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WASTE TONER POWDER IN CONCRETE INDUSTRY: AN APPROACH TOWARDS CIRCULAR ECONOMY

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Abstract

Substantial quantities of toner cartridges are produced and used in photocopiers and printers every year. Spent toner cartridges are classified as hazardous waste because they contain toner powder with specific chemical composition, making a recovery of waste toner cartridges a very important issue from the aspect of waste management and environmental protection. Spent toner cartridges are mechanically processed to exploit valuable materials such as metals, plastics and magnets and to separate toner powder as a toxic waste. In this work, the use of waste toner powder as an additive in concrete was studied. The toner powder was mixed with calcium-based additive in ratio 50:50 immediately after the mechanical treatment. The resulting mixture (hereafter: WTP) was added to concrete at different percentages (1%, 3,%, 5% and 10%) as a replacement for fine aggregate. All processes were performed on industrial scale. The addition of 1% and 3% of WTP lead to a concrete with the optimal properties. The possible impact on the environment was studied by the means of leaching test using valid regulations for a landfill. The modified concrete with 1%, 3%, 5% WTP can be classified as inert waste.

Key words: circular economy, concrete industry, environmental impact, recycling, waste toner

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1. Introduction

The European Union (EU) seeks to build a foundation for the development of a circular economy model, where waste is considered a raw material and thus is used in an efficient and sustainable manner (Charles et al., 2015; Cucchiella et al., 2015). The EU has focused on the processing of waste electrical and electronic equipment (WEEE) due to a series of explicit warnings (Cucchiella et al., 2015; Gurauskiene and Stasiskiene, 2018). The WEEE Directive (Directive 2012/19/EU) and the RoHS Directive (EC Directive, 2011) are the most relevant examples. The intention of circular economy is to achieve so called 'closed loop' of recycling in order to reduce environmental impacts. The manufacturing companies should take back their own waste products to secure their material resources (Charles et al., 2015; Singh and Ordoñez, 2016). In so called, 'open loop' recycling process, resources are mostly recirculated to make different types of product (Gnoni et al., 2017; Singh and Ordoñez, 2016). In such industrial symbiosis, material and waste management costs can be reduced, new revenue from waste and by-products can be generated, environmental emissions can be reduced, waste can be diverted from landfill particularly (Charles et al., 2015), innovative ways to optimize the value of the residues of processes from different industry are found (Domenech et al., 2019). One of the aims of circular economy is to minimize resources leakage through energy recovery and landfill.

The recovery of waste toner cartridges is a meaningful subject, not only from waste treatment but also from environmental protection point of view (Jujun et al., 2011; Sepperumal et al., 2014).

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Tremendous amounts of toner cartridges are produced and used worldwide in copiers and printers. For instance, approximately 115 tons of spent toner cartridges were collected and recycled in Republic of Croatia in 2017. Spent toner cartridges include the following components: 40 % steels, 35 % plastics, 5 % magnets, 12 % aluminum and 8 % toner powder (Patronov and Tonchev, 2011; Jujun et al., 2011).

The long-term common treatment practice of waste spent toner cartridges was landfilling and incineration. However, a disposal on landfills and incineration are not suitable treatment technologies for spent toner cartridges since plastics have very slow environmental degradation rate, and residual toner powder can leak into the environment, presenting the risk of pollution of soil and groundwater (Jujun et al., 2013). Controlled incineration of spent toner cartridges and waste toner powder is an acceptable waste management solution (Patronov and Tonchev, 2011). According to Patronov and Tonchev (2011), waste toner powder has higher calorific value than conventional fossil fuels (about 30 MJ/kg). Therefore, if the incineration is carried out under appropriate conditions, waste toner powder could be used as fuel. Some reports showed the drawbacks of traditional incineration due to decreased flammability of toner powder and huge resistance in combustion process caused by presence of inorganic materials (Jujun et al., 2013). Moreover, uncontrolled combustion could lead to emissions of PAHs, furans and dioxins. In addition, valuable materials remain uncirculated. As resource recovery reduces and eventually eliminates the need for incinerators and landfills, waste has been increasingly seen as a secondary raw material (Mihajlov and Stevanović - Čarapina, 2015).

The main idea of circular economy is to benefit economically and environmentally from making better use of finite and scarce resources and related valuable materials. The revised EU waste legislative sets clear targets for reduction of waste and establishes an ambitious path for waste management and recycling. Key elements of the revised legislative include common targets (by 2030) for recycling of municipal and packaging waste; reducing landfill to maximum of 10 % of municipal waste with a ban on landfilling of separately collected waste; concrete measures to promote re-use and stimulate industrial symbiosis, etc. (EC Directive 2018). The changes in EU legislative in collection targets could guarantee around 10 million tonnes of e-waste (or roughly 20 kg per capita) collected in the EU in 2020 (Awasthi et al., 2018).

Recent papers suggest that increased resource efficiency is possible and that it can bring major economic, environmental and social benefits. One way to assist the industry in transition to circular economy is to improve usage of materials obtained from waste recycling processes (Awasthi et al., 2018; Comanita et al., 2018). Waste toner cartridges are no different. However, dispersed toner dust reduces the options for identification, separation and recycling making classical mechanical recycling of waste cartridges a difficult task (Salhofer and Tesar, 2011). Thus, prior to any kind of recycling treatment, toner cartridges should be removed from printer/copiers (EC Directive, 2012). Approximately 10 % of toner powder remains in photocopiers (Koseki, 2014; Vignesh, 2015; Yildirim et al., 2004) of which 66 % is being recovered (Anić Vučinić et al., 2016).

Waste toner powder is of different particle size compared to the original toner and contaminated with dust picked up from paper. The quantity of this waste depends upon the usage of toner and the inability of the paper to grasp complete toner particles from the drum (Vignesh, 2015). The toner powder is not considered as an environmental hazard, it is not combustible or flammable. However, waste toner powder contains substances, some of which are toxic and carcinogenic for humans if inhaled (Salhofer and Tesar, 2011).

In air, waste toner powder may cause explosion due to the small particle size (2-12 µm) and high carbon content (Gminski et al., 2011; Yildirim et al., 2004). The dust explosions of toner cartridges have been reported throughout recycling facilities in Japan (Koseki, 2014). Trends even foster the production of finer toner powder with related hazards. In our previous paper, the addition of calcite in an inert atmosphere was used to decrease the risk of explosion (Anić Vučinić et al., 2013). Moreover, previous researches have been focused mostly on the exploitation of waste toner powders from printers and photocopy machines in asphalt and bitumen (Anić Vučinić et al., 2013; Essawy et al., 2013; Hansen et al., 2000; Khedaywi, 2014; Yildirim et al., 2004). Alternative application of toner powder include: basis for the bacteria growth (Sepperumal et al., 2014), pyrolysis oils and nanoparticles from waste toner through vacuum gasification (Dong et al., 2017; Jujun et al., 2017), a resource of ferrous (Gaikwad et al., 2017; Kumar et al., 2018), oxides for anode materials in lithium ion batteries (Li et al., 2018), a source of ferrous as sensitizer for the photocatalysts used in water purification (Cindrić et al., 2018), hydrophobic sponge from waste toner by one step heat for separation of oil from water (Shi et al., 2018), pigments (Moock Environmental Solutions Ltd., 2018). The possibility of waste toner powder recycling in concrete industry is poorly investigated (Mannion, 2010; Mohan, 2010; Newlands et al., 2012).

The mixture of waste toner powder with calcite is an output fraction from mechanical recycling of waste toner cartridges obtained from an authorized waste recycling company in Republic of Croatia. This mixture is separated from other materials obtained from this recycling process such as steel, aluminium and plastics which can be sold in their respective markets (Spectra Media Ltd, 2019).

Given that approximately 115 tons of waste toner cartridges are collected in the Republic of Croatia annually, after calcite addition, approximately 18 tons of toner powder and calcite mixture remains. Since there is no systematic disposal of this waste in the Republic of Croatia, it is usually transported out of the country for processing.

In current study, the possibility of using waste toner powder as replacement for fine aggregate (sand) in the concrete industry was presented. Optimal composition and possible environmental impact of final composite materials were given. The research was carried out in real industrial environment. The mixture was produced using common practice in the Zagorje Tehnobeton Plc (Varazdin, Croatia). The results showed the acceptable properties of modified concrete in terms of compressive and tensile splitting strength. The leaching tests performed according to legislation related to landfills showed acceptable DOC in fresh and aged samples. Since according to (Popovici et al., 2015) modern approaches must be based on green market waste, as well as on integrated environmental and economic policies, this work represents an effort towards circular economy and environmental protection.

2. Material and methods

2.1. Preparation of modified concrete

For the research, the recipe for concrete strength class C20/25 was used for preparation of testing samples. Used materials were identical to those that are incorporated into the concretes of real facility, the Zagorje Tehnobeton Plc from Varazdin, Croatia. Aggregates that were used were an industrial product of Colas Mineral Ltd from Varazdin, Croatia obtained by exploiting and refining gravel and sand on the exploitation field of Hrastovljan, Croatia. The cement Special CEM II/A-S 42.5 R was used as a binder. Preparation of concrete mixtures, moulding and evaluation of its properties was carried out according to standard procedures described in HRN EN 12390.

The mixture of waste toner powder and calcite is product of the mechanical treatment of waste toner cartridges and it was obtained from authorized waste recycling company Spectra Media Ltd from Donja Bistra (Croatia). Waste toner powder was obtained from bag-type dust collector upon shearing process; separated from all other components of waste toner cartridges (Fig. 1).

During mechanical treatment the calcite is mixed in ratio 50:50 wt% with waste toner powder to minimize possibility for explosion (Anić Vučinić et al., 2013). Above mentioned mixture was used as replacement for fine aggregate (0/4 mm) in following percentages: 1, 3, 5, 10 %. One reference concrete mixture was made and was used as control mixture.

2.2. Characterization

Air content and slump test (consistency) as properties of fresh concrete were tested according to standards HRN EN 12350-2:2009 (Croatian Standards Institute, 2009a) and HRN EN 12350-7:2009 (Croatian Standards Institute, 2009b), respectively. Compressive strength was carried out according to HRN EN 12390-3:2009 (Croatian Standards Institute, 2009c) and tensile splitting strength according to HRN EN 12390-6:2009 (Croatian Standards Institute, 2009d).

Leaching test was carried out according to standard HRN EN 12457-2:2002 Characterization of waste. Leaching. Compliance test for leaching of granular waste materials and sludges. One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction).

Leaching test was performed in Laboratory for environmental geochemistry on Faculty of Geotechnical Engineering (University of Zagreb). For experimental specimens of hardened concrete, content of dissolved organic carbon (DOC) from eluate was determined in apparatus Shimadzu TOC – V_{CPN} . Prior to analysis for heavy metals by Atomic Absorption spectrometry (Perkin Elmer Analyst 800). Chloride and fluoride ion concentrations in the filtrates were analysed by colorimetry using a Hach Lange DR 5000 spectrophotometer.

Test specimens used for compressive strength testing were crushed to demanded size and were used in leaching test.

3. Results and discussion

3.1. Properties of fresh concrete

Apart from its strength, the concrete is also characterized by its workability. The workability is described as the ease with which concrete can be mixed, placed, consolidated and finished.

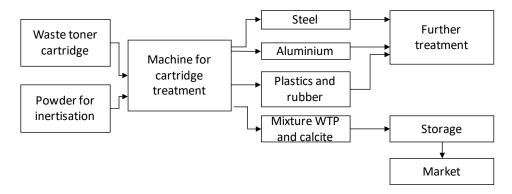


Fig. 1. Scheme for waste toner cartridge mechanical processing (Spectra Media Ltd, (2019), www.spectra-media.hr)

A mix that is difficult to place and consolidate will increase the cost of handling, and lead to poor strength, durability and appearance. Since it is practically impossible to devise test methods that can simultaneously check all these properties, the measurement of the workability of a concrete mixture is obtained indirectly through its 'consistency'. The consistency is defined as the relative mobility, or ability of freshly mixed concrete to flow. It is indicative of the mix wetness. Usually, wetter mixes are more workable, with some exceptions to this rule. Accordingly, the slump height is the workability criterion of concrete (Konstantinidis, 2013), commonly known as a consistency.

Anić Vučinić et al. (2016) have in their research determined properties of fresh concrete with replacement of fine aggregate with mixture, e.g. air content and consistency. The toner powder is normally a mixture of red, blue and yellow pigments with different organic structures (i.e. chromophores), charge control agents (Fe, Cr or Zn particles), polyester resin, wax, silica and carbon black (Simmons and Duffey, 2013). The components with hydrophobic character such as resins make at least 80% of toner composition according to MSDS specification from various manufacturers. contributing to the overall hydrophobicity of modified concrete mixture. Anić Vučinić et al. (2016) have reported higher air content with higher replacement percentages, but comparing to reference mixture, only mixture with 1% replacement shows decrease in air content. Mixtures with 5 and 10% replacement show high increase in air content when comparable to reference concrete, which can lead to suggestion that waste toner powder and additive can be used as an airentraining agent. Air-entraining agents (or admixtures) cause small stable bubbles of air to form uniformly through a concrete mix. The benefits of entraining air in the concrete products is to enhance their resistance to freeze-thaw degradation and increased cohesion and to improve compaction in lowworkability mixes (The Concrete Society, 2002).

In this particular case, the formations of air bubbles can be assign to the presence of silica and resins in the toner composition. It was reported that air bubbles were formed using partially hydrophobic silica nanoparticles as the stabilizer (Dickinson et al., 2004). The dispersion of nanoparticles in resins usually cause the formation of air bubbles (Liang and Wong, 2017). In case of toner powder, the dispersion of small dust particles in cement matrix could lead to the same effect.

Colouration of concrete is reported by Anić Vučinić et al. (2016) and Newlands et al. (2012). Newlands et al. (2012) have replaced part of the cement in concrete with patented mixture containing surfactants that enables better bonding of toner powder particles with cement-based products (gypsum, concrete, plaster). The reported consistency (slump test) was increased for all concrete mixtures regarding the reference concrete.

3.2. Properties of hardened concrete

Fresh concrete is being only a transit stage. The importance of this stage comes from the fact that the concrete strength is very seriously affected by the degree of its compaction. Therefore, the properties of hardened concrete are observed.

The test cubes were made to determine properties of hardened concrete. A greyish colouring was observed in cubes with toner powder. The intensity of colour increased with the increasing percentage of added WTP (Fig. 2).

All tests were made in triplicates and the average results observed for three cubes were reported.



Fig. 2. Colouring of test specimens depending on replacement percentage

Out of numerous tests connected to the concrete, compressive strength test is the extreme vital. All other mechanical parameters directly depend on the compressive strength of the concrete (Dash et al., 2016). Compressive strength of tested concrete composition should be higher of conditioned class (characteristic compressive strength) at least for size required to comply with requirements according to Appendix A of standard HRN EN 206-1, respectively approximately two times higher than expected standard deviation (e.g. from 6 MPa to 12 MPa) (Faculty of Civil Engineering and Institut IGH, 2012).

The results of compressive strengths of test cubes after 28 and 986 days are given in Fig. 3. The compressive strength is shown as f'_c : the specified compressive strength of concrete using standard cubes dimensions 150x150x150 mm.

The samples with 1% and 3% replacement give relatively close results to reference mix and mixtures with higher replacement show lower values of compressive strength. Concrete with 1, 3 and 5 % replacement fulfil both criteria for compliance with compressive strength class, while concrete with 10 % replacement fulfils criteria 2, but not criteria 1 of compliance and thus, it does not fulfil compliance with compressive strength requirements. The difference between new and aged samples is a result of normal process of concrete hardening with time.

Waste toner powder in concrete industry: an approach towards circular economy

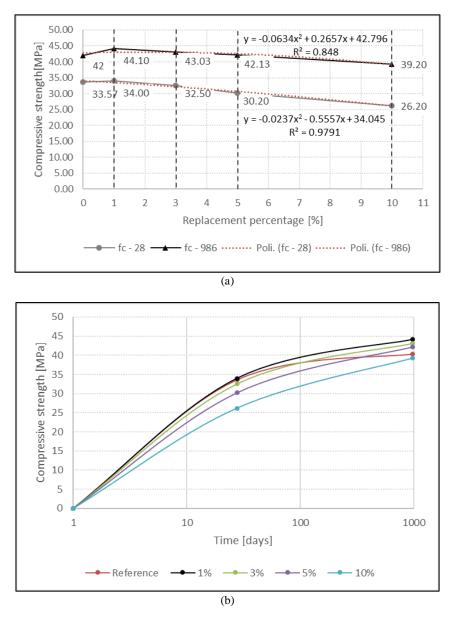


Fig. 3. Compressive strength of test specimens: a) dependent on the percentage of replacement with WTP and b) given as a function of time

The tensile strength is commonly defined in one of three ways: direct tensile strength, tensile splitting strength or flexural strength. It has been seen that different values are obtained from the different test methods. Because of high test variability of tensile testing, it is recognized that compliance should be based on the measurement of compressive strength, as reported above. It has also been suggested that the tensile splitting test is unsuitable as a conformity test for concrete (Bamforth et al., 2008).

Tensile strength is an important property of concrete due to structural vulnerability to tensile cracking upon loading of concrete and other effects. However, tensile strength of concrete is very low compared to the compressive strength. It was interested to observe the properties of modified concrete after 28 and 986 days in comparison. Hypothetically, a crucial structural defect in combination with environmental factors would eventually results in certain negative changes in the tensile strength. The results of tensile splitting test for experimental specimens are given in Fig. 4 compared to reference. The tensile strength is given as mean splitting tensile strength ($f_{ctm, sp}$). As shown, replacement of fine aggregate with waste toner powder and calcite (WTP) resulted in decreased tensile splitting strength in all samples.

Compared to the concrete samples with no replacement of fine aggregate, tensile splitting strength after 28 days decreased in 14.72% for concrete with 3% replacement and the highest percentage of replacement resulted in 30.43% lower tensile splitting strength. The results for tensile strength after 986 days are a bit different. Except for the sample with 3% WTP (20.84 % decrease), tensile strength is insignificantly lower even for samples with 10% replacement (4.43 % of decrease).

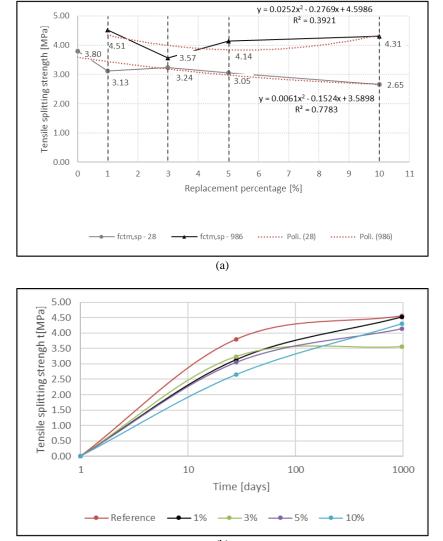
The reason for the slight deviation observed in this case could be the presence of polyester resins and wax that counts for 80-90 % of the total replacement. The resin could form chemical bonds with silica, alumina and other oxides from aggregate (gravel or sand). Those chemical bonds improve the tensile strength. The vinylester and epoxy resin were used to improve the concrete properties. Such polymer concrete is reported to have better mechanical properties than its counterpart, Ordinary Portland Cement (OPC) concrete (Burlacu et al., 2018; Lokuge and Aravinthan, 2012; Sosoi et al., 2018).

In mentioned patent (Newlands et al., 2012), compressive strength after 7 and 28 days, pressure water penetration, and capillary absorption were reported. The compressive strength was decreased, while the slump test was increased for all concrete regarding the reference concrete. Higher penetration of water under pressure in the concrete samples indicated a harmful lack of cement, which is the reason for poor results of compressive strength. The results of capillary water absorption indicate that the entry of water into test concrete is reduced at atmospheric pressure, which is attributed to the properties of toner powder to reject water and to clog pores due to very small particle size. Based on the results in current study those issues were evaded by the replacement of standard mixture content with only WTP in low percentages.

The results suggest that commonly used concrete formulation could be modified with waste toner powder and the addition of other additives (admixtures) is not necessary. Since all samples were tested in triplicates, standard deviations were calculated using (Eq. 1).

$$SD = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} \tag{1}$$

where x and \bar{x} stand for the experimental value observed for one test cube and the average value for triplicates of the same replacement percentage; *n* is the number of testes cubes (3).



(b)

Fig. 4. Tensile splitting strength of test specimens: (a) dependent on the percentage of replacement with WTP and (b) given as a function of time

Since than less than 1 m³ of concrete was prepared for each sample, a single cube should be enough for strength tests. However, according to the common EU standards and Indian Standard code of practice for general structural use of plain and reinforced concrete (Bureau of Indian Standards, 2000), for additional control in terms of sample homogeneity, the frequency/number of testing of compressive strength by cube test was increased to three. Calculated SDs of experimental compressive and tensile strengths for all samples are given in Table 1.

Based on the calculated SDs for f'_c , all samples follow the request that average 28 days compressive strength of at least three 150 mm concrete cubes prepared with water proposed to be used shall not be less than 90 % of average of strength of three similar concrete cubes prepared with distilled water (Bureau of Indian Standards, 2000).

The influence of the addition of WTP on compressive (f'_c) and tensile strength (f_{ctm}) are presented by the empirical (Eq. 2) and (Eq. 3). The coefficients a_0 , a_1 and a_2 are given in Table 1.

$$f'_c - X = a_{0,fc} + a_{1,fc} (WTP, \%) + a_{2,fc} (WTP, \%)$$
 (2)

$$f_{ctm, sp} - X = a_{0, sp} + a_{1, sp} (WTP, \%) + a_{2, sp} (WTP, \%)$$
(3)

Note that *X* stands for the number of days.

3.3. Leaching test

The WTP mixture is a non-explosive output fraction characterized with high DOC which classifies it as hazardous waste according to waste acceptance criteria although for other parameters complies with OG 114/2015, that are in accordance with European legislation.

Obtained results for leaching of concrete cubes after 28 and 986 days in terms of DOC are given in Fig. 5. It can be noticed that DOC in eluate increased exponentially with higher replacement percentage. The rate of DOC release per replacement percentage was found to be 0.21 and 0.12 %⁻¹ after 28 and 986 days, respectively. The insignificant change was observed after 3 years. The difference in DOC values determined upon leaching test after 28 days (marked as "After 28 days") and after 986 days (marked as "After 3 years") could be ascribed to experimental error due to comminution stage necessary for performance of leaching test according to OG 114/2015.

Table 1. Standard deviations of results of performed tests and coefficients of empirical equations

	f	" c	$f_{ctm, sp}$		
$X (days) \rightarrow$	28	986	28	986	
		SD			
1% WTP	0.61	1.65	0.88	0.28	
% WTP 0.70		1.92	0.17	0.63	
5% WTP 0.20		2.89	0.54	0.58	
10% WTP	% WTP 1.49		0.17	0.30	
reference	0.75	3.50	0.19	0.33	
		coefficients			
a ₀	34.045	44.525	3.590	4.599	
a ₁	-0.566	-0.446	-0.152	-0.277	
a ₂	-0.024	-0.009	0.006	0.025	

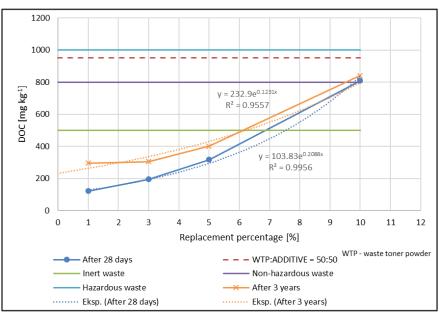


Fig. 5. Results of leaching test regarding DOC value

 Table 2. Classification of experimental concrete and control mixture after three years based on results of leaching test according to Ordinance 114/2015 (OG, 2015)

						Limit value of eluate parameters ****L/S = 10 l/kg		
Parameters	TO	T1	ТЗ	<i>T5</i>	T10	Landfill for inert waste	Landfill for non- hazardous waste	Landfill for hazardous waste
As (mg/kg)	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.5</td><td>2</td><td>25</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.5</td><td>2</td><td>25</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.5</td><td>2</td><td>25</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.5</td><td>2</td><td>25</td></dl<></td></dl<>	<dl< td=""><td>0.5</td><td>2</td><td>25</td></dl<>	0.5	2	25
Ba (mg/kg)	0.2067	0.2446	0.2418	0.2941	0.3134	20	100	300
Cd (mg/kg)	0.00041	0.00011	0.00030	0.00006	0.00007	40	1000	5000
Cr (mg/kg)	<dl< td=""><td><dl< td=""><td>0.18</td><td>0.6</td><td>0.36</td><td>0.5</td><td>10</td><td>70</td></dl<></td></dl<>	<dl< td=""><td>0.18</td><td>0.6</td><td>0.36</td><td>0.5</td><td>10</td><td>70</td></dl<>	0.18	0.6	0.36	0.5	10	70
Cu (mg/kg)	0.1	0.1	0.1	0.1	0.1	2	50	100
Hg (mg/kg)	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>10</td><td>200</td><td>2000</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>10</td><td>200</td><td>2000</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>10</td><td>200</td><td>2000</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>10</td><td>200</td><td>2000</td></dl<></td></dl<>	<dl< td=""><td>10</td><td>200</td><td>2000</td></dl<>	10	200	2000
Mo (mg/kg)	0.04738	0.04765	0.04948	0.07273	0.09656	0.5	10	30
Ni (mg/kg)	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.0018</td><td>0.0037</td><td>0.4</td><td>10</td><td>40</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.0018</td><td>0.0037</td><td>0.4</td><td>10</td><td>40</td></dl<></td></dl<>	<dl< td=""><td>0.0018</td><td>0.0037</td><td>0.4</td><td>10</td><td>40</td></dl<>	0.0018	0.0037	0.4	10	40
Pb (mg/kg)	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.5</td><td>10</td><td>50</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.5</td><td>10</td><td>50</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.5</td><td>10</td><td>50</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.5</td><td>10</td><td>50</td></dl<></td></dl<>	<dl< td=""><td>0.5</td><td>10</td><td>50</td></dl<>	0.5	10	50
Se (mg/kg)	0.09907	0.1406	0.1465	0.157	0.1601	0.1	0.5	7
Zn (mg/kg)	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>4</td><td>50</td><td>200</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>4</td><td>50</td><td>200</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>4</td><td>50</td><td>200</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>4</td><td>50</td><td>200</td></dl<></td></dl<>	<dl< td=""><td>4</td><td>50</td><td>200</td></dl<>	4	50	200
Cl ⁻ (mg/kg)	38	50	64	72	82	800	15000	25000
F ⁻ (mg/kg)	5	6.5	6.9	9.6	10.8	10	150	500
SO ₄ ²⁻ (mg/kg)	880	980	1060	1100	1120	1000	20000	50000
DOC (mg/kg)	123.0	296.0	305.0	401.4	841.1	500	800	1000
TDS (mg/kg)	4340	6360	6090	533	6040	4000	60000	100000

Note: DL – detection limit; 10 – control mixture; 11- concrete with 1% replacement; 15- concrete with 5% replacement; 15- concrete with 5% replacement; 15- concrete with 5% replacement

Namely, difference in the concrete particle size could alleviate the difference in DOC measurements due to "better" leaching of organic components of WTP from smaller particles. Regardless, 1, 3 and 5 % WTP are still suitable to be disposed of on the inert waste landfill, while the DOC parameter value points out that the 10% WTP is higher than criteria for landfill for non-hazardous waste.

Finally, the complete leaching tests was performed according to the valid legislation to assess the leaching of inorganic substances from aged concrete cubes. The results are given in Table 2. Results are compared with the ascribed limits for different types of landfills. Selenium (Se) was shown as the limiting element. The leaching of Se from concrete cubes with any percentage of replacement was above limits for inert waste. However, the concrete with WTP <10% could be disposed on landfills for non-hazardous waste.

The observed results could refer to the fact that the leachable concentration of DOC and Se could be a limiting factors in the use of the respective concrete mixtures, but also it is important to emphasize that this concentration is not necessarily above the legally permitted limit, as there is no unified legislation or guidelines at the level of our country or European Union which would define the parameters and the maximum values of leaching from such innovative concrete samples. The results clearly show that such types of concrete products (with a limited share of waste as a substitute for raw materials) can, at the end of their life cycle, be disposed of on landfill or could find some other use, such as a recycled aggregate in road construction.

The retention of potentially dangerous and harmful substances within the hardened material (concrete) through possible encapsulation of WTP and calcite mixture was achieved.

4. Conclusion

In this paper is presented the possibility of using mixture of waste toner powder and calcite obtained by mechanical treatment of waste toner cartridges as a substitute for fine aggregate granulation (0-4 mm) in concrete products in percentages of 1, 3, 5 and 10 %. This mixture of waste toner powder and calcite is unique and formed in real industrial conditions in the Republic of Croatia. The mixture of waste toner powder and additive is a non-explosive output fraction characterized with high DOC which classifies it as hazardous waste according to waste acceptance criteria although for other parameters it complies with landfill legislative.

The research was conducted on fresh and hardened concrete prepared according to recipe for concrete class C20/25 to determine technical characteristics of this experimental concrete. Leaching test was conducted to determine possible environmental impact from experimental concrete due to high DOC content in mixture used as replacement. The results showed that the mixture of waste toner powder and additive gives satisfactory results for 1, 3, 5 % replacement of fine aggregate in concrete both from environmental and technical aspects, while 10 % replacement gave unsatisfactory results from both aspects.

It is important to emphasize that concentrations of DOC and selenium that leaked from this innovative concrete are not necessarily above the legally permitted limit, as there is no unified legislation or guidelines at the level of our country or European Union which would define the parameters and the maximum values of leaching from such innovative concrete samples. Experimental samples with 1, 3, 5 % replacement are classified as inert waste, which leads to conclusion that concrete encapsulates this mixture and its possible harmful substances and represents a possibility of 'open – loop' recycling process. This research has shown that the concrete products with a limited share of waste as a substitute for raw materials can, at the end of their life cycle, be disposed of on landfill or could find some other use.

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