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Possibility of Using Vitreous Enamel Waste in the Construction Industry as the Concept of Cleaner Production

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Abstract: Waste vitreous enamels from the heating device production process were used for partial replacement of cement in the mortar and concrete production industry. This waste, due to the high content of heavy metals, is classified as hazardous waste. At the same time, waste vitreous enamels possess pozzolanic activity and belong to class 15 (WEP—generated during the production process of heating devices, premix technology), that is 5 (WETM—generated during the production process of heating devices, classic technology) of pozzolanic materials. The purpose of this research was to develop new composites from these wastes to reduce the deposition of the toxic compounds and reduce their environmental impact. The chemical and physical-chemical characterization and pozzolanic activity of the raw waste materials were studied by a mixture of complementary methods, as well as physical-mechanical characterization and a leaching test of mortar and concrete composites. The results indicate that the replacement of cement with WEP up to 30%, or with WETM up to 20% does not significantly affect the quality of concrete in comparison to the quality of the reference concrete prepared with 100% cement. The leaching test showed no significant release of toxic elements for both obtained composites.

Keywords: waste; vitreous enamel; cement replacement; construction material; environment protection

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1. Introduction

The concept of clean production is a preventive, comprehensive strategy applied to the entire production cycle. In recent years, industries have been confronted with strict legal standards regarding the reducing pollutant emissions to water, air and soil, and the generation of waste. In this context, the costs of disposing production waste as well as the cost of maintaining wastewater treatment plants are non-negligible investments for manufacturers. This makes the production of the final product(s) considerably more expensive. However, the application of a globally accepted strategy, in which each plant strives for clean production in accordance with green economy standards, maximizing the reuse of waste from production, offers the possibility of minimizing waste volumes and reducing pollution, which can consequently have significant economic benefits. The imperative is to create a new product with utility, with the least consumption of raw materials, energy and human resources and with a minimal negative impact on the environment. Moreover, industrial ecology is an integrated, emerging tool that guides the industry to reuse materials, save energy and reduce waste generation. Such a tool can consider industrial waste as a by-product or alternative material that can be fed to another industry [1,2].

While the construction sector has a major positive impact on society and the economy, it is also one of nature's biggest polluters and has massive impacts on the environment [3,4]. The typical construction process involves the use of various construction equipment and natural resources and generates many pollutants [5–7]. In terms of resources, it is common knowledge that sand, which a non-renewable resource, is most commonly used in the construction industry as it is suitable for the production of concrete. Due to the increase in construction activity around the world, there is a great demand for sand and natural resources are running out. This fact has recently led to the increased use of waste and by-products in the production of concrete instead of the most common cement, Portland cement [8]. Theoretically, any material containing oxides, such as silicon-dioxide (SiO_2), alumina (Al_2O_3), limestone ($CaCO_3$), iron oxide (Fe_2O_3) or magnesium oxide (MgO), can be used as a raw material for the production of Portland cement. In the literature, researchers have investigated different types of waste as partial substitutes for cement and have concluded that concrete can consume a significant amount of waste. The most commonly studied and used industrial wastes for these purposes are: silica fume [9–11], slag (obtained from various sources) [12–15], glass [16–19], fly ash [20–24], marble dust [25,26], etc. Moreover, many researchers investigate the possibility of incorporating agro-industrial wastes into the brick mixture, i.e., green cement brick has been proposed to be further checked for use in the construction industry [27,28].

Different waste types have different properties; therefore, it is necessary to examine them carefully before each application. The materials obtained must also meet all the criteria prescribed in the regulations for the particular application.

Glassy enameling is the best and most durable protection for metallic substrates against corrosion and plays a very important role in the production of coatings [29]. Thanks to unique properties such as excellent resistance to chemical degradation processes [30,31], good resistance to tribological phenomena such as abrasive wear [32] and high temperature resistance, vitreous enamels are widely used for coating a wide range of products and various appliances such as cooking pots, electric water heaters, and heaters. Depending on the application, certain properties of the enamel are required. In order for enamel coatings to be resistant to weathering or formulated to be resistant to strong acids or mild alkalis, certain additives must be added to them [33]. The composition of the frit is decisive for the properties of the coating. Glass frits used in glass enamels can contain up to 20 components [34]. The problem is that enamels, similar to other glassy materials or frits, are manufactured in a process that produces highly toxic chemicals that pollute the environment and natural resources when deposited in inappropriate places. One of these chemicals is a fluoride derivative found in the form of hydrofluoric acid in the waste gases from smelting furnaces. This chemical interacts with lime particles and turns into a by-product called micronized fluoride lime (MFL) [35]. In addition, nickel and cobalt oxides, which are known carcinogens, have often been used to improve the adhesion between the enamel coating and the metal surface [36,37]. According to EU and Serbian regulations on environmental protection and handling of waste containing hazardous substances, these wastes are considered hazardous. However, when used correctly, they can contribute to cost reduction, sustainable development and environmental protection, and in most cases improve the quality of the final product.

A considerable amount of glass enamel waste is produced in the manufacture of various types of heating appliances. The aspect of reducing glass enamel waste is particularly important, which means reducing waste treatment costs, saving material and water, increasing overall efficiency and productivity, and significantly reducing the amount of waste sent to landfill. In addition to protecting the environment, one of the main objectives of this research is to determine the useful value of glass enamel waste, i.e., to convert unusable and hazardous waste from the production of heating appliances into usable waste.

Waste vitreous enamels have significant potential and usability and with appropriate physical and chemical properties can be applied in the construction industry [1]. According to the available literature, the application of waste vitreous enamels to partially replace cement in the mortar and concrete production industry was not completely described. Mineralogically speaking, sand is composed predominantly of grains (granules) of quartz, musk flakes, and then grains of zircon, rutile, apatite, granite, magnetite, tourmaline, etc. Since the chemical composition of vitreous enamels is similar to sand, enamel can be an adequate replacement for cement. In addition, from the aspect of environmental protection, significant amounts of waste can be used with this extremely simple procedure.

The focus of the research was on the maximum amount of waste that could be used for the production of cement composites, solving the problem of their disposal, which is a great contribution to preserving a healthy environment. Pozzolanic activity and physical-chemical properties of waste vitreous enamels was investigated. Additionally, physical-mechanical characterization of the mortar and concrete composites according to standards was performed. To confirm the environmental safety of applied materials, a leaching test was carried out.

2. Materials and Methods

2.1. Sampling

Sampling was performed in factory of heating devices in South of the Republic of Serbia. In this factory, approximately 160 tons of waste vitreous enamel is generated during last four years. The two different kinds of raw samples of waste vitreous enamels generated during the production process of heating devices were taken from the plant for four months (batches 1–4) sample WEP—premix technology, and sample WETM—traditional method, 8 samples in total (Figure 1).

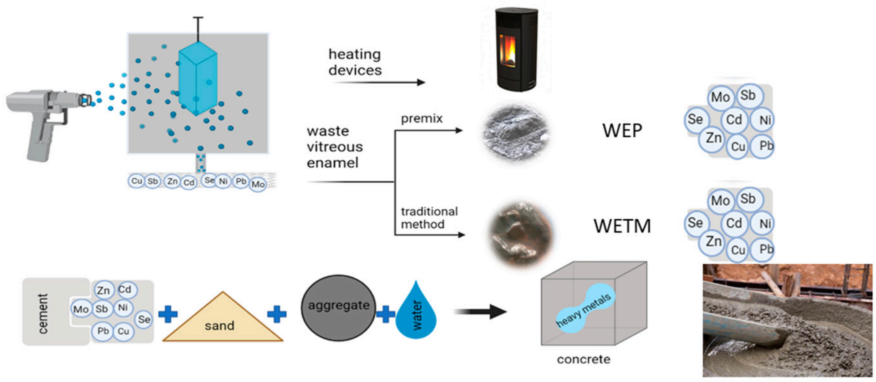

Figure 1. The representative samples of raw waste vitreous enamel samples and their use for cement partial replacement in the concrete and mortar production.

The representative samples were dried (105 °C for 24 h), mixed and homogenized. After drying, samples were crushed, ground and sieved so the size of particles was 100% with size < 63 μm.

Ordinary Portland cement CEM I 42.5R (CRH, Popovac, Serbia) was used, with the chemical and mineralogical composition determined in previous research, as shown in Table 1 [38].

Table 1. Chemical and mineralogical composition of CEM I 42.5R.

Chemical Composition								
SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
21.62	2.60	7.00	60.16	2.34	2.55	0.33	0.66	2.68
Mineral properties								
brownmillerite; calcium-silicate oxide; calcite; larnite; magnesium-silicate; calcium-hydroxide								

2.2. Physical-Chemical Analysis of Waste Vitreous Enamels

2.2.1. Chemical Analysis and Determination of the Content of Heavy Metals

Solid state of selected waste vitreous enamels samples were converted to a liquid by appropriate treatment. Chemical composition and heavy metal concentrations of raw samples and after the leaching test, were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) on a spectrometer Spectroflame (Spectro Analitical Instruments, Kleve, Germany). According to EPA 3051A procedure, arsenic concentrations were determined by microwave digestion.

2.2.2. X-ray Structural Analysis (XRPD)

Phase analysis of all samples was conducted by using an X-ray powder diffractometer (XRPD, Rigaku Ultima IV, Tokyo, Japan), with filtered CuKα1 radiation (λ = 0.154178 nm). X-ray diffraction data were collected over the 2θ range from 10° up to 90° with the step of 0.02° and scanning rate of 5°/min. Structural analysis was performed using the program Powder Cell [39,40]. The TCH pseudo-Voigt profile function gave the best fit to the experimental data. All the structural models for refinement were taken from the American Mineralogist Crystal Data Structure Base (AMCDSB) [41].

2.2.3. Fourier-Transform Infrared Spectroscopy (FTIR) with Attenuated Total Reflection (ATR)

The functional groups of all considered samples were studied using Attenuated total reflection (ATR), a technique used in conjunction with infrared spectroscopy and with direct examination of waste vitreous enamels in a solid state without further preparation. FTIR spectra were recorded on the Thermo SCIENTIFIC Nicolet iS10, Spectrometer. The operating range was 4000–450 cm^{-1} at room temperature (20 °C).

2.2.4. Determination of the Specific Surface by the BET Method

The specific surface areas of the waste vitreous enamels were determined based on the amount of adsorbed gas (adsorbate N_2) per unit mass of adsorbents (samples), depending on the relative pressure of the adsorbate. The calculations of the specific surface of all samples were performed based on the determination of adsorption and desorption isotherms of nitrogen under static conditions, at liquid nitrogen temperature (−196 °C). Micromeritics ASAP 2020 instrument was used for these measurements. Before starting the measurement, the samples were degassed at 120 °C and vacuumed for 24 h. The specific surface areas were calculated by the Brunauer, Emmett, and Teller (BET) method, which is based on the assumption that gas adsorption takes place in the monomolecular layer on every enamel [42].

The total pore volume (V_{tot}) was given at p/p_0 = 0.998. The pore size distribution was estimated by applying the BJH method [43] to the desorption branch of isotherms whereas mesoporous surface area and micropore volume were estimated using the high-resolution αs plot method [44–46]. Microporous surface area (S_{mic}) was calculated by subtracting S_{meso} from S_{BET}.

2.2.5. Field Emission Scanning Electron Microscopy (FE-SEM)

For investigation of the morphological and microstructural properties of generated waste vitreous enamels, FESEM measurements were carried out. The microstructure of samples was examined using the TESCAN Mira3XMU instrument at 20 kV (Tescan; Kohoutovice, Czech Republic). The electronic images of the surfaces were obtained with secondary electrons (SEI mode) with a magnification of ×5000 and an operating voltage of 10.0 kV. Before analyses were conducted, the samples were sputter-coated with Au/Pd alloy, using the sputter coater Polaron SC503 Fision Instrument (Quorum Technologies Ltd., Lewes, UK).

2.3. Pozzolanic Activity of Waste Vitreous Enamels

Pozzolanic Class, the activity index, water requirement, Initial and Final setting time examinations were performed so that application potential of the use of waste enamels as the type II addition in the production of concrete in accordance with standard EN 206 could be determined. Standard SRPS B.C1.018 was used to determine Pozzolanic Class, standard EN 450-1 to determine the activity index. Standard EN 450-1 Annex B was used for determining Water requirement, while standard EN 196-3 was used for determining Initial setting time and Final setting time and Soundness.

2.4. Preparation and Testing of Mortar with Waste Enamels

For mortar preparation, river sand (fraction 0/2 mm), with a specific gravity of 2610 kg/m^3 and water absorption of 1.52% was used. In the mortar mixtures preparation, production and curing of specimens, Standard EN 196-1 was applied. Different mortar mixes were made: a reference mixture (M-E), four mixtures (WEP-M-10, WEP-M-20, WEP-M-30, and WEP-M-40) in which cement was replaced with 10, 20, 30 and 40% of WEP and four mixtures (WETM-M-7.5, WETM-M-15, WETM-M-22.5, and WETM-M-30) in which cement was replaced with 7.5, 15, 22.5, and 30% of WETM. In order to quantify binder and sand, i.e., water and binder, respectively, the mass ratio 1:3 and 1:2 was used in all mixtures. An identical amount of superplasticizer was used in all mixtures to improve the workability of mortar mixtures. Table 2 shows quantities of material for making one series of mortar specimens (3 prisms with dimensions 40 mm × 40 mm × 160 mm) in the laboratory mixer "Hobart N-50". Quantities of materials are given in mass ratio.

Table 2. Mix proportion of mortar for one series of samples.

Designat. of Mortar	Cement [g]	WEP [g]	WETM [g]	River Sand 0/2 mm [g]	Water [g]	Superplasticizer [g]
M-E	450.00	0	-	1350.00	225.00	1.00
WEP-M-10	405.00	45.00	-	1350.00	225.00	1.00
WEP-M-20	360.00	90.00	-	1350.00	225.00	1.00
WEP-M-30	315.00	135.00	-	1350.00	225.00	1.00
WEP-M-40	270.00	180.00	-	1350.00	225.00	1.00
WETM-M-7.5	416.25	-	33.75	1350.00	225.00	1.00
WETM-M-15	382.50	-	67.50	1350.00	225.00	1.00
WETM-M-22.5	348.75	-	101.25	1350.00	225.00	1.00
WETM-M-30	315.00	-	135.00	1350.00	225.00	1.00

2.5. Preparation and Testing of Concrete with Waste Enamels

For making concrete, a crushed gabbro with fractions 4/8 mm and 8/16 mm was used as the coarse aggregates with a specific gravity of 2890 kg/m^3 and water absorption of 0.58%. As the fine aggregates, river sand with a fraction of 0/4 mm, specific gravity of 2620 kg/m^3, and water absorption of 1.42% was used.

Preparation of concrete mixtures, production and curing of specimens was performed according to the standard EN 12390-2. A total of 7 different mixtures were used, in which cement was replaced with waste enamel in the 0, 10, 20, 30 and 40% (labels C–E, WEP-C-10, WEP-C-20, WEP-C-30, WEP-C-40, WETM-C-10, WETM-C-20 and WETM-C-30). Superplasticizer on the base carboxylates was added to all concrete mixtures. Quantities of materials in a mass ratio for 1 m^3 of concrete mixtures are given in Table 3.

Table 3. Mix proportion of concrete mixtures for 1 m^3.

Designat. of Concrete	Cement [kg]	WEP [kg]	WETM [kg]	River Sand 0/4 mm [kg]	Crushed Agg. 4/8 mm [kg]	Crushed Agg. 8/16 mm [kg]	Water [kg]	Superplasticizer [kg]
M-E	380.0	-	-	808.0	376.0	696.0	180.0	3.04
WEP-C-10	342.0	38.0	-	808.0	376.0	696.0	180.0	3.04
WEP-C-20	304.0	76.0	-	808.0	376.0	696.0	180.0	3.04
WEP-C-30	266.0	114.0	-	808.0	376.0	696.0	180.0	3.04
WEP-C-40	228.0	152.0	-	808.0	376.0	696.0	180.0	3.04
WETM-C-10	342.0	-	38.0	808.0	376.0	696.0	180.0	3.04
WETM-C-20	304.0	-	76.0	808.0	376.0	696.0	180.0	3.04
WETM-C-30	266.0	-	114.0	808.0	376.0	696.0	180.0	3.04

2.6. Methods of Investigations of Properties of Mortar and Concrete

The investigation of physical-mechanical properties of the mortar samples was carried out across determination of: Consistency—by flow table (Standard EN 1015-3); bulk density of fresh mortar (Standard EN 1015-3); bulk density of hardened mortar (Standard EN 1015-10); flexural strength and compressive strength (Standard EN 196-1); water absorption at atmospheric pressure (Standard EN 13755); drying shrinkage (Standard SRPS B.C8.029:1979 (ASTM C 596)).

Consistency—slump test (Standard EN 12350-2); density of fresh concrete (Standard EN 12350-6); air content in fresh concrete (Standard EN 12350-7); density of hardened concrete (water saturated) (Standard EN 12390-7); flexural strength (Standard EN 12390-5); compressive strength (Standard EN 12390-3); tensile splitting strength (Standard EN 12390-6); secant modulus of elasticity (EN 12390-13); depth of penetration of water under pressure (Standard EN 12390-8); freeze–thaw resistance with de-icing salts—scaling (Standard CEN-TS_12390-9); determination of ultrasonic pulse velocity (Standard EN 12504-4) were implemented to examine the physical-mechanical properties of the concrete.

EN 12457-2 standard was used to perform the leaching test. The test was performed on the mortar mixture where the maximal amount of cement was replaced with WEP or. WETM. The percentage content of waste material in concrete is lower compared to mortar and for this reason the concrete was not tested. The testing procedure was described in details in Nedeljković et al. [34].

3. Results and Discussion

3.1. Physical-Chemical Characterization of the Waste Vitreous Enamels

3.1.1. Chemical Analysis and Determination of the Content of Heavy Metals

The chemical composition and the content of heavy metals of waste vitreous enamels are tabulated in Table 4.

In both investigated samples the content of certain heavy metal ions (Mo, Sb, Se, Cu, Zn, Ni, Cd and Pb) exceeds the maximum values allowed for the classification of waste as non-hazardous. According to Standard "Službeni Glasnik 56/2010" as well as EN 12457/EN 16192: 2011 standard which applies in the Republic of Serbia, these samples can be classified as hazardous waste, so disposal and immobilization of such a category of waste should be a priority. In addition, in the Republic of Serbia, the use of waste in the construction industry is prescribed by the "Rulebook on restrictions and prohibitions on the production, placing on the market and use of chemicals" as well as "Rulebook on the categories, testing and classification of waste" which do not restrict the use on the basis of the concentration of heavy metals in raw materials which are used. Bearing that in mind, the waste vitreous enamel can find practical application as raw material in the cement industry.

Table 4. Chemical composition and the content of heavy metals in waste enamels.

Batch	Content, mg/kg								Maximum Values for Disposal
	1		2		3		4		
Parameter	**WEP**	**WETM**	**WEP**	**WETM**	**WEP**	**WETM**	**WEP**	**WETM**	
Mo	**449.5**	4.5	**439.5**	4.5	**399.5**	3.5	**387.5**	5.5	10 * 30 **
Hg	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	0.2 * 2.0 **
Sb	**38.0**	<0.5	**35.0**	<0.5	**39.0**	<0.5	**42.0**	<0.5	0.7 * 5.0 **
Se	**4.5**	**1.5**	**3.5**	**1.5**	**3.5**	**2.5**	**3.5**	**1.5**	0.5 * 7.0 **
Sr	100.5	25.0	101.5	23.0	112.5	27.0	112.5	26.0	/ */ **
Ba	int	2.5	54.5	2.5	64.3	2.5	32.5	1.5	100 * 300 **
Ca	13,700.0	1550.0	13,720.0	1560.0	13,722.0	1549.0	13,765.0	1548.0	/ */ **
Mg	1315.0	5245.0	1313.0	5235.0	1333.0	5248.0	1315.0	5244.0	/ */ **
Ti	1200	71.0	1220	75.0	1235	78.0	1228	78.0	/ */ **
V	18.0	2.5	19.0	3.5	18.0	2.5	18.0	2.0	/ */ **
Mn	6850.0	8750.0	6840.0	8758.0	6843.0	8758.0	6885.0	8722.0	/ */ **
Fe	7300.0	26,000.0	7320.0	26,080.0	7322.0	260,256.0	7301.0	26,033.0	/ */ **
Co	4245.0	45.0	4225.0	46.0	4244.0	42.0	4248.0	44.0	/ */ **
Cu	**3350**	26.0	**3251**	20.0	**3368**	28.0	**3368**	**27.0**	50 * 100 **
Zn	**127.5**	6.5	**128.5**	12.5	**123.5**	**409.5**	**122.0**	**422.5**	50 * 200 **
Ni	**150.0**	2.0	**151.0**	2.0	**155.0**	**61.0**	**151.0**	**62.0**	10 * 40 **
Cd	**2.0**	**1.5**	**2.5**	0.5	**3.0**	**6.5**	**2.0**	**5.5**	1 * 5.0 **
Al	2280.0	1220.0	2281.0	1225.0	2200.0	1225.0	2266.0	1248.0	/ */ **
Pb	**26.5**	10.0	**23.5**	9.0	**22.5**	10.0	**25.0**	10.0	10 * 50 **
As	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	2 * 25 **
Be	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	/ */ **
Cr	3.5	11.2	3.5	13.5	3.5	12.2	5.5	10.2	10 * 70 **
Tl	54.5	73.5	52.0	75.5	50.5	70.5	49.5	68.5	/ */ **
Sn	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	/ */ **

According to Standard "Sl. Glasnik 56/2010": * values refer to the disposal of non-reactive hazardous waste at non-hazardous waste landfills in cassettes not used for the disposal of biodegradable waste. ** values refer to the disposal at a hazardous waste landfill.

3.1.2. Results of X-ray Structural Analysis (XRPD)

In order to reveal the main mineralogical composition of waste vitreous enamel, phase analysis was performed by X-ray powder diffraction analysis. Waste vitreous enamels from the process of manufacturing heating devices (sample WEP and WETM) were sampled four times (batches 1–4). The obtained mineralogical compositions are presented in Figure 2.

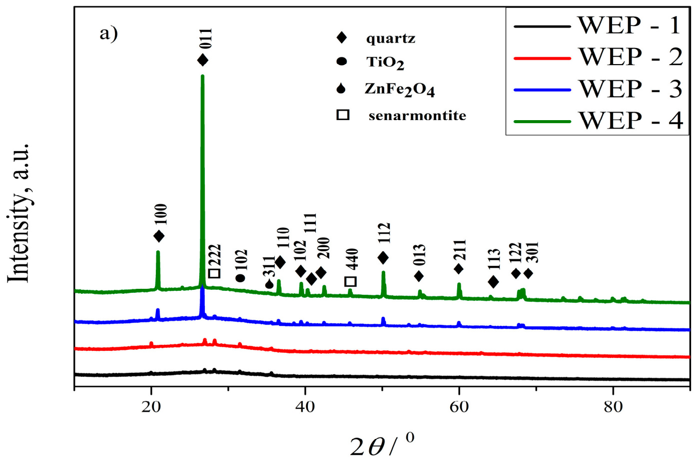

Figure 2. *Cont.*

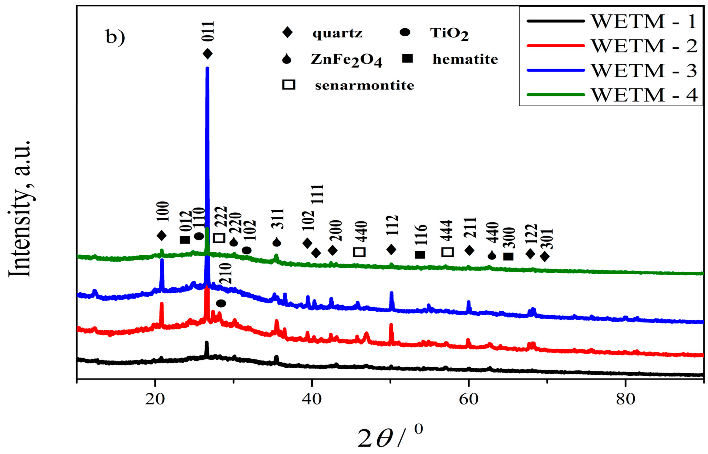

Figure 2. XRPD diagrams of the waste vitreous enamels: (**a**) WEP and (**b**) WETM.

Based on XRPD analyses, quartz (silicon oxide, ICSD No. 174) was identified as a dominant mineral in both groups of samples. Furthermore, small amounts of the oxides of metals Sb, Ti, Fe and Zn, appear in the form of supporting minerals such as senarmontite (antimony oxide, ICSD No. 1944), TiO_2 (titanium oxide, ICSD No.657748), $ZnFe_2O_4$ (zinc diiron(III) oxide, ICSD No. 24496) [47] and hematite (iron(III) oxide—alpha, ICSD No. 22505), were as well identified in waste vitreous enamel. The presence of metal oxides in WETM samples is more pronounced than their amounts in WEP samples.

3.1.3. Results of Fourier-Transform Infrared Spectroscopy (FTIR)

Results of the structural properties of waste vitreous enamels generated from the plant are presented in Figure 3.

From obtained results, it may be concluded that for each sample there are some very small deviations in structural properties for both WEP and WETM samples. The spectral change at ~3673 cm^{-1} is correspondent to a significant conversion of bridged hydroxyls (–OH) to isolated hydroxyls (Ti(IV)–OH) [48]. The peaks at 1134 cm^{-1}, 667 cm^{-1}, 515 cm^{-1} and 458 cm^{-1} are attributed to Ti–O bond (Figure 3b). The peak at 1134 cm^{-1} and 667 cm^{-1} refer to symmetric O–Ti–O stretch while the peak at 458 cm^{-1} and 515 cm^{-1} are due to the vibration of Ti–O bond [49]. Iron oxide shows peaks between 2955 cm^{-1} and 2857 cm^{-1} in both samples [50]. The peaks occurring in the range of ~827 to ~732 cm^{-1} are due to the Sb–O–Sb vibrations [51,52]. The metal oxide $Zn_2Fe_2O_4$ stretching bonds at tetrahedral and octahedral sites are observed at absorption bands in the range of 700–400 cm^{-1} [51–55]. The spectral band at ~827 cm^{-1} may be an indication of the presence of organic compounds in the investigated waste material and are assigned to the C–O–C and C–OH ring vibrations of carbohydrates [53]. On the other hand, the bands at 1030, 1005 and 962 cm^{-1} are characteristic for Si-O vibrations and indicated the presence of silica. The asymmetric stretching vibration of Si–O was characterized at 1072 cm^{-1}, the symmetric stretching vibration of Si–O in quartz appeared at 802, 798, 794 and 779 cm^{-1} [56].

3.1.4. Results of Determination of the Specific Surface by the BET Method

The results of the total specific surface area (Sp) of starting samples of the waste vitreous enamels generated from the plant, are presented in Table 5.

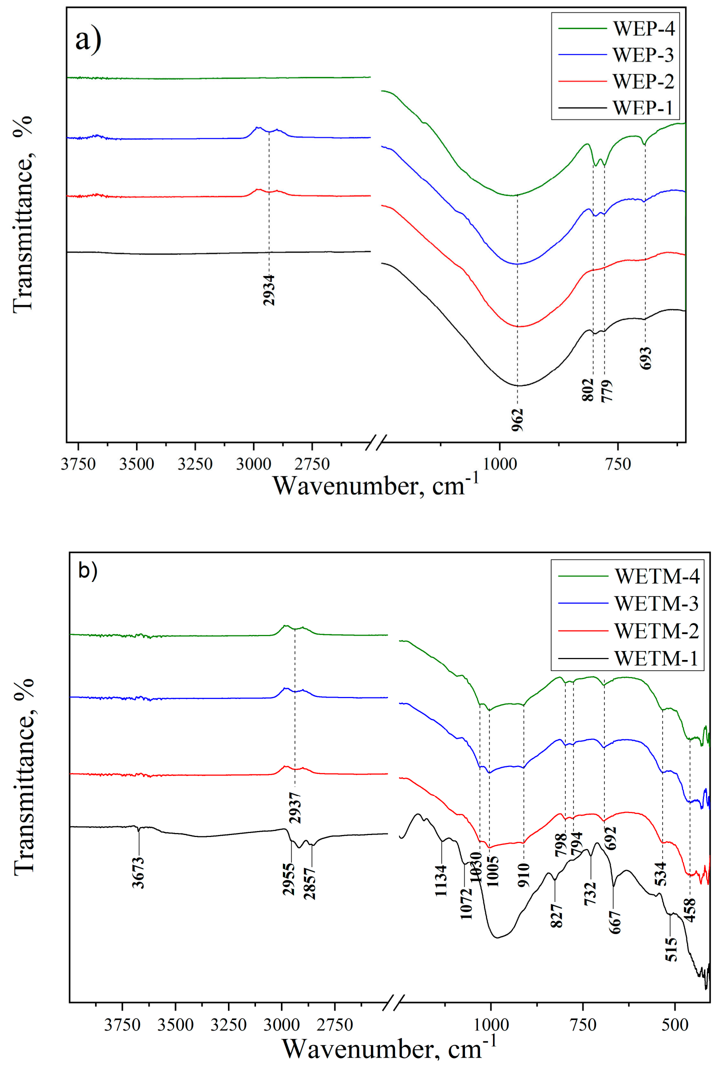

Figure 3. FTIR spectra of the waste vitreous enamels: (**a**) WEP and (**b**) WETM.

Table 5. Porosity parameters of the waste vitreous enamels generated from the plant (batches 1–4).

Sample	**WEP**						**WEMT**					
Batch	**S_p, m^2/g**	**V_{total}, cm^3/g**	**V_{meso}, cm^3/g**	**V_{micro}, cm^3/g**	**D_{sr}, nm**	**D_{max} *, nm**	**S_p, m^2/g**	**V_{total}, cm^3/g**	**V_{meso}, cm^3/g**	**V_{micro}, cm^3/g**	**D_{sr}, nm**	**D_{max} *, nm**
1	8.75	0.0818	0.0633	0.0185	10.87	2.48	6.08	0.0040	0.0002	0.0038	6.49	2.32
2	7.8	0.0816	0.0562	0.0254	9.92	2.53	7.06	0.0057	0.0003	0.0054	7.03	2.36
3	22.3	0.0708	0.0682	0.0026	9.80	2.25	20.08	0.0689	0.0622	0.0067	9.33	2.36
4	8.92	0.0816	0.0632	0.0184	10.95	2.59	6.23	0.0060	0.0002	0.0058	6.57	2.15

* D_{max}—the diameter of the pores that take the largest part of the volume.

The specific surface area of the waste vitreous enamel for both investigated samples in the raw state, was below 10 m^2/g generated in all months except batch 3 when it was 22.3 m^2/g and 20.08 m^2/g for WEP and WETM samples, respectively (Table 5). The appearance of smaller values of specific surface areas of the generated samples is in agreement with the higher degrees of agglomeration. In general, mesopores are formed between particles, while micropores are formed on the particles themselves. However, the standard "EN 197-1-Cement—Part 1 which is applicable in the Republic of Serbia and the EU (Standard EN 13263-1), prescribes that the specific surface area of the waste material should be greater than 15 m^2/g in order to be used as a type II admixture for the production of concrete in accordance with EN 206. This would mean that, due to parameters of textural properties, only samples from batch 3 meet the criteria and can be used as a replacement of cement. In order to overcome this problem and met the required criteria, it is also to further crush all other samples at particle sizes below 45 µm.

3.1.5. Results of Field Emission Scanning Electron Microscopy (FESEM)

The FESEM analysis was conducted for all sampled waste vitreous enamels. Considering that, the investigated surface of the samples was similar for all batches, only representative batch 3 of WEP and WETM, are shown in Figure 4.

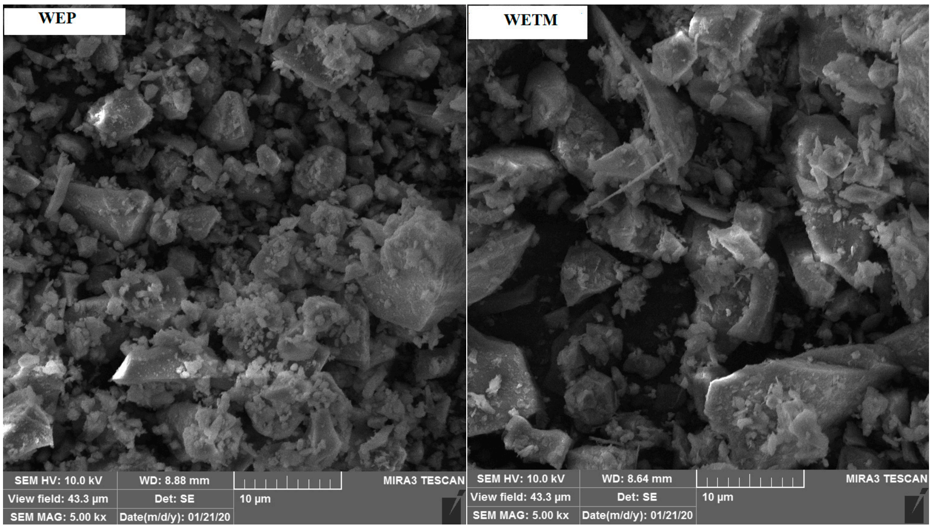

Figure 4. FESEM micrographs of the waste vitreous enamel (batch 3).

Observation at a magnification of 5.00 kX of the microstructure of the generated waste materials shows the appearance of different sizes of particles mainly with polygonal form and pronounced edges in both samples. It is obvious that the application of different production methods does not affect significantly the density or the size and morphology of the particles. Smaller particles, more uniform particle distribution and higher porosity are characteristic of the WEP sample. On the other hand, the WETM sample show larger particles and bimodal particle distribution.

It is known from the literature that smaller white particles of irregular shape and sharp edges, can correspond to fluxes or other components added to the frit [57]. Distinguishing the other particles with a more amorphous shape is difficult since some cover the others, but as mentioned earlier in the introduction, the components of the frit are mainly silica with additives such as alumina, flux and metals (Ti, Zn, Sb and Fe as adhesive agents) to provide chemical adhesion in the interphase between enamel and steel. Larger particles commonly correspond to the silica, while smaller ones correspond to the alumina, and other white particles with a polygonal form are probably belong to metal oxides. This analysis is in good correlation with results obtained by ICP, XRPD and FTIR analysis.

Based on the literature [27], it is known that smaller particles can much more easily slip in the gaps between coarse aggregates and undergo pozzolanic reactions, which indicates that the WEP sample should possess better pozzolanic activity in comparison to WETM. These pozzolanic reactions are able to reduce the water and air pockets in the concrete matrices, which indicates that the concrete mixture containing WEP will have better properties and higher density compared to the mixture containing WETM.

3.2. Results of Determination of the Pozzolanic Activity, Parameters of Cement Paste, Mortar and Concrete Produced with the Addition of Waste Enamels

3.2.1. Determination of the Pozzolanic Activity of Waste Enamels

In order to determine the feasibility of using of the waste vitreous enamels generated from the plant for four mounts (batches 1–4): as a type II admixture for the production of concrete in accordance with EN 206, first was tested their pozzolanic activities and determined activity indexes and the results are presented in Tables 6 and 7.

Table 6. Pozzolanic activity and parameters of cement paste with the addition of WEP.

Property	Parameters/Results				Requirement
	Batch 1	Batch 2	Batch 3	Batch 4	
Class of pozzolanic materials	Flexural strength: 4.5 mPa Comp. strength: 17.2 mPa	Flexural strength: 4.1 mPa Comp. strength: 16.8 mPa	Flexural strength: 2.1 mPa Comp. strength: 7.0 mPa	Flexural strength: 2.1 mPa Comp. strength: 7.4 mPa	>2.0/4.0 mPa (class 5/15) >5.0/15.0 mPa (class 5/15)
Activity index	After 28 days: 80.80% After 90 days—87.48%	After 28 days: 77.62% After 90 days—87.49%	After 28 days: 75.24% After 90 days—85.74%	After 28 days: 76.24% After 90 days—86.28%	>75% >85%
Water requirement	93%	94%	93%	94%	<95%
Standard consistency	29.5%	29.5%	30%	29.5%	not prescribed
Initial setting time	135 min	145 min	150 min	140 min	<230 min
Final setting time	160 min	180 min	180 min	170 min	not prescribed
Roundness	1.0 mm	1.0 mm	1.0 mm	1.0 mm	<10 mm

Table 7. Pozzolanic activity and parameters of cement paste with addition of WETM.

Property	Parameters/Results				Requirement
	Batch 1	Batch 2	Batch 3	Batch 4	
Class of pozzolanic materials	Flexural strength: 2.8 mPa Comp. strength: 8.4 mPa	Flexural strength: 2.1 mPa Comp. strength: 7.0 mPa	Flexural strength: 2.1 mPa Comp. strength: 6.9 mPa	Flexural strength: 2.2 mPa Comp. strength: 7.2 mPa	>2.0/4.0 mPa (class 5/15) >5.0/15.0 mPa (class 5/15)
Activity index	After 28 days: 73.45% After 90 days—85.10%	After 28 days: 78.62% After 90 days—89.29%	After 28 days: 75.86% After 90 days—86.13%	After 28 days: 76.78% After 90 days—87.08%	>75% >85%
Water requirement	98%	97%	100%	98%	<95%
Standard consistence	31.0%	30.5%	31.5%	31.0%	not prescribed
Initial setting time	175 min	165 min	185 min	170 min	<230 min
Final setting time	200 min	190 min	210 min	200 min	not prescribed
Soundness	0.5 mm	0.5 mm	0.5 mm	0.5 mm	<10 mm

An examination of the pozzolanic activity of the waste enamels WEP (batches 1 and 2) (Table 6) showed that it belongs to the class of 15 pozzolanic materials (the largest class), while by the values of its pozzolanic activity for batches 3 and 4 it belongs to class 5 of pozzolanic materials (lowest class). Waste enamel WETM, according to the values of pozzolanic activity also belongs to the class 5 of pozzolanic materials (Table 7). Additionally, both waste enamels meet the criteria for the activity index according to EN 450-1, which refers to their possible use as a type II admixture for the production of concrete in accordance with EN 206.

Waste enamels WEP in terms of water requirement, initial setting time and soundness meet the criteria prescribed by the Standard. Waste enamels WETM, in terms of initial setting time and soundness met the criteria prescribed by the Standard, while the water requirement was slightly above the allowed value. Replacement of cement with 25% of waste enamels did not significantly affect the standard consistency of the cement paste. After confirming the pozzolanic activity of waste enamels, the effect of partial replacement of cement with waste materials on the properties of mortar and concrete was further investigated. Given that WEP showed a higher class of pozzolanic activity (class 15) compared to WETM (class 5), the replacement of cement in the production of mortar and concrete in further research was in the range of 0–40% for WEP, i.e., 0–30% for WETM. These results of pozzolanic activity are in good correlation with the results of FESEM analysis, which indicated better properties of the concrete mixture containing WEP in comparison with the mixture containing WETM.

3.2.2. Effects of Waste Enamels on Mortar Properties

Test results of the physical and mechanical properties of mortar mixtures with the addition of waste enamels are given in Tables 8–11 and Figures 5–10.

Table 8. Physical properties of mortar mixtures with WEP.

Property	Unit	M-E	WEP-M-10	WEP-M-20	WEP-M-30	WEP-M-40
Consistency—by flow table	mm	135 ± 2.0	141 ± 3.0	137 ± 2.5	130 ± 2.0	125 ± 3.0
Bulk density of fresh mortar	kg/m^3	2299 ± 8	2295 ± 7	2288 ± 6	2279 ± 8	2270 ± 9
Bulk density of hardened mortar	kg/m^3	2294 ± 7	2290 ± 9	2283 ± 7	2276 ± 6	2265 ± 8
Water abs. at atm. pressure	%	7.54 ± 0.12	7.70 ± 0.10	7.81 ± 0.08	7.91 ± 0.11	7.99 ± 0.10

Table 9. Physical properties of mortar mixtures with WETM.

Property	Unit	M-E	WETM-M-7.5	WETM-M-15	WETM-M-22.5	WETM-M-30
Consistency—by flow table	mm	135 ± 2.0	137 ± 2.5	143 ± 3.5	134 ± 3.0	125 ± 2.5
Bulk density of fresh mortar	kg/m^3	2299 ± 8	2301 ± 6	2285 ± 9	2272 ± 7	2265 ± 8
Bulk density of hardened mortar	kg/m^3	2294 ± 7	2297 ± 7	2281 ± 8	2268 ± 9	2260 ± 7
Water abs. at atm. pressure	%	7.54 ± 0.12	7.66 ± 0.11	7.75 ± 0.10	7.84 ± 0.12	7.94 ± 0.09

Table 10. Drying shrinkage of the mortar mixtures with WEP.

Designation of Mortar	M-E	WEP-M-10	WEP-M-20	WEP-M-30	WEP-M-40
Age [Days]			$\varepsilon_{sm,sr}$[mm/m]		
3	0.00	0.00	0.00	0.00	0.00
4	0.25 ± 0.02	0.25 ± 0.02	0.24 ± 0.02	0.23 ± 0.02	0.23 ± 0.02
7	0.38 ± 0.03	0.36 ± 0.03	0.34 ± 0.01	0.31 ± 0.02	0.30 ± 0.03
14	0.59 ± 0.01	0.59 ± 0.03	0.60 ± 0.03	0.60 ± 0.03	0.61 ± 0.01
21	0.69 ± 0.03	0.73 ± 0.02	0.78 ± 0.02	0.82 ± 0.02	0.85 ± 0.02
28	0.91 ± 0.02	0.93 ± 0.02	0.97 ± 0.03	0.99 ± 0.03	1.02 ± 0.03
56	0.93 ± 0.02	0.94 ± 0.01	0.99 ± 0.01	1.01 ± 0.02	1.04 ± 0.02
90	0.94 ± 0.03	0.95 ± 0.03	1.01 ± 0.02	1.03 ± 0.01	1.06 ± 0.02

Table 11. Drying shrinkage of the mortar mixtures with WETM.

Designation of Mortar	M-E	WETM-M-7.5	WETM-M-15	WETM-M-22.5	WETM-M-30
Age [Days]			$\varepsilon_{sm,sr}$[mm/m]		
3	0.00	0.00	0.00	0.00	0.00
4	0.25 ± 0.02	0.23 ± 0.02	0.20 ± 0.03	0.18 ± 0.02	0.17 ± 0.03
7	0.38 ± 0.03	0.37 ± 0.03	0.34 ± 0.02	0.32 ± 0.01	0.30 ± 0.01
14	0.59 ± 0.01	0.58 ± 0.03	0.58 ± 0.01	0.56 ± 0.03	0.55 ± 0.03
21	0.69 ± 0.03	0.71 ± 0.02	0.73 ± 0.02	0.74 ± 0.02	0.76 ± 0.02
28	0.91 ± 0.02	0.92 ± 0.02	0.93 ± 0.03	0.93 ± 0.01	0.94 ± 0.03
56	0.93 ± 0.02	0.94 ± 0.01	0.96 ± 0.02	0.96 ± 0.03	0.97 ± 0.02
90	0.94 ± 0.03	0.96 ± 0.02	0.99 ± 0.01	0.99 ± 0.02	1.01 ± 0.02

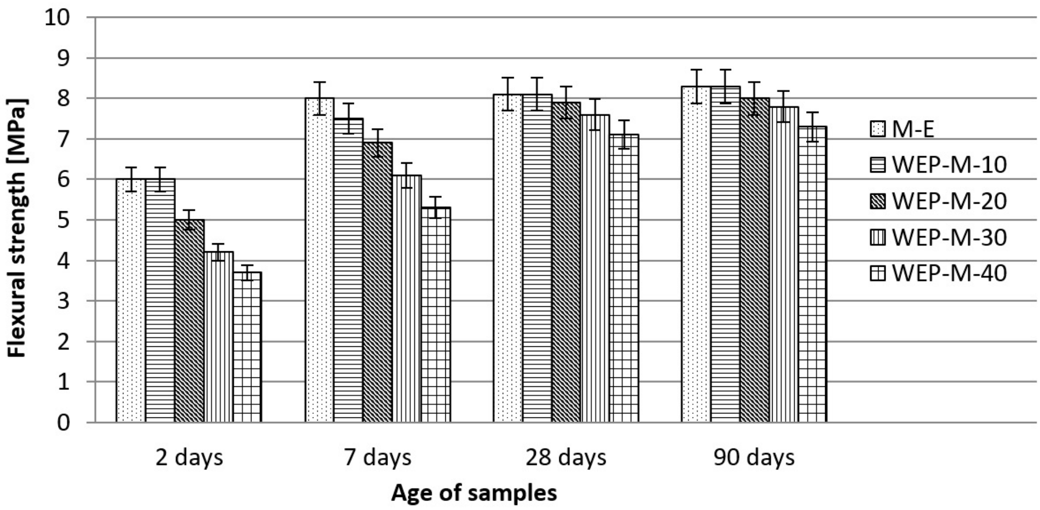

Figure 5. Flexural strength of mortar samples with WEP.

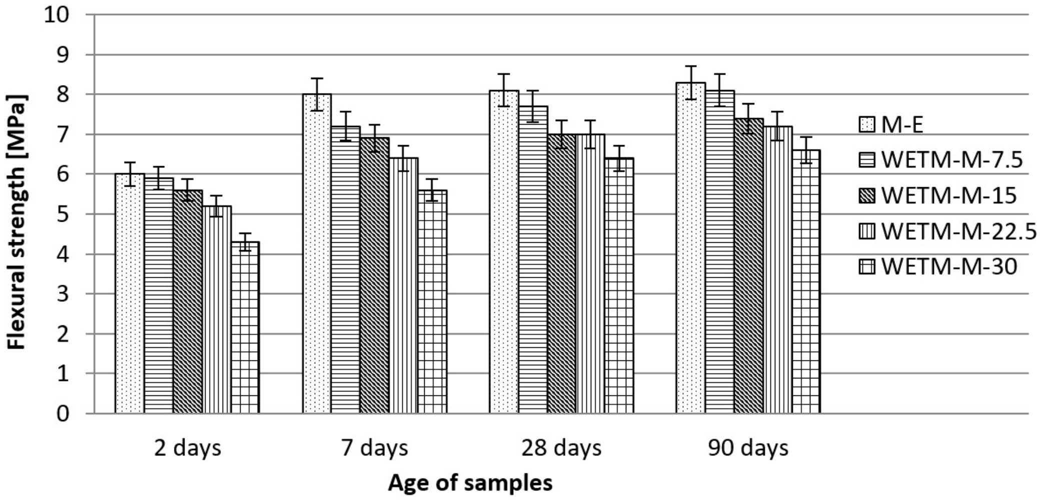

Figure 6. Flexural strength of mortar samples with WETM.

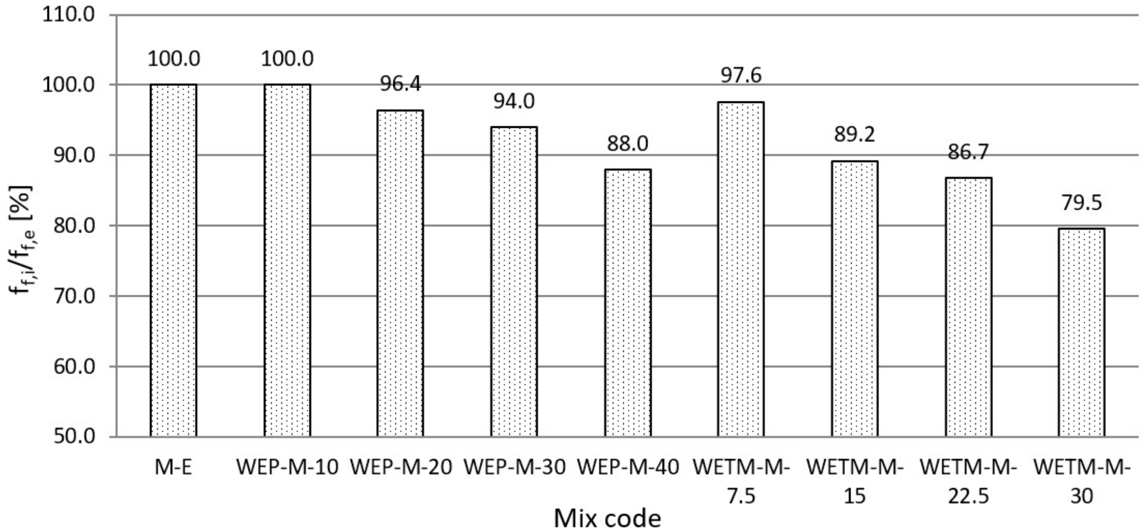

Figure 7. Percentage ratio of flexural of mortar with waste enamels and reference mortar at 90 days.

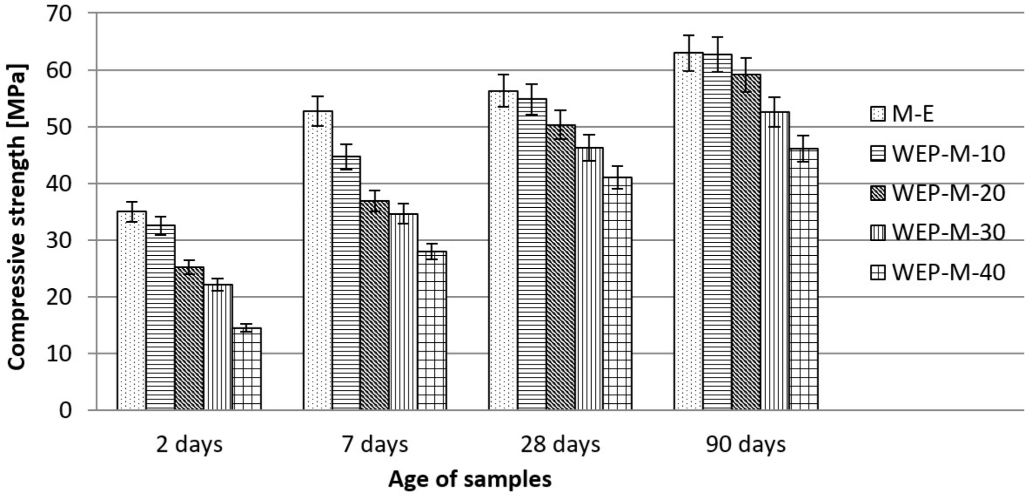

Figure 8. Compressive strength of mortar samples with WEP.

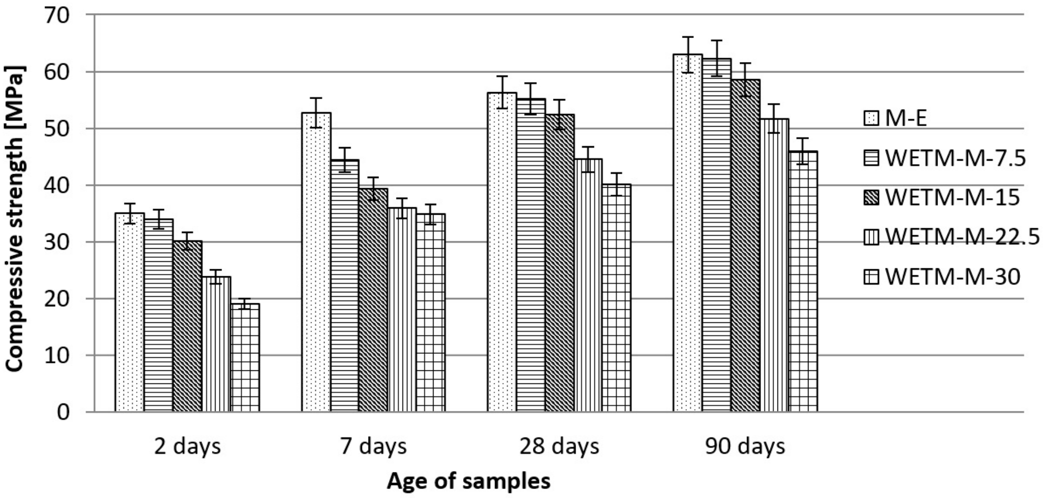

Figure 9. Compressive strength of mortar samples with WETM.

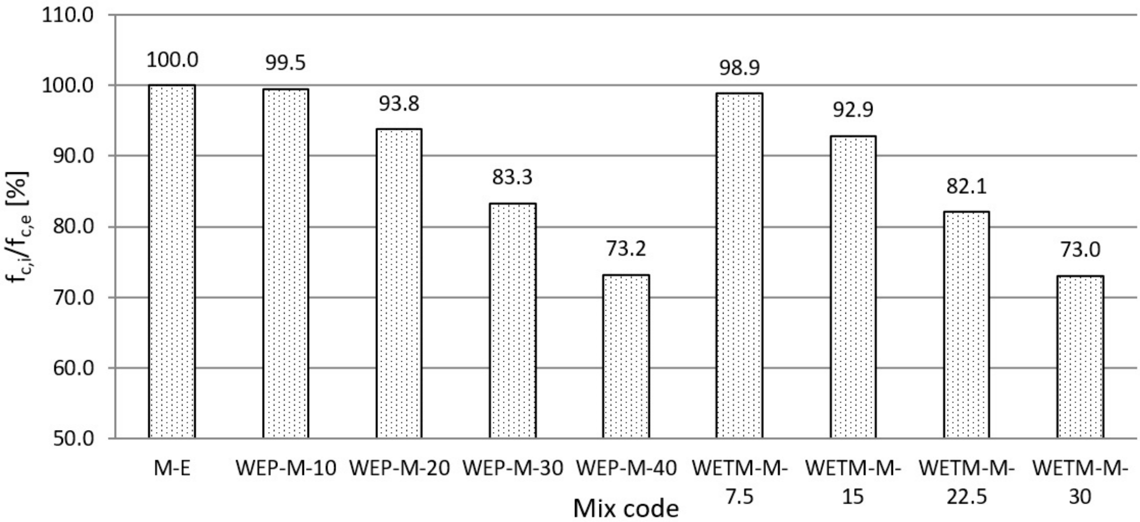

Figure 10. The percentage ratio of compressive strength of mortar with waste enamels and reference mortar at 90 days.

The physical properties of mortar were not considerably influenced by the use of waste materials as the substitution for cement. As it may be seen from the presented results, the consistency of the mortar, i.e., the spreading, grew slightly, and then decreases with the increase in the replacement of cement with waste enamels. The spreading variation is within ±10 mm. Generally, all types of mortars meet the criteria prescribed by the Standard for plastic consistency of mortar. Apart from that, the results of the substitution of cement with WEP and WETM samples show a small decline in the bulk density of the mortar in the fresh and hardened state. This reduction is greater in mortars with the addition of WETM. The absorption of water at atmospheric pressure was the lowest on the reference mortar, and with an increase in the percentage of cement replacements in the mixtures, the absorption of water slightly increase. A possible reason is the higher porosity interfacial transition zone between cement paste and aggregate in a mortar with waste enamels compared to reference mortar.

Drying cement mortar shrinkage measurement results show that mortar mixtures with waste materials added demonstrated lower shrinkage values in the initial hardening phase (first 7 days) in comparison with the reference mortar. At 14 days, mortar mixtures with WEP featured almost the same shrinkage values, while mortar mixtures with WETM demonstrated somewhat higher shrinkage than the reference mortar. In the later hardening phase (days 21 to 90), the reference mortar showed a lower shrinkage than the mortars in which waste materials partially substituted the cement. Greater shrinkage was observed in mortars where cement was replaced by waste enamel WEP. This does not match with the fact that in the cement hydration process, the pozzolanic reaction occurs later and after the formation of Portland (calcium-hydroxide), which is necessary for its initiation. The hydration products shrank due to the pozzolanic reaction, which caused increased shrinkage of the mortars with waste enamels added [58–60].

The quality of cement composites primarily depends on mechanical strengths, especially compressive strength. The flexural and compressive strength tests were performed at the mortar specimen age of 2, 7, 28 and 90 days. A graphical representation of the results is shown in Figures 5–10. Based on the test results, it was observed that for 2 and 7 days, increasing the amounts of cement replacements causes a decrease in the mortar strengths, regardless of the type of waste enamel. On the other hand, for 28 and 90 days, the strength of mortar prisms with waste materials slowly approaches the values of the reference mortar. That may be attributed to the pozzolanic reaction of the waste materials, which is manifested at a later stage of hardening. Due to higher pozzolanic activity, mortar samples with WEP waste enamel have a faster increase in mechanical strengths compared to samples with WETM addition. For that reason, the percentage of possible replacement of cement is estimated on the basis of strengths at 90 days and can be up to 20% for all tested materials. If the drop in strength of mortar samples at 90 days in the amount of 20% is acceptable, then the maximum replacement of cement with WEP is 30%, and with WETM is slightly more than 20%.

3.2.3. Effects of Waste Enamels on Concrete Properties

Related to testing the pozzolanic activity of used materials it was concluded that WEP has a higher pozzolanic activity (Class of pozzolanic materials is 15) compared to WETM waste material (Class of pozzolanic materials is 5). Therefore, it was decided that the replacement of cement with waste material WEP should be up to 40%, and the replacement of cement WETM should be up to 30%.

The different steps of replacing cement with WEP and WETM (10% for WEP, i.e., 7.5% for WETM, etc.) do not affect the final result of the research. In addition, for all tests performed on composites, there are results of both, WEP and WETM, samples with 30% added waste.

Test results of physical, mechanical and durability properties of concrete mixtures with addition of waste enamels are given in Tables 12–15 and Figures 11–13.

Table 12. Physical properties of concrete mixtures with WEP.

Property	Unit	C-E	WEP-C-10	WEP-C-20	WEP-C-30	WEP-C-40
Consistency—slump test	mm	200 ± 10	210 ± 11	220 ± 10	180 ± 10	170 ± 12
Density of fresh concrete	kg/m^3	2466 ± 12	2452 ± 0	2490 ± 12	2488 ± 11	2492 ± 11
Air content in fresh concrete	%	2.6 ± 0.19	2.0 ± 0.15	1.8 ± 0.17	1.7 ± 0.16	1.5 ± 0.18
Density of hardened concrete (water saturated)	kg/m^3	2455 ± 10	2442 ± 11	2483 ± 10	2482 ± 12	2485 ± 11
Determination of ultrasonic pulse velocity	km/s	5.21 ± 0.022	5.15 ± 0.015	5.21 ± 0.017	5.19 ± 0.018	5.19 ± 0.016

Table 13. Physical properties of concrete mixtures with WETM.

Property	Unit	WETM-C-E	WETM-M-10	WETM-C-20	WETM-C-30
Consistency—slump test	mm	200 ± 10	160 ± 11	110 ± 9	100 ± 10
Density of fresh concrete	kg/m^3	2466 ± 12	2488 ± 10	2479 ± 9	2455 ± 11
Air content in fresh concrete	%	2.6 ± 0.19	2.7 ± 0.17	2.5 ± 0.15	2.3 ± 0.16
Density of hardened concrete (water saturated)	kg/m^3	2455 ± 10	2484 ± 11	2471 ± 12	2447 ± 10
Determination of ultrasonic pulse velocity	km/s	5.21 ± 0.022	5.19 ± 0.021	5.16 ± 0.017	5.12 ± 0.016

Table 14. Mechanical and durability properties of concrete mixtures with WEP.

Property		Unit	C-E	WEP-C-10	WEP-C-20	WEP-C-30	WEP-C-40
Flexural strength	28 days 90 days	mPa	7.0 ± 0.2 7.4 ± 0.3	5.1 ± 0.3 5.5 ± 0.3	4.9 ± 0.2 5.4 ± 0.1	4.7 ± 0.2 5.1 ± 0.3	4.6 ± 0.2 5.0 ± 0.2
Compressive strength		mPa	See Figure 11				
Tensile splitting strength	28 days	mPa	3.9 ± 0.2	3.8 ± 0.3	3.7 ± 0.2	3.5 ± 0.3	3.2 ± 0.2
Secant modulus of elasticity	28 days	gPa	33.0 ± 0.3	34.2 ± 0.3	34.9 ± 0.2	33.5 ± 0.2	32.7 ± 0.3
Dept of penetration of water under pressure		mm	12 ± 2	10 ± 2	14 ± 3	12 ± 2	13 ± 3
Freeze–thaw resistance with de-icing salts—Scaling		kg/m^2	0.14 ± 0.02	0.16 ± 0.03	0.12 ± 0.03	0.15 ± 0.02	0.18 ± 0.03

Table 15. Mechanical and durability properties of concrete mixtures with WETM.

Property		Unit	WETM-C-E	WETM-C-10	WETM-C-20	WETM-C-30
Flexural strength	28 days 90 days	mPa	7.0 ± 0.2 7.4 ± 0.3	6.3 ± 0.1 6.7 ± 0.2	5.9 ± 0.3 6.5 ± 0.223	5.7 ± 0.2 6.2 ± 0.3
Compressive strength		mPa	See Figure 12			
Tensile splitting strength	28 days	mPa	3.9 ± 0.2	3.8 ± 0.3	3.6 ±0.2	3.5 ± 0.2
Secant modulus of elasticity	28 days	gPa	33.0 ± 0.3	32.6 ± 0.3	32.3 ± 0.3	31.8 ± 0.2
Dept of penetration of water under pressure		mm	12 ± 2	14 ± 2	15 ± 3	17 ± 3
Freeze–thaw resistance with de-icing salts—Scaling		kg/m^2	0.14 ± 0.02	0.14 ± 0.03	0.16 ± 0.02	0.19 ± 0.03

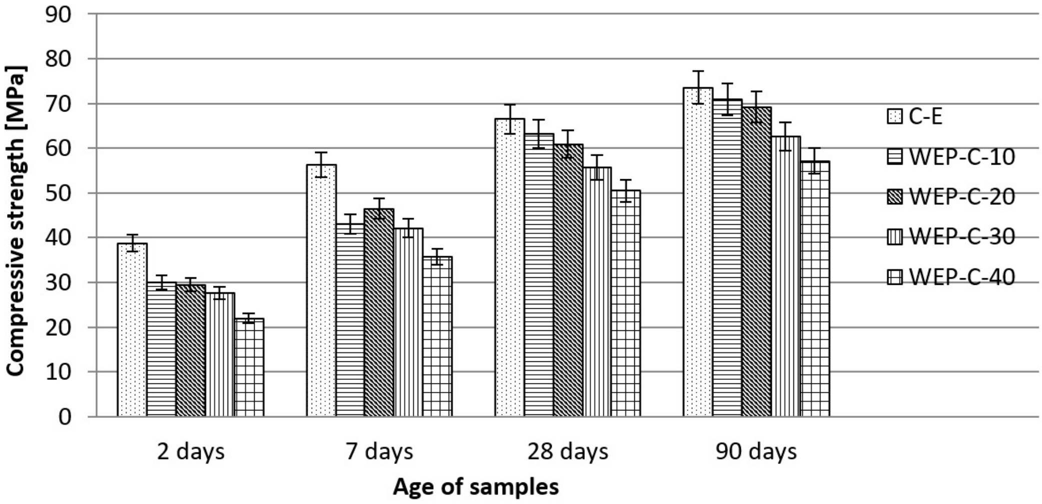

Figure 11. Compressive strength of concrete samples with WEP.

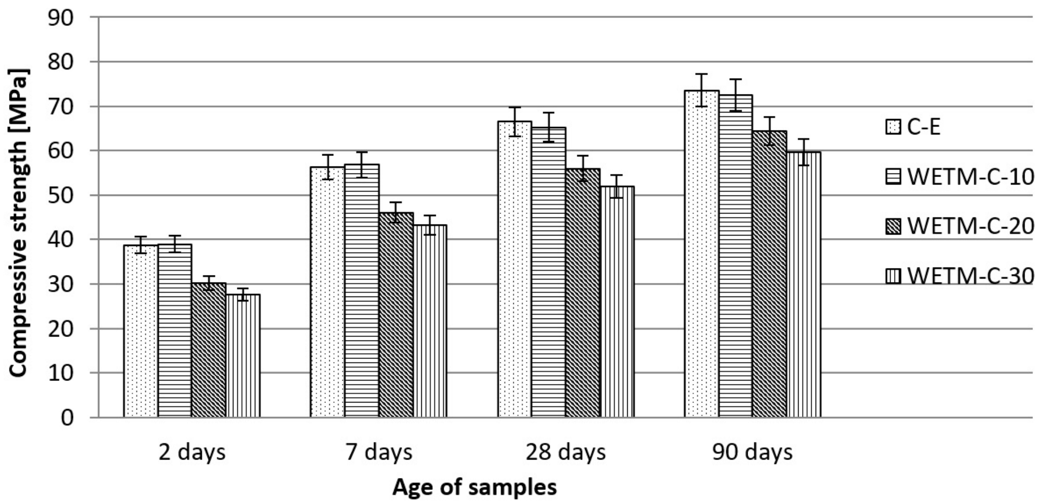

Figure 12. Compressive strength of concrete samples with WETM.

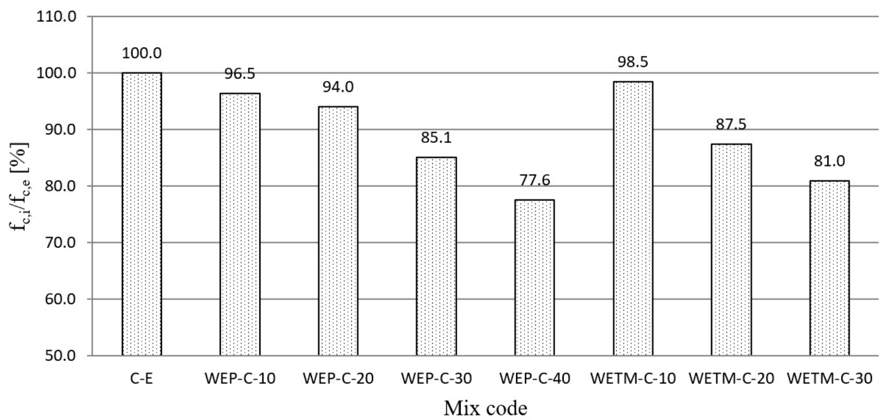

Figure 13. The percentage ratio of compressive strength of concrete with waste enamels and reference concrete at 90 days.

As can be seen from the results of the concrete consistency test, the replacement of cement with WEP up to 20% caused an increase in the slump, while a further increase in WEP amount decreased the slump. On the other hand, an increase in the amount of WETM caused a significant decrease in the slump. That may be due to the porosity of WETM and its ability to retain water and thereby reducing the amount of free water in the concrete mixture and therefore its consistency.

The content of entrained air into fresh concrete decreased with an increasing percentage of cement replacement, which can be attributed to the better placement of concrete prepared with waste enamels. The replacement of cement with waste materials caused an improper change in bulk density. However, those changes vary within the limits up to ±1%, which is acceptable.

The most important factors that affect ultrasonic pulse velocity through concrete are the concrete porosity, aggregate type and interfacial transition zone (ITZ). Based on the results presented in Tables 12 and 13, all concrete mixtures had values of ultrasonic velocity higher than 4.5 km/s which is a limit for strong concrete [60]. The differences in the values of the ultrasonic velocities in concretes with the addition of WEP and WETM were insignificant, which indicates that all concrete mixtures had an approximately uniform quality in terms of physical and mechanical characteristics.

The test was performed at 28 and 90 days, the samples were tested to flexural strength. Based on results presented in Tables 13 and 14, one can conclude that the flexural strength declined with an increase in the percentage of cement substitution, and the decline compared with reference concrete was the in the range 26–32% for concretes with WEP and 9–16% for concretes with WETM at a test samples age of 90 days.

Compressive strength is the most important property of concrete and test samples of 2, 7, 28 and 90 days were used to determine it. Based on the results shown at Figures 11 and 12, it can be observed that with the increase in the content of waste enamels, the compressive strength of concrete samples decreased at all ages of concrete, except for the "WETM-C-10" mixture at 2 and 7 days. In the first 7 days, the concrete mixtures "C-E" and "WETM-C-10" had the highest compressive strength increase, while with increasing age, the compressive strength of concrete treated with waste enamels approached the value for reference due to a delayed pozzolanic reaction. With the increasing concrete age, a small decline in compressive strength was observed with an increase in the percentage of cement replacement by waste materials. The authors [17,58,59] in the study of the properties of concrete with the addition of recycled glass and waste vitreous enamel had comparable inferences.

Figure 13 shows the percentage ratio of compressive strength of concrete with waste enamels and reference concrete at 90 days. With an increasing percentage of cement replacement, a small decline in compressive strength can be observed, irrespective of the type of waste enamel used. As for the compressive strength, the cement substitution with waste enamel WEP turned out to be more effective. If the level of compressive strength reduction of 15% is acceptable, it can be concluded that up to 30%, i.e., 20% of the cement can be replaced with WEP, i.e., WETM in concrete production.

The results from Tables 14 and 15 show that the tensile splitting strength slightly declined with the increase in the percentage of cement substitution, irrespective of the waste enamel type used. The highest strength value (3.9 mPa) was observed for the reference concrete, while the concrete mixtures with 30% cement substitution by WEP and WETP showed 10% lower tensile splitting strength.

At a sample age of 28 days, the secant modulus of elasticity of concrete was examined. Observable in Tables 14 and 15 is that the modulus of elasticity of concrete increased with the increase in the percentage of cement substitution by WEP of up to 20% when it reaches the maximum value (34.9 gPa). With the further increase in the substitution share of cement, the modulus of elasticity slowly declined to reach a minimum for concrete with 40% cement substitution (32.7 gPa). In the event of substituting cement with WETM, with an increase in the percentage of cement substitution, the values of the secant modulus of elasticity of concrete slightly declined.

Depth of penetration of water under pressure and freeze–thaw resistance with de-icing salts are the properties of concrete that relate to its durability. The results of the testing of these properties are given in Tables 14 and 15. The results of concrete with the addition of

WEP showed that the depth of penetration of water is in the range of 12 ± 2 mm, where there is no proper dependence between the depth of penetration and the percentage of cement replacement. On the other hand, with an increase in the percentage of cement replacement by WETM, the depth of penetration of water slightly increased. The concrete mixture WETM-C-30 (17 mm) demonstrated the greatest depth of penetration of water. According to Neville and Brooks [60], since no concrete mixture demonstrates a penetration greater than 30 mm all concrete mixtures can be considered as waterproof. It can be inferred that there is no negative effect of waste enamels on the mixtures resistance to pressurized water action.

Test results of freeze–thaw resistance with de-icing salts are given in Tables 14 and 15. The concrete mixture with 20% substitution of cement by WEP (0.12 kg/m^2), which is slightly less than standard concrete (0.14 kg/m^2) showed the least scaling of the concrete surface after 56 freezing-thaw cycles with de-icing salt. The values of surface scaling of concrete with the addition of WEP were in the range of 0.12–0.18 kg/m^2. On the other hand, with the percentage increase in the substitution of cement by WETM, the scaling of the concrete surface slightly increased. The greatest scaling of the concrete surface was recorded in the case of the concrete mixture marked WETM-C-30 (0.18 kg/m^2).

3.2.4. The Leaching Test

In order to confirm the environmental safety of using mortar mixtures, the leaching test was performed on the mixtures with maximally allowed cement replacement, where the mortar mixtures were made with 30% of WEP, and 20% of WETM. The results are shown in Table 16.

Table 16. The concentration of the released elements after the leaching test.

Released Element	Concentration, µg/dm^3		* Allowed Values, µg/dm^3
	WEP	WETM	
Cu	34	5	<100
Zn	21	15	<1000
Ni	10	20	<100
Cd	1	1	<10
Pb	20	30	<100
Cr	7	2	<500
Hg	48	4	<1
As	22	31	<50
Mg	8	5	-
Fe	1270	31,000	-
Co	<10	<10	-
Al	2280	544	-
Sn	698	5	-
Si	470	420	-
Mo	1	<1	-
Sr	600	140	-
Ca	100	400	-
Mn	<1	<1	-
V	10	<10	-

* According to the Rulebook on permitted quantities of hazardous and harmful substances in soil and irrigation water and methods of their testing, "Službeni glasnik RS 23/1994"—applicable in Serbia. Dashes mean that the Rulebook does not prescribe limits.

From obtained results, it can be seen that, according to the Rulebook which is applicable in Serbia, the concentrations of the released elements from both examined mortar mixtures were much lower than allowed.

In order to fully confirm that the application of waste vitreous enamel is safe for the environment, the leaching test was continued and performed for the next 60 days. The concentration of released elements did not differ significantly in comparison with those shown in Table 16, for the whole examined time interval.

Thus, it may be concluded that the application of the waste vitreous enamel as a partial replacement for cement in mortar and concrete productions is completely acceptable from ecological and human health safety aspects.

4. Conclusions

The production of heating devices generates solid wastes that are harmful to the environment but can be managed. This paper presents research into the possibility of using waste enamels for the production of cement composites. According to the experimental results and results of testing the pozzolanic activity of waste vitreous enamels, as well as their influence on the properties of cement paste, mortar and concrete, several major conclusions are drawn as follows:

1. Used waste enamels possess pozzolanic activity and belong to class 15 (WEP), that is 5 (WETM) of pozzolanic materials. Additionally, both waste enamels meet the criteria for the activity index according to EN 450-1, which refers to their possible use as a type II admixture for the production of concrete in accordance with EN 206. Waste enamels WEP and WETM in terms of water requirement, initial setting time and soundness meet the criteria prescribed by the Standard.
2. Examinations of the physical and mechanical properties of mortars with waste enamels have shown that these materials can be used as a replacement for cement in the production of mortar, where is recommended a maximum cement replacement in the amount of 30% for WEP, and 20% for WETM. These replacements of cement with waste enamels in mortar do not significantly affect its physical and mechanical characteristics in comparison with the characteristics of the reference mortar prepared with 100% cement.
3. The use of waste enamels in concrete, as a partial replacement of cement, contributes to a slight decrease in physical and mechanical properties, while on the other hand, it does not compromise the durability of the concrete. Test results indicate that the replacement of cement with WEP up to 30%, or WETM up to 20% does not significantly affect the quality of concrete compared to the quality of the reference concrete prepared with 100% cement.
4. Bearing in mind that vitreous waste enamels can be used for the production of cement composites, the problem of their disposal is solved, which is a great contribution to preserving a healthy environment.
5. Further research should be focused on studying the behavior of reinforcement in concrete produced with the addition of waste enamels, as well as the possibility of the production of concrete paving flags and blocks.

In general, by finding a useful value for vitreous enamel waste materials and their application, the process will be improved and contribute to cleaner production, as the most suitable for industrial application.

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