active Cu—Zn mine (Neves Corvo, Portugal).

The Plombières Pb—Zn mine (Eastern Belgium) was exploiting a Mississippi Valley Type (MVT) ore deposit (Evrard et al., 2015) from 1844 until 1882 (Sweneen et al., 1994). After closure of the mine, imported ores were still smelted at the Plombières site until 1922 (Dejonghe et al., 1993). The dumped material from the mining operations consists of red to black iron oxides, coal-rich black material, slag material, ash, Zn—Pb mining waste, bricks, ceramic pipes, old ceramic bricks and clay mixed with fine-grained dolomite ($\text{CaMg}(\text{CO}_3)_2$) sand

as a mineral dressing waste (Kucha et al., 1996). All this waste is stored in huge mine tailing dams, which are covered with soils and metallurgical waste, such as slags, from the processing plants. In total, approximately 11.4 Mt. of mining waste material is stored at the Plombières mining site (Helser and Cappuyns, 2021). The Plombières tailing material was sampled on-site through a hand excavated pit-hole and about 25 kg of material was taken from a yellow clayish layer (classified as yellow tailings) at 1.10 m depth (SUL_PL_62_I – Fig. 2), being the most prominent layer in this tailing dam, with a thickness of ± 5 m (Bevandić et al., 2021). Before sampling, the first meter of heterogeneous material (from appearance: soil, slag, black sand material, ceramic pipes, ceramic bricks, brown silt material and other remaining material) was removed.

The Freiberg Cu-Zn-Pb mine (Eastern Germany) exploited a hydrothermal polymetallic vein-type ore deposit (Seifert and Sandmann, 2006) from 1168 until 1969 (Fritz and Jahns, 2017). Mining waste materials, specifically from the Davidschacht tailing, which were deposited between 1951 and 1964, consist of a quartz (SiO_2) bearing ore with arsenopyrite (FeAsS), pyrite/marcasite (FeS_2), pyrrhotite (Fe_{1-x}S), Fe-rich sphalerite (ZnS), stannite ($\text{Cu}_2\text{FeSnS}_4$), chalcopyrite (CuFeS_2), cassiterite (SnO_2), tetrahedrite ($\text{Cu}_6(\text{Cu}_4\text{S}^{2+})\text{Sb}_4\text{S}_{12}\text{S}$), bornite (Cu_5FeS_4), and galena (PbS) (Redwan et al., 2012). Small amounts of carbonates (calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), siderite (FeCO_3) and rhodochrosite (MnCO_3)) can also be found in the main gangue mineral quartz (Seifert and Sandmann, 2006). The amount of this mine tailing is estimated at 1.3 Mt. (GEOS, 1993). At the Freiberg Cu-Zn-Pb mining site, tailing material (SUL_FR_01 - Fig. 2) from the first meter of the Davidschacht tailing dam was sampled on-site using a digger. A subsample of around 7 kg was brought to Belgium in a sealed bag.

The Neves Corvo Cu—Zn active mine (Southern Portugal) is exploiting a heterogeneous Volcanogenic Massive Sulphide (VMS) type ore deposit (Wardell Armstrong International, 2017), which is located within the western part of the world-class Iberian Pyrite Belt. It started its underground exploitation in 1982 (Wardell Armstrong International, 2017) and the production started at the end of 1988 (Real and Franco, 1990). This waste rock material is used in the Tailings Management Facility (“Instalação de Resíduos do Cerro do Lobo”) for the construction of contention berms for a deposit of thickened tailings and for the first layer of final cover, a process known as co-deposition. The final cover of the deposit is a multilayer and low flux cover, consisting of a capillary break, clean rock and topsoil, on the top of the waste rock layer (Wardell Armstrong International, 2017). In the last 10 years (2010–2019) the total amount of fresh waste rock material (SUL_NC_01) produced was 5.6 Mt. After being hoisted from underground mining operations, the waste rock material can be either transported to the Tailings Management Facility (TMF) or temporarily stored in a waste rock pile, exposed to weathering, turning into an oxidised stored waste rock material. At the end of 2019, there was 3.1 Mt. of stored waste rock material (SUL_NC_03) available, and 7.1 Mt. that has been used, during the last 10 years (2010–2019), for the TMF vertical expansion, which is indirectly available. At Neves Corvo Cu—Zn mine, these two waste rock materials were sampled on-site, the fresh waste rock (SUL_NC_01) from the hoisted rock and the stored waste rock (SUL_NC_03) from an open-air waste rock pile storage (Fig. 2). Around 50 kg of each waste rock material was shipped to Belgium in sealed containers.

According to the European List of Waste (European Commission, 2014), both Plombières and Freiberg tailing materials can be classified as “acid-generating tailings from processing of sulphide ore” (code 01 03 04*) and both Neves Corvo waste rock materials (fresh and stored) used in this study can be classified as “wastes from mineral metalliferous excavation” (code 01 01 01). Any waste with asterisk (*) in the list of wastes shall be considered as hazardous waste pursuant to Directive 2008/98/EC (European Commission, 2008), unless Article 20 (Hazardous waste produced by households) of that Directive applies.



Fig. 2. Overview of the materials used to produce the ceramic mixtures after necessary pre-treatment.

2.1.2. Company's raw materials

For the production of the company-specific blend for clay roof tiles (Pottelberg plant, Belgium) 3 different primary raw materials (local clay, local sand and imported clay) and 1 secondary raw material (imported filler G, which is a by-product from an industrial grinding activity of natural stone processing) were used (Fig. 2). Local clay and local sand were collected from local quarries and the imported clay and imported filler were collected from the Pottelberg production plant storage.

For the production of a company-specific blend for inner wall blocks (Zonnebeke plant, Belgium) 5 different primary raw materials (local clay, regional sand, regional filler, imported filler B and imported filler R) and 1 waste material (imported waste, which is a by-product of the paper industry) were used (Fig. 2). Local clay was collected from a local quarry and all the other materials were collected from the Zonnebeke production plant storage.

2.1.3. Modified blends for clay roof tiles and inner wall blocks

The company-specific blend for clay roof tiles (PM: Pottelberg Mixture) was modified on lab scale, by partly replacing 2 primary raw materials (local clay and local sand) by 4 different mining waste materials (SUL_PL_62_I, SUL_FR_01, SUL_NC_01 and SUL_NC_03). Knowing in advance that we were dealing with sulphidic mining waste we only introduced 5 wt% of waste in the standard roof tile blend, as high sulphidic and sulphuric contents can cause drying and/or firing efflorescence on the ceramic test pieces. The aesthetical aspect of ceramic roof tiles is an

important feature, therefore limiting the sulphur, sulphides and/or sulphates is recommended.

The company-specific blend for inner wall blocks (ZM: Zonnebeke Mixture) was also modified on lab scale, by completely replacing 1 primary raw material (local sand) and partially replacing 1 of the fillers (imported filler R) by 4 different mining waste materials (SUL_PL_62_I, SUL_FR_01, SUL_NC_01 and SUL_NC_03). As the aesthetical aspect is less relevant for inner wall blocks, 10 wt% of mining waste was introduced in the standard block blend.

These new unfired blends were subjected to the same physical, chemical and thermal characterisation as the mining waste materials and company-specific raw materials.

2.2. Methods

2.2.1. Pre-treatment, physical, chemical and thermal characterisation of materials

2.2.1.1. Pre-treatment All of the collected materials were kept in appropriate sealed containers and transported safely to the laboratory. They were all dried overnight at 105 °C in a ventilated drying stove (Heraeus UT 6060). Once dried, the Neves Corvo waste rock materials (SUL_NC_01 and SUL_NC_03) and the clays used in the ceramic roof tiles (local clay and imported clay) and in the blocks (local clay) were grinded by using a shredding machine (Hosokawa-Alpine MZ-25). The grain size of the Neves Corvo waste rock materials was reduced (<1.4 mm) as the received material was far too coarse to be used as such in the ceramic mixtures. The clays were shredded as this facili-

tates their integration into the ceramic mixtures. This process doesn't change the original grain size distribution of these clays at all. In the same way, once dried, 3 company-specific raw materials used in the ceramic blocks (regional filler, imported filler R and imported filler B) were grinded using a jaw crusher machine (Retsch BB 200) and sieved at < 1.4 mm, as this process is comparable to what is used for the industrial production. The local and regional sands, the imported filler G as well as the tailing materials from Plombières (SUL_PL_62_I) and Freiberg (SUL_FR_01), were fine enough and did not receive a mechanical pre-treatment. For physical, mineralogical, chemical and thermal sample characterisation, the pre-treated samples were homogenised and a representative sample was, if necessary, grinded (Morgan Advanced Materials porcelain mortar and pestle) and sieved (Retsch sieves) at < 2 mm, < 250 µm, < 200 µm and < 180 µm, depending on the intended analysis. For the environmental compliance tests, performed by an accredited laboratory, sample pre-treatment was performed according to CMA/5/B.3 method (CMA, 2020), and included grain-size reduction (< 4 mm, 95 wt%) with a jaw crusher machine and split divider. The analysis of water content and dry residue was done according to the CMA/2/II/A.1 method (CMA, 2020).

2.2.1.2. Physical characterisation The moisture content from the materials, expressed in wt% on wet, was determined on the samples as received. For this purpose, samples were dried overnight in a ventilated drying stove (Heraeus UT 6060) at 105 °C. Grain size distribution analysis was performed on the representative samples sieved at < 2 mm. Wet sieving on a 50 µm sieve splits the sample in two fractions. The fraction < 50 µm was further analysed by the sedigraph sedimentation method (Pye and Blott, 2004) using a Micromeritics SediGraph 5100 machine, while the > 50 µm fraction was analysed, after drying, on a mechanical shaking sieve column with sieves ranging from 1.4 to 0.09 mm (Retsch AS 200 control). The specific surface area (SSA) was determined by methylene blue adsorption (Hegyési et al., 2017) on grinded and sieved (< 250 µm) samples.

2.2.1.3. Mineralogical characterisation The qualitative mineralogical composition was determined by X-ray powder diffraction (XRD) using a diffractometer (Philips Analytical X-ray, model PW1830 generator with a PW3710 mpd control) with CuK α radiation and 30 mA based on the Rietveld method. Sample preparation included mixing 1.8 g of powdered sample (< 180 µm) with addition of 0.2 g of zincite (ZnO) powder as standard. For mineral identification the Profex software (version 3.14.3) was used.

2.2.1.4. Chemical characterisation The total elemental composition analyses were performed on the powdered samples (< 250 µm) by X-ray fluorescence (XRF) spectrometry (Panalytical Axios-Minerals, using superQ software with Omnia module) using beads prepared with C₆H₈O₇ and LiBr solutions for major elements, and by inductively coupled plasma optical emission spectrometry (ICP-OES Varian Vista MPX) after HNO₃/HClO₄/HF digestion for trace elements (mainly for Ba, Cr, Cu, Ni, Pb and Zn). The total carbon and sulphur content was analysed by a non-dispersive infra-red (NDIR) analyser (Leco SC632) by firing the powdered samples (< 250 µm) at 1450 °C, according to the standard ISO 10694:1995. During preparation of the beads for XRF analysis, some sulphur can be volatilised, therefore the measurements done by NDIR are considered more precise. Lime content was determined by titration of CO₂ from the decomposed carbonates of the powdered samples (< 250 µm) using a Mettler Toledo T70 and Phototrode DP5, with N-N-dimethylformamide, ethanolamine and thymolphthalein as absorbents, and 0.1 N tetrabutylammonium hydroxide solution as titrans. Subtracting the inorganic C (calculated from the CO₂ content by titration) from the total C (determined with NDIR) gives the organic C. To determine the gross loss on ignition (LOI), samples were fired at 1000 °C, based on the standard NBN EN 15935:2012. Soluble anions (SO₄²⁻) were measured on the powdered samples (< 250 µm) by Ion chromatography (Metrohm 761 Compact IC), according to the standard NBN EN ISO 10304-1:2009. For the sulphidic mining waste material the standard L/S ratio of 3 l/kg was changed as we expected high

amounts of soluble sulphates. Initially all samples were diluted at L/S = 8.3 l/kg, but even further dilutions were necessary for Neves Corvo fresh waste rock (SUL_NC_01) sample (L/S = 30 l/kg) and for both Freiberg tailing (SUL_FR_01) and Neves Corvo stored waste rock (SUL_NC_03) samples (L/S = 100 l/kg). Inductively coupled plasma optical emission spectrometry (ICP-OES Varian Vista MPX) was used to analyse soluble cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺). For both analyses, samples were prepared by refluxing with distilled water for 6 h.

2.2.1.5. Thermal characterisation Thermogravimetry and Differential Scanning Calorimetry (TG-DSC) were performed using a Netsch STA 449 F3 machine, by firing the powdered samples (< 200 µm) at 1050 °C in a platinum crucible, under oxidising conditions.

2.2.1.6. Environmental compliance TESTS For the environmental compliance tests regarding the possible use of waste materials as building products in Flanders (Belgium), a sequence of analyses were performed on the mining waste materials according to VLAREMA (2012) regulations. As aforementioned these analyses were performed by an accredited laboratory. After sample digestion, concentrations of metal(loid)s (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn) were determined by inductively coupled plasma mass spectrometry (ICP-MS) according to method CMA/2/I/B.5 (CMA, 2020) following the ISO 17294-2:2003 standard. Total concentrations of organic compounds were measured by HS-GC-MS according to method CMA/3/E (CMA, 2020) for aromatics (benzene, toluene, ethylbenzene and xylenes), styrene, hexane, heptane and octane; by GC-FID according to method CMA/3/R.1 (CMA, 2020) for mineral oil; by GC-MS for Polychlorinated Biphenyls (PCB) according to method CMA/3/I (CMA, 2020) and for Polycyclic Aromatic Hydrocarbons (PAHs) according to method CMA/3/B (CMA, 2020). The column leaching test (L/S_{cum} = 10 l/kg, 7 fractions) was performed according to method CMA/2/II/A.9.1 (CMA, 2020) following the NEN 7373:2004 standard. This test aims to simulate the flow of percolating groundwater through a porous bed of granular material (Siddique et al., 2010). Finally, element concentration in the leachates was determined by ICP-MS, according to method CMA/2/I/B.5 (CMA, 2020) following the ISO 17294-2:2003 standard. The main criteria for the certification of waste as raw material intended for use as a building product need to comply with the following points (VLAREMA, 2012):

1. The maximum total concentrations of organic compounds cannot exceed the VLAREMA limit values (Appendix A). If the total concentrations exceed the limit values of organic compounds, the material can never be declared as raw material and keeps the status of waste;
2. The maximum total concentrations of metal(loid)s (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn) are guidance values (Table 4). If the total concentrations exceed the limit values for free use of excavated soil (Annex V of VLAREBO, 2008) the leachability has to be determined (column test for non-shaped building products and diffusion test for shaped building products);
3. The maximum leachability values (column test) of metal(loid)s in the waste material for use in or as non-shaped building product should not exceed the VLAREMA limit values (Table 4). If these limit values are not exceeded, the waste material can be considered as raw material for use in or as non-shaped building product (e.g.: cover layer, earth-rock filled dams). In case of deviating leachability, specific weight and intended application height, the calculated immission limit values of the waste material must comply with VLAREMA immission limit values (Annex 2.3.2.C of VLAREMA, 2012);
4. The leachability values (diffusion test) of metal(loid)s in the shaped building products, in which the waste material is used, must comply with VLAREMA immission limit values (Annex 2.3.2.C of VLAREMA, 2012).

In summary, when the total concentrations of organic compounds are below the VLAREMA limit values and the total concentrations of metal(loid)s are higher than the guidance values, the waste materials

can still get the status of “raw material” (also referred to as “end of waste status”) if the building product itself complies with the leachability limit values after the diffusion test for shaped products, or with the leachability limit values after the column test for non-shaped products. In the present study, only the mining waste materials were tested (total concentrations of metal(loid)s and organic compounds, and leaching with a column test). The environmental compliance of shaped building products with mining waste incorporation will be investigated in a follow-up study.

2.2.2. Preparation of ceramic blends

After characterisation of the company-specific raw materials and mining waste materials, new blend compositions were calculated (Table 1) using 5 wt% of mining waste for the roof tile blends and 10 wt% for the block blends. For these test mixtures special attention was given to the > 50 µm fraction, knowing that too high sieve residues (> 50 µm) affect not only aesthetic but also technical properties. The standard roof tile and block blend were used as reference.

For each blend, the right amount of each material was weighed, as well as the estimated quantity of water to be added. In order to have a favourable plasticity, the roof tile mixtures needed around 16 wt% of water content, while the block mixtures needed around 18 wt%.

For the lab preparation of roof tile and block test specimens (Fig. 3), the following general procedure was followed:

1. Initial hand-mixing: started by gradually mixing by hand, clays, sand, fillers and waste materials with the addition of small amounts of water. 0.5 wt% of BaCO₃ was added to every roof tile mixture to fix the soluble sulphates, thus preventing drying efflorescence;

2. Mixing machine: subsequently, the mixture went twice through a mixing machine for additional homogenisation (two different grid sizes were used). Plasticity was checked and, if necessary, adjusted;
3. Vacuum extruder: the homogeneous mixture was extruded under vacuum conditions using an extruder machine with a 58 × 16 mm die;
4. Wet test specimens: after vacuum extrusion, 12 wet test pieces per mixture are cut at a length of around 116 mm. Each wet test piece receives a unique identification code and is marked using a caliper (100 mm mark) in order to calculate its drying and firing shrinkage.

The shaping of the blends and the drying and firing behaviour of the vacuum extruded test pieces were assessed on lab scale and compared with the behaviour of the standard. The required technical (plasticity, drying and firing shrinkage, water absorption and modulus of elasticity), aesthetic (firing colour and efflorescence) and chemical (total carbon and sulphur, and soluble ions) properties were evaluated.

2.2.3. Technical, aesthetic and chemical properties of the vacuum extruded test specimens

2.2.3.1. Technical properties The plasticity of the wet mixtures was measured according to the Pfefferkorn (Pfef) method (Andrade et al., 2011). The moisture content of the wet mixtures was determined after drying the mixtures overnight at 105 °C in a ventilated drying stove (Heraeus UT 6060), and expressed in wt% on wet. The drying behaviour of the wet test specimens (speed of weight loss, drying shrinkage, drying efflorescence and appearance of cracks) was studied and compared to the standard on lab scale. For that purpose, some of the test specimens were submitted to different drying programmes using a climate test chamber (Vötsch VC3 4060 with SIMPATI® software). The different drying programmes are characterised by different tempera-

Table 1
Composition (dry weight %) of ceramic mixtures for roof tiles (A) and blocks (B).

A Roof tile mix	Local clay	Local sand	Imported clay	Imported filler G	Additive (BaCO ₃)	SUL_PL_62_I	SUL_FR_01	SUL_NC_01	SUL_NC_03	TOTAL ^a	
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	
SUL_PM_1	31.0	28.0	24.0	17.0	0.5					100.5	
SUL_PM_2	27.0	27.0	24.0	17.0	0.5	5.0				100.5	
SUL_PM_3	31.0	23.0	24.0	17.0	0.5		5.0			100.5	
SUL_PM_4	31.0	23.0	24.0	17.0	0.5			5.0		100.5	
SUL_PM_5	31.0	23.0	24.0	17.0	0.5				5.0	100.5	
B Block mix	Local clay	Imported filler B	Regional filler	Imported filler R	Imported waste	Regional sand	SUL_PL_62_I	SUL_FR_01	SUL_NC_01	SUL_NC_03	TOTAL
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
SUL_ZM_1	44.8	19.3	16.6	11.4	2.3	5.6					100.0
SUL_ZM_2	44.8	19.3	16.6	7.0	2.3		10.0				100.0
SUL_ZM_3	44.8	19.3	16.6	7.0	2.3			10.0			100.0
SUL_ZM_4	44.8	19.3	16.6	7.0	2.3				10.0		100.0
SUL_ZM_5	44.8	19.3	16.6	7.0	2.3					10.0	100.0

^a BaCO₃ (0.5 wt%) was added on top of each roof tile mixture.

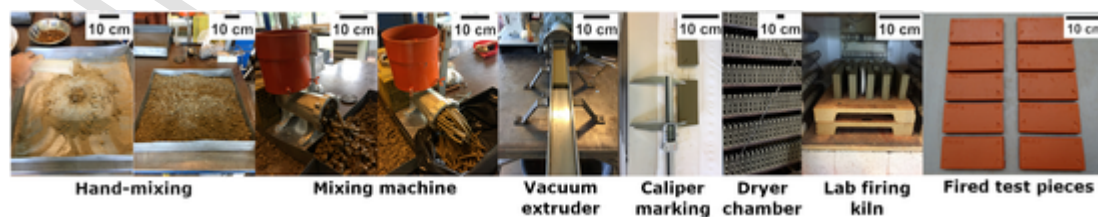


Fig. 3. Production of roof tile and block test specimens (preparation, drying and firing).

tures and different relative humidity. Per programme, one wet test piece per blend was studied. The other wet test pieces were dried, all together, in an industrial drying chamber (60 h of drying time with a max. Temperature of 65 °C). The drying shrinkage was measured and compared to the standard. The industrial dried test pieces were then fired in electric lab kilns (Fours H&C SPRL, Type 25 and 100) at 985 °C and 1000 °C, at a speed of 90 °C/h and dwell time of 1 h, for the roof tile blends and at 965 °C, at a speed of 23 °C/h and dwell time of 30 min, for the block blends. The firing shrinkage of all the fired test specimens was measured and the total shrinkage was calculated and compared to the standard. In addition, water absorption, using different methods, was determined for the fired test specimens. For roof tiles a progressive water immersion test (E_{prog}) and a full vacuum water immersion test (E_{fullvac}) are common, while for blocks a 24 h water immersion test ($E_{24\text{h}}$) is the standard. The saturation level (ratio between E_{prog} and E_{fullvac} , expressed in percentage), which is an important parameter in the prediction of the frost resistance for roof tiles, was also calculated. For blocks this is not an important parameter as they are used in protected masonry. Finally, the modulus of elasticity, E -modulus, was determined on the fired test specimens by a non-destructive method based on the impulse excitation technique (ASTM E1876-15 standard) using a J.W. Lemmens GrindoSonic machine, model MK5 Industrial, with a frequency between 20 Hz to 100 kHz. This instrument measures the transient natural vibration of a test object after a light mechanical impulse, which results in a highly accurate measurement of the natural frequency (J.W. Lemmens, 2004). The E -modulus (GPa) was calculated using the software GEN-EMOD, as well as the dimensions (length, height and width), weight and natural vibration (R value, expressed in μs) of the fired test specimens.

2.2.3.2. Aesthetical properties Drying efflorescence on dried test specimens was studied after industrial drying and during the drying behaviour tests in the lab climate test chamber (Vötsch VC3 4060 with SIMPATI® software). The fired test specimens underwent an in-house efflorescence test in order to assess the sensibility to efflorescence of each blend, for different firing temperatures. In this test, pieces were laid horizontally (roof tiles) or vertically (blocks) in around 5 mm of demineralised water. Water enters the fired body by capillarity. If salts are present they migrate together with the water to the drying surface. After 3 days the test pieces were dried at 50 °C in a ventilated stove (Heraeus UT 6060). This process was repeated 3 times and, finally, the pieces were dried overnight at 105 °C in a ventilated stove (Heraeus UT 6060). The firing colour of all fired test specimens were visually compared to the standard.

2.2.3.3. Chemical properties The elemental composition of the unfired (major and trace elements, total carbon and sulphur) and fired (total carbon and sulphur) blends was analysed by the same methods used for the mining waste and company-specific raw materials (see 2.2.1.4). The soluble anions (especially SO_4^{2-}) and soluble cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) in the unfired and fired blends were analysed by the same methods used for the chemical characterisation of the mining waste and company-specific raw materials (see 2.2.1.4). For both analyses, samples from the unfired blends (dried, grinded and sieved at $<250 \mu\text{m}$) were refluxed with distilled water during 6 h ($L/S = 3 \text{ l/kg}$), while the fired blend samples (also dried, grinded and sieved at $<250 \mu\text{m}$) were shaken in distilled water for 1 h at 120 strokes/min ($L/S = 10 \text{ l/kg}$).

3. Results and discussion

3.1. Characterisation of the mining waste materials

The results of the physical and chemical characterisation of each mining waste material and the company-specific raw materials that were replaced in roof tile and block blends, are presented in Table 2.

Plombières tailing (SUL_PL_62_I) is a fine grained material (86 wt% $<50 \mu\text{m}$), whereas Freiberg tailing (SUL_FR_01) is somewhat coarser

(48 wt% $<50 \mu\text{m}$). The grain size distribution of the Neves Corvo waste rock samples was determined after shredding, as they were too coarse to integrate as such in the ceramic blends. Even though both waste rock materials were shredded, they still showed a coarser fractions ($>50 \text{ wt\%}$ 1400–200 μm). Being a fine material makes Freiberg tailing, but especially Plombières tailing, a potential suitable fit for the roof tile blends, as the desirable maximum grain size for this company-specific roof tile blend is around 300 μm , as shown in the standard roof tile mix SUL_PM_1 (Table 5). As the maximum grain size for the company-specific block blend used in this study can be up to 1 mm (standard block mix SUL_ZM_1 in Table 6), all mining waste materials could be used for this company-specific block blend.

The moisture content (MC) of the Plombières and Freiberg tailing materials, as received, is very similar and around 16 wt% (Table 2). The MC of the Neves Corvo waste rock materials is low ($<10 \text{ wt\%}$) and, most probably, their differences are related the nature of the material and the way of storing them.

The Plombières tailing material has the highest specific surface area (SSA). The Plombières tailing also has the highest fine fraction ($<2 \mu\text{m}$), which it is often composed of clay minerals. Clay minerals tend to have a high SSA (Tournassat et al., 2015). The other studied mining waste materials (Freiberg and Neves Corvo), having less $<2 \mu\text{m}$ fraction, show low SSA values. Nevertheless, the Neves Corvo stored waste rock material (SUL_NC_03) has a somewhat higher SSA when compared to the fresh waste rock material (SUL_NC_01), most probably due to its higher $<2 \mu\text{m}$ fraction (23 wt%).

The XRD qualitative results (Table 3) showed that all the studied mining waste materials are mainly composed of quartz and phyllosilicates (e.g.: muscovite $\text{KAl}_2(\text{F}, \text{OH})_2$, or $(\text{KF})_2(\text{Al}_2\text{O}_3)_3(\text{SiO}_2)_6$) and chlorite). Moreover, Plombières tailing (SUL_PL_62_I) showed the presence of feldspar (e.g.: plagioclase) and an amorphous phase (probably metallurgical slag – Helser and Cappuyns, 2021). Freiberg tailing (SUL_FR_01) showed the presence of pyrite, carbonates (e.g.: siderite) and sulphates (e.g.: gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Concerning Neves Corvo waste rock samples, the fresh waste rock sample (SUL_NC_01) showed the presence of Fe-bearing minerals (pyrite and siderite); while the stored waste rock sample (SUL_NC_03) presented not only pyrite, but also feldspar (e.g.: plagioclase) and common weathered sulphate minerals (e.g.: gypsum and jarosite).

The Plombières tailing material has a very low carbon (0.1 wt% C) and sulphur (0.01 wt% S) content when compared to the other mining waste materials, with the Freiberg tailing material having the highest carbon (0.8 wt% C) and sulphur (9.6 wt% S) content, followed by Neves Corvo fresh (0.7 wt% C and 6.8 wt% S) and stored (0.5 wt% C and 4.5 wt% S) waste rock material. The high S content makes the Freiberg tailing and Neves Corvo waste rock materials less favourable for use in ceramics as they most probably will cause high SOx emissions, as well as soluble sulphates, which can lead to efflorescence formation.

The very high loss on ignition (LOI) values of the Freiberg and the Neves Corvo materials (Table 2) are related to the high total C and S contents. The high LOI of the Neves Corvo stored waste rock material (14.9 wt%) is, most probably, due to the presence of weathered sulphate minerals (e.g.: gypsum and/or jarosite) - Table 3. The DSC curve of SUL_NC_03 shows an endothermic peak at around 100 °C and the TG curve shows a progressive initial weight loss up to 250 °C (Fig. 4), which can indicate the water release from the weathered minerals (e.g.: gypsum). Fig. 4 also shows an exothermic peak of pyrite (FeS_2) decomposition at around 460 °C (Labus, 2017), as well as the apparent difference in pyrite content between Neves Corvo fresh and stored waste rock.

The Plombières tailing material has the lowest lime content (0.07 wt% CaCO_3), and the Freiberg tailing material the highest (6.68 wt% CaCO_3). A high lime content, especially when it is a coarse grained lime, can cause lime pits after firing. This happens when free

Table 2

Physical properties and chemical composition of mining waste materials (A) and replaced company-specific raw materials (B).

A Mining waste material	1400-1000 μm	1000-200 μm	200-50 μm	50-2 μm	< 2 μm	MC*	SSA	CaCO ₃	CO ₂ carbonates	C _{total}	C _{organic}
	wt%	wt%	wt%	wt%	wt%	wt%	m ² /g	wt%	wt%	wt%	wt%
SUL_PL_62_I	3	3	8	47	39	15.6	93	0.1	0.03	0.1	0.1
SUL_FR_01	1	5	46	35	13	15.8	16	6.7	2.9	0.8	0.03
SUL_NC_01	12	58	11	9	10	5.1	12	3.2	1.4	0.7	0.3
SUL_NC_03	8	45	13	11	23	8.9	36	0.1	0.1	0.5	0.5
A Mining waste material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	MnO	LOI	S _{total}
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
SUL_PL_62_I	74.0	12.0	4.3	0.9	0.6	0.9	1.1	2.4	0.2	3.3	0.01
SUL_FR_01	32.1	4.4	20.0	0.3	1.1	0.6	<LOD	1.3	0.4	14.2	9.6
SUL_NC_01	42.9	12.0	17.1	0.6	0.5	1.7	<LOD	2.1	0.2	9.3	6.8
SUL_NC_03	39.2	10.9	15.8	<LOD	1.8	1.4	<LOD	2.7	<LOD	14.9	4.5
A Mining waste material	Ba	Cr	Cu	Ni	Pb	Zn	Soluble SO ₄ ²⁻	Soluble Ca ²⁺	Soluble Mg ²⁺	Soluble Na ⁺	Soluble K ⁺
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	wt%	mg/kg	mg/kg	mg/kg	mg/kg
SUL_PL_62_I	366	60	23	31	30	137	0.01	52	5	13	22
SUL_FR_01	158	34	858	68	5143	14,686	3.2	7616	1123	28	63
SUL_NC_01	306	59	2226	47	797	3725	1.1	3727	265	390	166
SUL_NC_03	420	56	7039	53	614	1890	7.3	11,185	3493	35	24
B Company-specific raw material	1400-1000 μm	1000-200 μm	200-50 μm	50-2 μm	< 2 μm	MC*	SSA	CaCO ₃	CO ₂ carbonates	C _{total}	C _{organic}
	wt%	wt%	wt%	wt%	wt%	wt%	m ² /g	wt%	wt%	wt%	wt%
Local clay	0	0	1	43	56	26.5	241	1.5	0.7	0.5	0.3
Local sand	0	11	85	4	0	13.8	23	0.1	0.03	0.02	0.01
Regional sand	0	89	11	0	0	3.1	23	0.1	0.03	0.01	0.001
Imported filler R	18	48	12	8	14	10.0	72	1.6	0.8	0.4	0.2
B Company-specific raw material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	MnO	LOI	S _{total}
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Local clay	60.9	15.7	6.7	0.9	1.0	2.1	0.5	3.2	<LOD	7.3	0.6
Local sand	96.1	1.1	1.1	0.1	0.1	0.1	<LOD	0.6	<LOD	0.6	<LOD
Regional sand	99.2	0.3	0.1	<LOD	<LOD	<LOD	<LOD	0.1	<LOD	0.2	<LOD
Imported filler R	58.1	21.1	6.4	1.0	0.7	1.8	0.6	3.9	0.0	5.9	0.03
B Company-specific raw material	Ba	Cr	Cu	Ni	Pb	Zn	Soluble SO ₄ ²⁻	Soluble Ca ²⁺	Soluble Mg ²⁺	Soluble Na ⁺	Soluble K ⁺
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	wt%	mg/kg	mg/kg	mg/kg	mg/kg
Local clay	290	120	21	53	19	94	0.2	353	48	579	509
Local sand	91	39	7	11	8	16	0.01	97	36	8	211
Regional sand	43	2	5	1	7	7	0.01	22	3	23	19
Imported filler R	154	103	45	62	11	103	0.1	274	9	333	434

<LOD: below the limit of detection.

All analyses were performed on pre-treated samples, except for MC (*) that was performed on samples as received.

Table 3

Mineralogical composition of mining waste materials (qualitative XRD method).

Mining waste material	Mineral						
	Quartz	Phyllosilicates	Feldspar	Carbonates	Pyrite	Sulphates	Amorphous
SUL_PL_62_I	+++	++	++				++
SUL_FR_01	+++	+++		++	++	+	
SUL_NC_01	+++	+++		++	++		
SUL_NC_03	+++	+++	++		++	++	

+++ major components; ++ minor components; + traces.

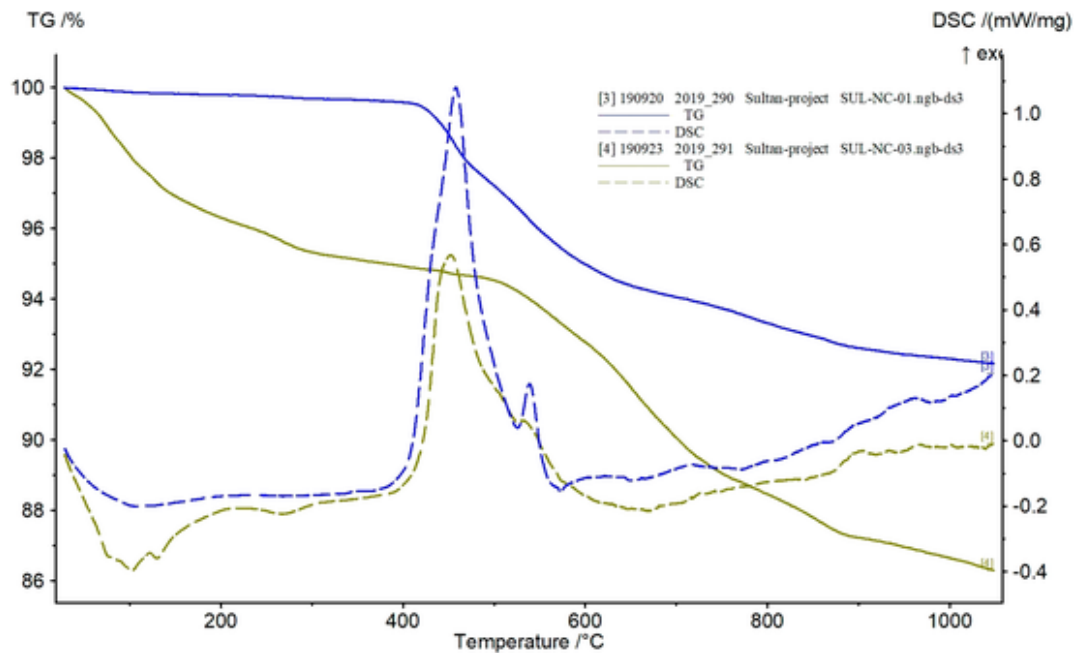


Fig. 4. TG-DSC curves of Neves Corvo waste rock materials (SUL_NC_01 and SUL_NC_03).

CaO reacts with the air moisture and CO₂, forming respectively Ca(OH)₂ and at a later stage CaCO₃, resulting in a volume expansion and lime pits may occur (Ruiz-Agudo et al., 2013).

The important amounts of Si and Al in the Plombières tailing material (Table 2) are in line with mineralogical results, as the material is mainly composed of quartz, phyllosilicates (e.g.: muscovite) and feldspars (e.g.: plagioclase). The presence of high Fe and total sulphur content (S_{total}) in the other mining waste materials can be linked to the occurrence of the iron sulphide mineral, pyrite.

ICP-OES results for trace elements show that the Plombières tailing sample is very poor in Cu (23 mg/kg), Pb (30 mg/kg) and Zn (137 mg/

kg). The tailing material from Freiberg still contains considerable amounts of Zn (14,685 mg/kg) and Pb (5142 mg/kg) and some Cu (858 mg/kg), while the Neves Corvo samples are rich in Cu and Zn (2226 mg/kg Cu and 3724 mg/kg Zn in the fresh waste rock sample, 7039 mg/kg Cu and 1890 mg/kg Zn in the stored waste rock sample).

The soluble sulphate content in the Plombières tailing material is very low. High concentrations of soluble sulphates were found in the samples from Freiberg and Neves Corvo. As the stored waste rock sample from Neves Corvo is a weathered material, the soluble sulphate content amounts 7.3 wt%, which is half of the total sulphur content in this sample.

Table 4

Total materials compared with limit values from elements leached during the column leaching test (B) compared with guidance and limit values from Flemish environmental regulations.

A								
Total element concentration								
Mining waste material	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Guidance values (VLAREMA, 2012 ^a)	250	10	1250	375	5	250	1250	1250
Limit values (VLAREBO, 2008 ^b)	35	1.2	91	72	1.7	48	120	200
SUL_PL_62_I	10	0.6	51	14	<0.10	24	29	87
SUL_FR_01	6300	150	35	890	0.15	23	5100	15,000
SUL_NC_01	970	9.9	49	2000	6	32	800	3600
SUL_NC_03	1000	3.4	50	5200	5	33	480	1700
B								
Element concentration leached during column leaching test (cumulative release)								
Mining waste material	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Limit values (VLAREMA, 2012 ^c)	0.8	0.03	0.5	0.5	0.02	0.75	1.3	2.8
SUL_PL_62_I	0.04	0.001	0.065	0.05	0.0004	0.05	0.05	0.18
SUL_FR_01	0.46	29	0.02	<2.6	0.0004	5	2.5	2600
SUL_NC_01	0.12	0.0037	0.03	0.047	0.00039	0.055	0.046	0.62
SUL_NC_03	0.7	0.99	0.31	1200	<0.00084	8.5	0.12	530

^a Values according to the Flemish environmental regulations VLAREMA (2012) Annex 2.3.2.A.

^b Values according to the Flemish environmental regulations VLAREBO (2008) Appendix V.

^c Values according to the Flemish environmental regulations VLAREMA (2012) Annex 2.3.2.B.

The environmental compliance tests were performed to check the possible use of waste materials as building products, according to the procedures described in the Flemish regulations (VLAREMA, 2012). Table 4 shows the results for the total concentrations of metal(loid)s as well as the metal(loid) concentrations from the leachates of the column test and the total concentrations of organic compounds are given in Appendix A.

None of the mining waste materials exceeded the limits for organic compounds stipulated in the Flemish environmental regulations (Appendix A). For the total metal(loid) concentrations (for As, Cd, Cr, Cu, Ni, Zn and Pb), only Plombières tailing material (SUL_PL_62_I) stays below the guidance values for the total concentration of metal(loid)s (VLAREMA, 2012) and even below the limit values for free use of excavated soil (VLAREBO, 2008) (Table 4). This means that Plombières tailing material, without the need for an additional column leaching test, can be used in or as non-shaped building product (e.g. cover layers, river beds, earth-rock filled dams, etc.). The results of the column leaching test, performed on all the mining waste materials, showed that besides SUL_PL_62_I also SUL_NC_01 stayed below the VLAREMA limit values (Table 4), which means that Neves Corvo fresh waste rock material (SUL_NC_01) can also be used in or as non-shaped building product (e.g. cover layers, river beds, earth-rock filled dams, etc.). All mining waste materials are below the limits for organic compounds, which means that they are still possible candidates to get a “raw material declaration”. They can be used in or as a shaped building product (e.g. roof tile and block) and in or as a non-shaped building product (e.g. aggregate and composite) if the final product itself does not exceed the immersion limit values (Annex 2.3.2.C of VLAREMA, 2012) after the column (for non-shaped products) or diffusion (for shaped products) tests.

3.2. Incorporation of mining waste in ceramic mixtures

3.2.1. unfired roof tile mixtures

The results of the physical and chemical characterisation for each roof tile mixture are presented in Table 5.

For the roof tile mixtures, where local clay and local sand were partly replaced by 5 wt% of mining waste material, the physical and chemical properties of the unfired mixtures showed that the mix with Plombières tailing material (SUL_PM_2) is very similar to the standard mixture (SUL_PM_1), for all parameters (Table 5). Concerning the other 3 unfired blends, even though only 5 wt% of mining waste was used in the roof tile mixtures, some clear differences are evident, especially in chemistry (total S and heavy metals content for Cu, Pb and Zn) when compared to the standard and the mix with Plombières tailing material (Table 5).

Compared to the reference, higher LOI values were found for the unfired blends where S rich mining waste materials were added, with the highest LOI values coming from the Freiberg tailing mix (SUL_PM_3). The unfired blends with Freiberg tailing and both Neves Corvo waste rock materials show higher contents for Fe₂O₃, Cu, Zn and Pb, in accordance with the metallogenic origin of the mining waste materials. Relatively high Ba content in all unfired mixtures was found, due to the addition of BaCO₃ in order to prevent drying efflorescence. The BaCO₃ in the roof tile mixtures, reacts with the free sulphates (SO₄²⁻) and forms insoluble BaSO₄. This is the reason why the soluble sulphate content in all unfired blends is low to very low.

The highest total S content is, as expected, found in the Freiberg tailing mix (SUL_PM_3: 0.8 wt% S), followed by Neves Corvo fresh waste rock mix (SUL_PM_4: 0.4 wt% S), Neves Corvo stored waste rock mix (SUL_PM_5: 0.4 wt% S) and Plombières tailing mix (SUL_PM_1: 0.1 wt% S) (Table 5).

Concerning the soluble sulphate content, the Neves Corvo stored waste rock mix (SUL_PM_5) still has 0.2 wt% of soluble sulphates, and the Freiberg tailing mix (SUL_PM_3) 0.1 wt%. The reference mixture (SUL_PM_1), the mixture containing the Plombières tailing (SUL_PM_2) and the mixture with Neves Corvo fresh waste rock (SUL_PM_4) don't show almost any presence of soluble sulphates. Although BaCO₃ was added to all wet mixtures (fixed amount of 0.5 wt% was added per mixture), it is clear that this amount is not enough for the SUL_PM_3 and SUL_PM_5 mixtures. Nevertheless, none of the unfired mixtures showed efflorescence after drying.

For all roof tile unfired mixtures, technical properties (Table 7), such as plasticity and drying shrinkage, were in the same range as the standard. Moreover, there was no clear difference in drying behaviour of the test pieces for the different climatic test programmes.

3.2.2. Unfired block mixtures

The results of the physical and chemical characterisation for each block mixture are presented in Table 6.

All block mixtures, where 10 wt% of mining waste material was used instead of the regional sand (total amount) and the imported filler R (partial amount), contain less coarse material (> 50 µm) and more silt (50–2 µm) or clay (< 2 µm) fractions, compared to the standard mix. By consequence, SSA increases slightly in these unfired mixtures.

The results of the unfired block mixtures show that the Plombières tailing mixture (SUL_ZM_2) is comparable to the standard (SUL_ZM_1) and the Freiberg tailing mixture (SUL_ZM_3) presents the highest total sulphur content with 1.7 wt% S, followed by the Neves Corvo fresh waste rock mixture (SUL_ZM_4) with 0.9 wt% S and by Neves Corvo stored waste rock mixture (SUL_ZM_5) with 0.8 wt% S. Considering major and trace elements analyses, Freiberg and Neves Corvo mixtures present higher amounts of Fe₂O₃, Cu, Pb and Zn compared to the standard.

Neves Corvo stored waste rock mixture presents the highest soluble sulphate content (1.0 wt%), followed by the Freiberg tailing mix (0.7 wt%) and Neves Corvo fresh waste rock mix (0.5 wt%). The Plombières tailing mix presents the same soluble sulphate content as the reference (0.4 wt%). Although the soluble sulphate content is quite high, drying efflorescence was not visible.

For all the block mixtures, the plasticity and drying shrinkage (Table 7) were in the same range as the standard. No clear difference in drying behaviour was found on the test pieces for the different climatic test programmes.

3.2.3. Fired roof tile mixtures

The fired roof tile (985 °C and 1000 °C) test specimens were characterised for their technical, aesthetical and chemical properties.

Regarding technical properties, the fired pieces containing Plombières' tailing material are close to the standard fired pieces (Table 7).

The three other fired mixtures using Freiberg and Neves Corvo mining waste materials differ for firing shrinkage, water absorption and E-modulus values. This can be linked to the presence of a black core in these fired pieces. As the unfired blends contain considerable amounts of C and especially S (Table 5), the CO₂ and SO_x (from pyrite decomposition) release during firing creates a reducing atmosphere in the body. Therefore these mixtures are sensible to black core formation (Fig. 5). The reducing atmosphere in the body causes the reduction of Fe₂O₃, forming Fe₃O₄, which gives the black core (Gredmaier et al., 2011).

The black core in the fired test piece of SUL_PM_5 mix is less pronounced than the one from SUL_PM_4, as the total sulphur content in the unfired mixture of SUL_PM_5 comes not only from pyrite (FeS₂) but also from the soluble sulphates. The fired test piece with Freiberg tail-

Table 5
Physical properties and chemical composition of roof tile mixtures.

Unfired roof tile mix	1400-1000 μm	1000-200 μm	200-50 μm	50-2 μm	<2 μm	MC	SSA	CaCO ₃	CO ₂ carbonates	C _{total}	C _{organic}	
	wt%	wt%	wt%	wt%	wt%	wt%	m ² /g	wt%	wt%	wt%	wt%	
SUL_PM_1	0	3	27	20	50	15.9	120	2.5	1.1	0.4	0.1	
SUL_PM_2	0	3	27	21	49	15.8	118	2.5	1.1	0.4	0.1	
SUL_PM_3	0	3	25	23	49	15.8	118	2.8	1.2	0.4	0.1	
SUL_PM_4	1	5	23	22	49	15.6	118	2.6	1.2	0.4	0.1	
SUL_PM_5	0	5	24	21	50	16.0	117	2.3	1.0	0.4	0.1	
Unfired roof tile mix	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	MnO	LOI	S _{total}	
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	
SUL_PM_1	70.1	11.8	5.5	0.7	1.5	1.1	0.5	2.4	0.1	5.0	0.2	
SUL_PM_2	70.4	11.4	5.7	0.7	1.6	1.2	0.6	2.6	0.1	4.8	0.1	
SUL_PM_3	66.1	11.6	6.7	0.8	1.6	1.3	0.7	2.6	0.1	5.7	0.8	
SUL_PM_4	67.4	12.1	6.5	0.7	1.6	1.3	0.5	2.7	0.1	5.3	0.4	
SUL_PM_5	66.4	12.6	6.3	0.8	1.8	1.2	0.7	2.9	<LOD	5.6	0.4	
Unfired roof tile mix	Ba	Cr	Cu	Ni	Pb	Zn	Soluble SO ²⁻ ₄	Soluble Ca ²⁺	Soluble Mg ²⁺	Soluble Na ⁺	Soluble K ⁺	
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	wt%	mg/kg	mg/kg	mg/kg	mg/kg	
SUL_PM_1	3530	98	26	40	<LOD	73	0.03	255	66	349	421	
SUL_PM_2	3606	114	26	56	<LOD	76	0.03	218	5	269	375	
SUL_PM_3	3175	117	72	59	154	781	0.1	309	5	313	383	
SUL_PM_4	3543	99	120	43	16	270	0.04	385	13	334	505	
SUL_PM_5	3719	100	278	44	1	144	0.2	613	9	339	591	
Fired roof tile (985 °C)	C _{total}	S _{total}	Soluble SO ²⁻ ₄			Soluble Ca ²⁺		Soluble Mg ²⁺		Soluble Na ⁺		Soluble K ⁺
	wt%	wt%	wt%			mg/kg		mg/kg		mg/kg		mg/kg
SUL_PM_1	0.03	0.2	0.3			1383		9		11		21
SUL_PM_2	0.005	0.2	0.4			1567		7		10		17
SUL_PM_3	<LOD	0.3	0.5			2038		20		19		34
SUL_PM_4	<LOD	0.3	0.6			2177		38		109		58
SUL_PM_5	0.004	0.3	0.5			2146		13		14		28
Fired roof tile (1000 °C)	C _{total}	S _{total}	Soluble SO ²⁻ ₄			Soluble Ca ²⁺		Soluble Mg ²⁺		Soluble Na ⁺		Soluble K ⁺
	wt%	wt%	wt%			mg/kg		mg/kg		mg/kg		mg/kg
SUL_PM_1	0.003	0.1	0.3			1471		7		9		14
SUL_PM_2	0.002	0.1	0.3			1393		7		10		17
SUL_PM_3	0.003	0.3	0.4			1679		19		108		61
SUL_PM_4	0.01	0.2	0.4			1618		12		17		23
SUL_PM_5	0.03	0.2	0.4			1520		9		11		19

<LOD: below the limit of detection.

ing material (SUL_PM_3) shows the biggest black core formation, which can be linked to the high total sulphur (pyrite) content of the unfired mix (Table 5). This black core reflects lower water absorption, higher firing shrinkage and higher *E*-modulus values (Table 7).

In general, all the fired mixtures showed satisfying saturation levels (Table 7). This means that, theoretically, frost resistance problems should not occur. However, it is well known that black cores make the body less frost resistant (Pavlovets et al., 2020). This is mainly due to the different physical behaviour of the inner (black core) and outer layer (red rim) during the freeze-thaw cycles (Gredmaier et al., 2011).

The firing colour of all of the fired roof tiles test specimens are comparable to the standard on both studied temperatures (Fig. 5).

Compared to the unfired mixtures, the total sulphur content in the fired standard mix and the mix using Plombières tailing, remains constant. In contrast, fired mixtures containing Freiberg tailing and Neves Corvo waste rock materials have a lower total sulphur content compared to the unfired blends (Table 5). In the standard and Plombières

blend there is enough free CaO (decomposition of lime through calcination), which acts as a sorbent for the SO_x, coming mainly from the decomposition of FeS₂, and forming CaSO₄, which is the most common sulphate in heavy clay ceramics (Gredmaier et al., 2011). In the 3 other mixtures, the volatile SO_x content is too high for the available amount of free calcium oxide, which results in more SO_x emissions. Firing at higher temperatures (1000 °C) decreases the total sulphur and soluble sulphates content, as part of the sulphates further decomposes (Fig. 6).

The CaSO₄ content and the porometry (capillary flow) is the reason why efflorescence occurs on the surface of the fired test pieces during the efflorescence test (Fig. 7).

Concerning efflorescence, Plombières fired test pieces (985 °C and 1000 °C) show small, but visible, efflorescence stains even though their soluble sulphate content is almost the same as for the standard. This can be explained by the higher porosity (water absorption) of the fired test pieces with Plombières tailing material (Table 7), since efflores-

Table 6
Physical properties and chemical composition of block mixtures.

Unfired block mix	1400-1000 μm	1000-200 μm	200-50 μm	50-2 μm	<2 μm	MC	SSA	CaCO ₃	CO ₂ carbonates	C _{total}	C _{organic}
	wt%	wt%	wt%	wt%	wt%	wt%	m ² /g	wt%	wt%	wt%	wt%
SUL_ZM_1	2	27	9	20	42	17.3	142	2.0	0.9	3.9	3.7
SUL_ZM_2	2	22	7	21	48	17.6	140	1.9	0.8	3.8	3.6
SUL_ZM_3	2	21	11	25	41	18.0	141	2.3	1.0	4.2	3.9
SUL_ZM_4	3	24	8	19	46	17.3	142	2.2	1.0	4.2	4.0
SUL_ZM_5	2	24	9	21	44	17.6	141	1.7	0.7	4.2	4.0
Unfired block mix	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	MnO	LOI	S _{total}
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
SUL_ZM_1	57.7	15.1	6.5	1.0	1.8	2.0	0.7	3.4	0.1	10.6	0.3
SUL_ZM_2	57.5	15.4	6.7	1.0	1.8	2.2	0.7	3.3	<LOD	10.4	0.3
SUL_ZM_3	52.3	14.6	8.2	0.8	1.8	2.2	0.8	3.4	0.1	11.7	1.7
SUL_ZM_4	54.4	15.4	8.0	0.8	1.6	2.1	0.9	3.2	<LOD	11.3	0.9
SUL_ZM_5	54.6	15.3	7.6	0.8	1.7	2.2	0.8	3.5	0.1	11.7	0.8
Unfired block mix	Ba	Cr	Cu	Ni	Pb	Zn	Soluble SO ²⁻ ₄	Soluble Ca ²⁺	Soluble Mg ²⁺	Soluble Na ⁺	Soluble K ⁺
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	wt%	mg/kg	mg/kg	mg/kg	mg/kg
SUL_ZM_1	70	90	34	45	<LOD	96	0.4	1144	20	426	750
SUL_ZM_2	48	95	33	47	<LOD	91	0.4	1097	26	417	708
SUL_ZM_3	46	95	97	49	211	1188	0.7	2425	144	439	839
SUL_ZM_4	94	112	176	58	29	395	0.5	1404	24	466	809
SUL_ZM_5	77	93	444	53	20	235	1.0	3387	121	417	811
Fired block (965 °C)	C _{total}	S _{total}	Soluble SO ²⁻ ₄	Soluble Ca ²⁺	Soluble Mg ²⁺	Soluble Na ⁺	Soluble K ⁺				
	wt%	wt%	wt%	mg/kg	mg/kg	mg/kg	mg/kg				
SUL_ZM_1	0.1	0.3	0.4	1585	91	73	138				
SUL_ZM_2	0.6	0.3	0.5	1615	158	155	220				
SUL_ZM_3	0.2	1.2	2.8	8505	1361	347	1041				
SUL_ZM_4	0.4	0.7	1.3	4031	439	153	371				
SUL_ZM_5	0.3	0.6	0.9	2890	371	167	467				

<LOD: below the limit of detection.

Table 7
Technical properties of roof tile and block test specimens.

	Plasticity (Pfefferkorn)	Drying shrinkage	Firing/total shrinkage	Water absorption	Saturation level (E _{prog} /E _{fullvac})	E-modulus				
	in-print (mm)	%	%	wt%	%	GPa				
Roof tile mix	Unfired mix	Industrial dryer	Lab 985 °C	Lab 1000 °C	E _{prog} 985 °C	E _{prog} 1000 °C	Lab 985 °C	Lab 1000 °C	Lab 985 °C	Lab 1000 °C
SUL_PM_1	7.3	6.4	1.5/7.8	1.9/8.3	7.3	6.3	72	65	17.6	19.6
SUL_PM_2	8.0	6.2	1.5/7.7	2.0/8.2	7.7	6.9	73	69	16.5	18.5
SUL_PM_3	7.0	6.1	1.7/7.9	2.4/8.6	6.6	5.1	68	57	20.9	22.8
SUL_PM_4	6.7	6.0	1.6/7.6	2.1/8.1	6.7	5.3	70	60	20.0	22.2
SUL_PM_5	6.1	6.0	1.8/7.7	2.3/8.3	7.1	5.8	72	65	19.7	22.8
Block mix	Unfired mix	Industrial dryer	Lab 965 °C	E _{24h} 965 °C	Lab 965 °C	Lab 965 °C				
SUL_ZM_1	7.3	5.4	0.8/6.2	11.4	NA	14.0				
SUL_ZM_2	6.0	5.3	0.7/6.0	10.1	NA	18.2				
SUL_ZM_3	6.3	5.6	0.7/6.3	11.0	NA	17.6				
SUL_ZM_4	6.3	5.4	0.6/6.0	11.2	NA	16.4				
SUL_ZM_5	5.0	5.4	1.1/6.4	11.4	NA	17.4				

NA: not analysed.

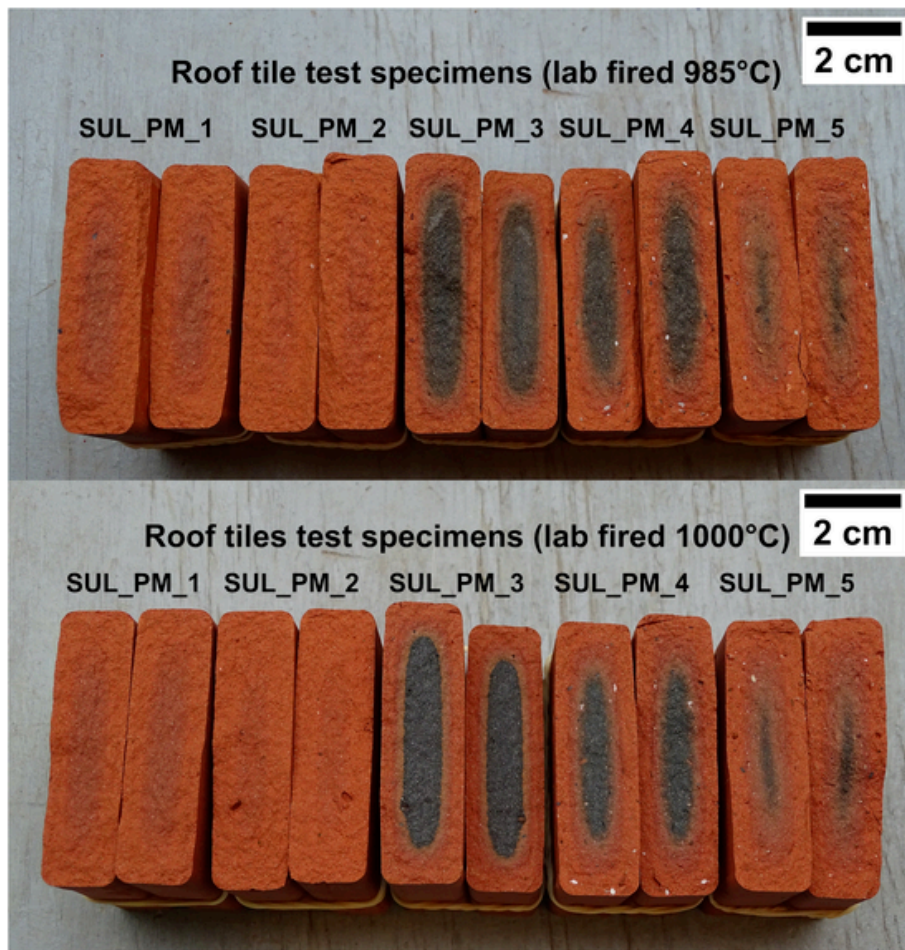


Fig. 5. Black core formation in fired roof tile test specimens (985 °C and 1000 °C).

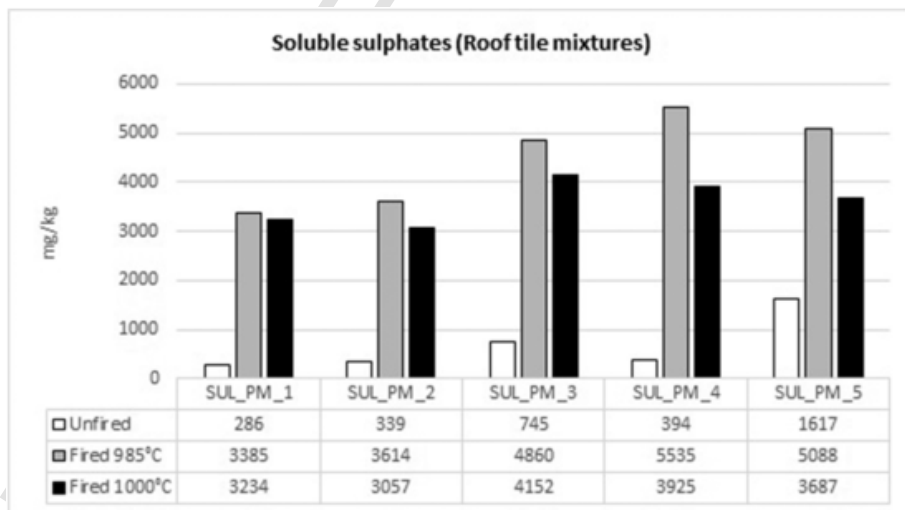


Fig. 6. Soluble sulphates content in unfired and fired (985 °C and 1000 °C) roof tile mixtures.

cence is the result of the available soluble sulphates and the porometry of the fired body (Chwast and Todorović, 2015).

3.2.4. Fired block mixtures

For the fired block test specimens (fired at 965 °C), there are no clear differences in technical properties compared to the standard (Table 7). The only remarkable difference is the increase of E-modulus

values (Table 7) in all the test specimens using mining waste, as a consequence of a more pronounced black core (Fig. 8). The pronounced black core formation in SUL_ZM_3, SUL_ZM_4 and SUL_ZM_5 comes from the higher content of volatiles (CO₂ and especially SO_x) and the reducing atmosphere that they create (Gredmaier et al., 2011). For the Plombières fired test piece (SUL_ZM_2), the more pronounced black core is related to the granulometry of the mixture, having the highest



Fig. 7. Efflorescence test result on the fired roof tile test specimens (no. 12 fired at 985 °C and no. 14 fired at 1000 °C).

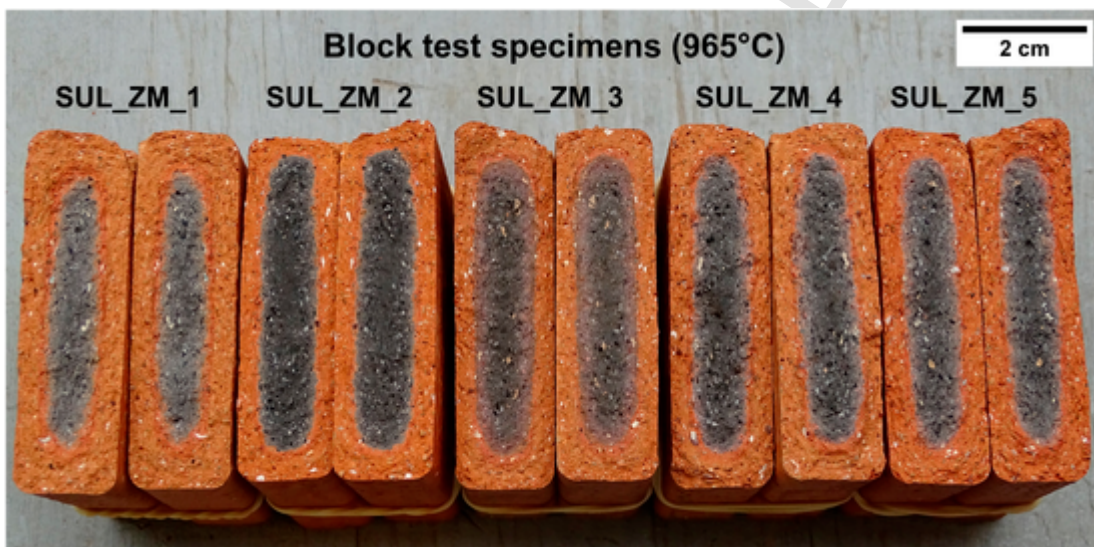


Fig. 8. Black core formation in fired block test specimens (965 °C).

<2 µm fraction (48 wt%, Table 6). For inner wall blocks, saturation levels are not analysed as they are not exposed to freeze-thaw cycles. Therefore, black core formation is less critical in this ceramic product with even the standard (SUL_ZM_1) presenting a black core (Fig. 8).

The firing colour of all of the fired block test specimens is comparable to the colour of the standard test specimen (Fig. 8).

Efflorescence results (Fig. 10) are in line with the soluble sulphates content of each fired block mixture (Fig. 9) with the strongest efflorescence appearing on the fired test piece with Freiberg tailing

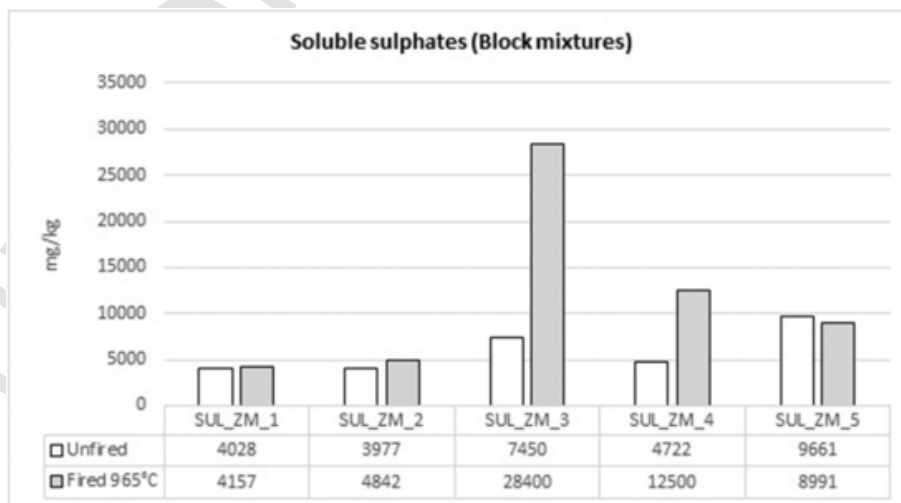


Fig. 9. Soluble sulphates content in unfired and fired (965 °C) block mixtures.

(SUL_ZM_3), followed by the fired block test pieces with Neves Corvo fresh (SUL_ZM_4) and stored (SUL_ZM_5) waste rock material (Fig. 10). The unfired mixtures with the highest total sulphur content (mainly present as FeS_2), SUL_ZM_3 and SUL_ZM_4, are characterised by a substantial increase in soluble sulphates when fired ($965\text{ }^\circ\text{C}$) due to the reaction between the volatile SO_x and free CaO coming from the decomposition of lime (CaCO_3). For the three other mixtures (SUL_ZM_1, SUL_ZM_2 and SUL_ZM_5), the soluble sulphate content stays more or less constant after firing (Fig. 9).

The presence of CaSO_4 , as well as the porometry (capillary flow), explains the efflorescence on the surface of the fired test pieces (Fig. 10).

4. Conclusions

Studying the behaviour of secondary sources, such as mining waste materials, in other industry applications is a must to shift towards a more resource efficient and sustainable world. In the present study, the use of uncleaned mining waste materials from three different mining sites (Plombières, Freiberg and Neves Corvo), as a total or partial substitute of primary resources, for the production of ceramic roof tiles and blocks was investigated. The study focus on environmental compliance tests of the mining waste materials, and on production parameters (shaping, drying and firing behaviour) and product quality (technical, aesthetical and chemical properties) of the produced ceramic bodies.

Plombières and Freiberg tailing materials are fine enough to be integrated in ceramic blends without any mechanical pre-treatment. Neves Corvo fresh and stored waste rock materials need to be grinded and sieved before use, which is an additional cost. The high concentrations

of sulphur, mainly coming from pyrite, and heavy metals (especially Cu, Zn and Pb) in the Freiberg tailing and both Neves Corvo waste rock materials make them less suitable to replace primary raw materials in ceramic roof tile and block blends, even in small amounts (5 wt% and 10 wt%, respectively). The high sulphur content resulted in higher SO_x emissions, efflorescence (caused by soluble sulphate sulphates), and black core formation.

Regarding the Flemish environmental regulations for the sustainable management of material cycles and waste (VLAREMA, 2012), Plombières tailing material (SUL_PL_62_I) as well as Neves Corvo fresh waste rock (SUL_NC_01) stayed below the established limit values for total and leached metal(loid) concentrations. Therefore, they can be used in or as non-shaped building products. The other mining waste materials, Freiberg tailing (SUL_FR_01) and Neves Corvo stored waste rock (SUL_NC_03), exceed limit values for total and leached metal(loid) concentrations. Nevertheless, because none of the mining waste materials exceed the limits for organic compounds, they stay possible candidates to get a “raw material declaration” if they comply with the immission limit values for soil (Annex 2.3.2.C of VLAREMA, 2012) after the diffusion test (in case of use in or as a shaped building product) the column test (in case of use in or as non-shaped building products).

The Plombières fine tailing material used in this study has a very low sulphur and heavy metal (Cu, Zn and Pb) content as well as a satisfying environmental performance. The technical, aesthetical and chemical properties of the fired bodies, in which the Plombières tailing material was used, were very similar to the standard fired roof tile and block bodies. Therefore, Plombières tailing material can be considered the best fit to partially or totally replace some primary raw materials

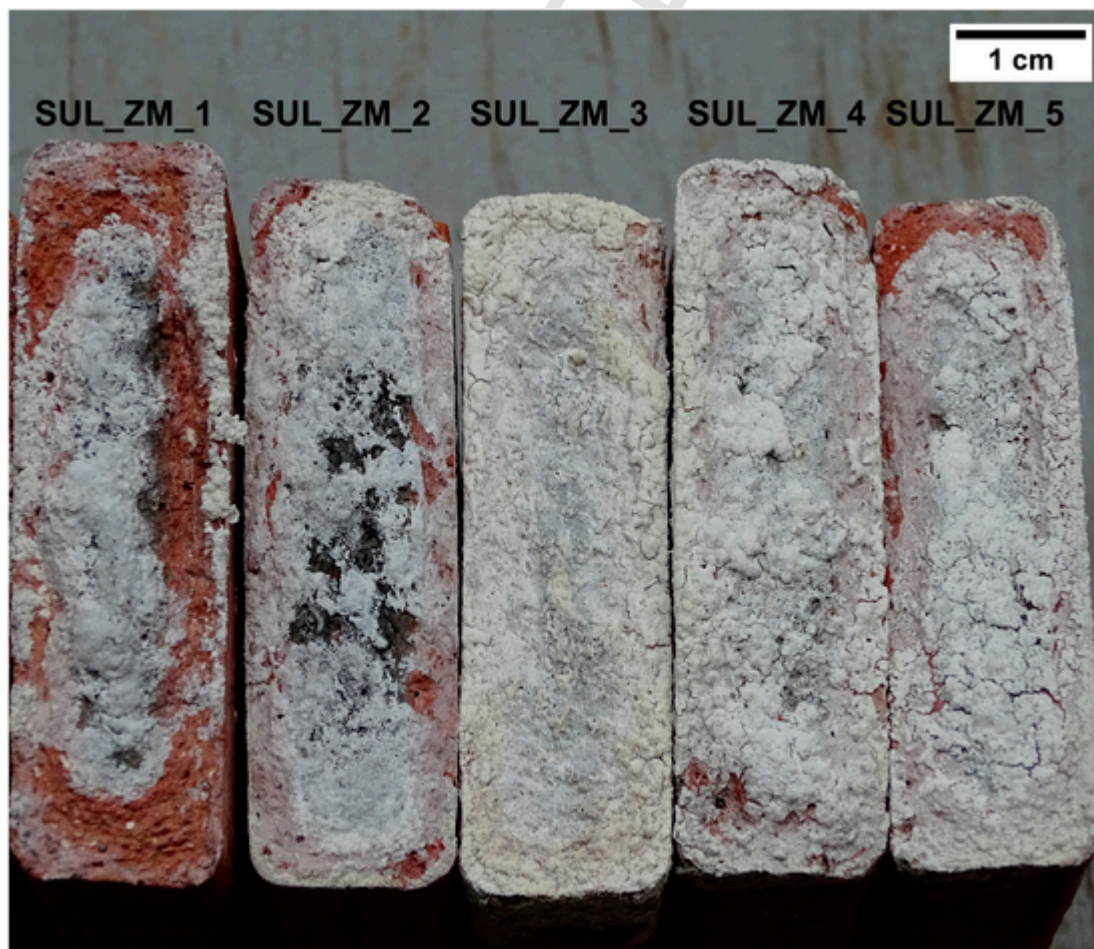


Fig. 10. Efflorescence test result on the fired block test specimens ($965\text{ }^\circ\text{C}$).

(mainly clay and sand) used in the production of ceramic roof tiles and blocks. Future research will focus on using higher amounts of Plombières tailing material, not only in roof tiles and blocks but also in other ceramic products, such as pavers and facing bricks.

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Uncited reference

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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