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Article

Circular Economy Approach: Recycling Toner Waste in Cement-Based Construction Materials

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Abstract: Based on a waste generated survey by companies in the area of the city of Bahia Blanca (Argentina), the possibility of incorporating part of them in a Portland cement matrix was examined. Among the waste is toner (TW), which is obtained from cartridges used in photocopiers, laser printers, and faxes. This paper aims to analyze the physical and mechanical properties of cement pastes and mortars using toner as a Portland cement replacement compared to a reference sample without toner. The mixes were made with 2.5, 5, 10, and 15 wt.% replacement of cement by toner, and it was measured the flow, normal consistency, setting time, calorimetry, and Frattini test in pastes and mechanical strengths in mortars employing standardized tests. Also, an analysis of the leachate in the curing water was carried out after 56 days to look for contaminating materials. The replacement of up to 5% cement with toner did not produce substantial alterations in the final setting time or mechanical properties. No heavy metals were found in the leachate, so TW can be immobilized in a cementitious matrix as it does not cause leaching above the established limits. Therefore, TW from a local industry can be used in construction materials and could contribute to a reduction of up to 14% of CO_2 emissions with a cement replacement of 15% in cement-based materials.

Keywords: toner waste; cement mortars; life cycle assessment; circular economy

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1. Introduction

Nowadays, several methods exist to control the amount of waste produced by humanity. Waste management involves all activities necessary for supervising waste from the time that it is generated until it is collected, transported, and positioned at its final destination (disposal, incineration, or recycling) [1].

The electronics industry, driven by societal demands, produces a substantial quantity of solid waste, commonly referred to as electronic waste (e-waste), which consists of metals such as iron, steel, aluminum, copper, certain heavy metals, screen glass, and many plastics. Different approaches and procedures have been implemented to facilitate the recovery of specific components from e-waste. To recover e-waste components, a dismantling process is carried out. The devices are separated into different parts, such as metal frames, printed circuits, power supplies, and plastics [2,3]. Some materials are incinerated, although the combustion process is harmful to the environment due to the emission of toxic gases.

The main problems in the recycling of e-waste are the high content of toxic and polluting materials and the complexity of the technologies to carry out adequate separation. The inclusion of shredded electronic waste (plastics and glass properly separated from the contaminating components) in concrete as a partial replacement of the coarse aggregate has been studied [4,5]. The growing global demand for ink and toner cartridge production has led to a significant accumulation of such waste that threatens the environment [6,7]. Using it as a secondary raw material in other industries is a promising approach to ink waste management [8,9]. The circular economy (CE) is based on the principles of ecology and proposes a change from the "reduce, reuse, recycle" paradigm to a more profound and lasting transformation aimed at reducing the impact of human activities on the environment [10]. This model gives a prominent role to waste and focuses on its reuse. In this approach, waste loses its status as such and becomes "raw material" for natural cycles or is transformed to form part of new products, with minimal energy expenditure [11]. In contrast to the traditional "produce, use, throw away" cycle, the CE advocates a minimum reduction in the extraction of natural resources and aims to extend the useful life of materials by promoting reuse, recycling, and recovery [12]. CE has become one of the potential approaches for addressing the huge amount of waste generated by maintaining products and materials as long as possible in the economy. CE is essential for the e-waste sector as it contains toxic substances and precious metals [13,14]. Farrell et al. [15] state that adopting CE principles can help offset environmental factors like manufacturing emissions and increase recycling and recovery rates.

Toner is a fine powder, mainly composed of carbon and iron, that, due to electrostatic or magnetographic attraction, pressure, and heat, is fixed to the paper to print images or text. The composition of toner exhibits significant variation among different color variants. The main components of colored toners are chromium, copper, inorganic cyanides, acrylic polymers, photographic developers, and thermoplastic particles. The chemical composition and particle size make the final disposal of toner a serious problem, whereby inadequate disposal practices may lead to environmental contamination [16]. For example, prolonged suspension of fine toner particles (<10 µm) in the air can pose a risk to human health [17]. Toner can cause granulomatous pneumopathy (a condition in the lungs with tumor formation) and mediastinal adenopathy (a condition in a lymph node between the pleura of the lungs) due to the size of its particles. Additionally, if proper precautions are not taken, it can lead to respiratory tract alterations such as sneezing, chronic cough, skin and eye irritations, and even headaches [18]. In practice, printer ink cartridges are typically discarded into the home waste system without any additional regulation, contaminating sanitary landfills, yet toner cartridges should be removed from printers before recycling them. The waste amount of copiers and printers reaches 18 million tons per year [19]. Since about 10% of the toner powder remains in the cartridges [20], it is estimated that about 7200 tons of toner waste are discarded annually [19].

The use of toner from recycled cartridges in the production of asphalt mixes for flexible pavements has been reported to be successful [21,22]. The recycled powder is homogenized and then agglomerated to produce a particle of 1 to 3 mm in diameter. During the agglomeration process, one or more additional materials can be added, such as recycled motor oil. The final product is used as a polymer-based additive to produce asphalt with significant advantages of energy savings (the toner mixture is heated to a temperature 20 to 50 °C lower than normal asphalt, using less energy for its production), reduction of landfills (it allows for a decrease in the number of cartridges that end up in landfills), reduction of crude oil used in roads (it reduces the use of a crude oil-derived material), generating a high-strength product that reduces the formation of cracks in roads, minimizes maintenance costs, and increases durability [23]. Additionally, it was reported that the rheological characteristics of the asphalt binder were improved by increasing the amount of toner added to 12% [24], and polymer-modified binders showed an increase in viscosity [25].

The feasibility of recycling waste toner powder in the concrete industry has not been thoroughly investigated. A strength decrease was observed when toner recovered from printer cartridges was used as a pigment for cement to toner replacement of 5, 10, and 20 wt.%, although no impact on the hydration rate of the pastes was observed [26].

The use of supplementary cementitious materials (SCMs) from the waste of other industries or industrial by-products contributes to reducing landfill waste and CO_2 emissions [27]. The use of SCMs as a cement replacement may improve the performance of the concrete mix and, therefore, reduce its cost [28]. However, when the mix design and batching of the concrete are not appropriate, it can lead to a loss of strength and worsen durability.

In order to promote CE and evaluate the environmental impact of material production, this paper aims to investigate the use of black toner waste (TW) as a supplementary cementitious material in cement pastes and mortars. The objective is to improve the disposal of hazardous waste and the recovery of electronic waste. It includes the study of the pozzolanic activity of TW, the influence of the use of TW on flowability, heat of hydration, water requirement in blended cement pastes, and compressive strength and contaminant leaching in blended cement mortars.

2. Materials and Methods

Toner incorporated in the mixes was obtained from 200 cartridges discarded at printing shops, and it was homogenized through mixing. Only black toner waste (TW) was used in order to have the same chemical composition and because it is the most frequently used. The sample for testing was selected via the quartering method. TW was placed on a flat and clean surface. Subsequently, it was divided into four approximately equal parts with the aid of a spatula, and one of these parts was selected while the other three were discarded. The selected part was then further divided into four parts, and one of these subdivisions was chosen for analysis.

TW was used in pastes and mortars as a partial replacement for ordinary Portland cement (OPC), considering four replacement levels by weight: 2.5% (T2.5), 5% (T5), 10% (T10), and 15% (T15). A reference sample was also produced without the replacement of OPC by TW (T0).

OPC was used to produce pastes and mortars, and demineralized water was used for mixing and curing samples.

The OPC has a density of 3.09 g/cm^3. It is equivalent to CEM I 42.5 N, and its chemical composition was determined by XRF.

2.1. Black Toner Waste Characterization

TW was characterized physically, chemically, and mineralogically. Physical characterization was performed by density determination (average of three different measurements) and microscopic observation of the TW particles, using a scanning electron microscope (SEM) Zeiss model EVO MA10 (Carl Zeiss, Jena, Germany). Chemical analysis was determined by X-ray fluorescence (XRF), using a Malvern Panalytical Axios Fast instrument (Malvern Panalytical, Almelo, The Netherlands). Mineralogical characterization was conducted by X-ray diffraction (XRD) analysis, using a Rigaku D-Max III C diffractometer (Rigaku Denki Co., Ltd., Tokyo, Japan). XRF and XRD were performed in external laboratories.

From the examination under the SEM, the presence of particles smaller than 10 µm is observed with respect to the cement (Figure 1). It is an important feature since small particles can be inhaled and penetrate the smallest regions of the lungs [29]. The density of TW is 1.1 g/cm^3. It is replaced by weight, and since it has a density 2.81 times lower than cement, TW occupies a greater volume compared to cement.

Table 1 reports the chemical composition of toner determined by XRF. The XRD pattern (Figure 2) of TW displays sharp diffraction peaks at $2\theta = 29.369°$ (64.1%), 30.166° (72.5%), 35.525° (100%), 43.198° (48.4%), and 57.044 (28%) coincident with pyridoxylidene hydrazine (Pi). Pi indicates the presence of carbon (C), hydrogen (H), iron (Fe), nitrogen (N), oxygen (O), and sulfur (S).

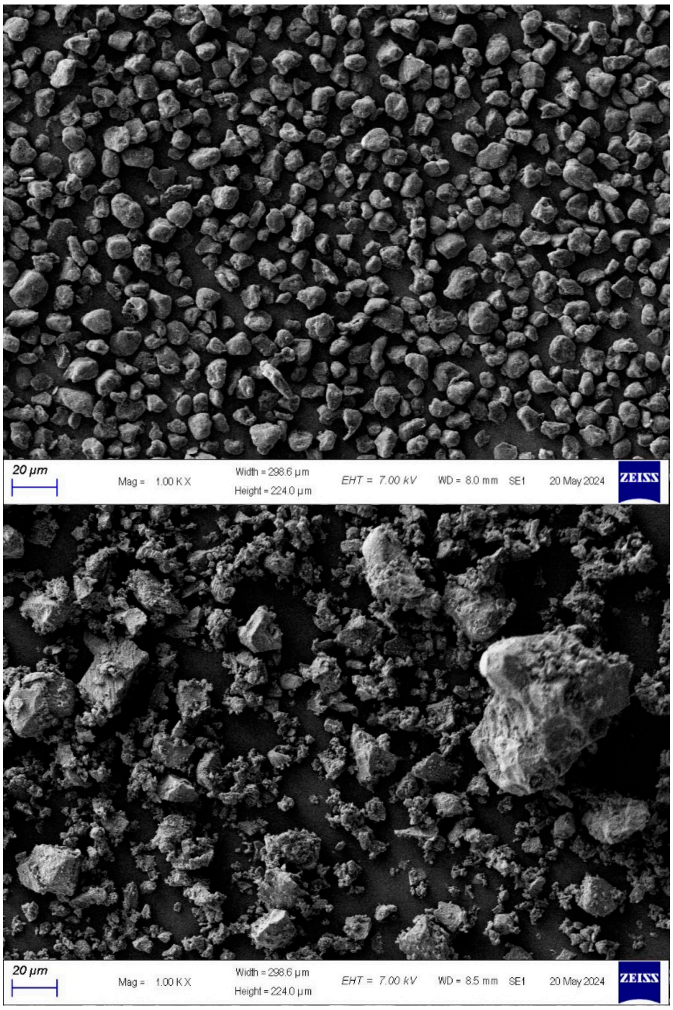

Figure 1. Images of TW (**up**) and OPC (**down**) with SEM.

Table 1. Chemical characteristics composition of OPC and TW (%).

Material	Al_2O_3	BaO	CaO	Cr_2O_3	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SO_3	SiO_2	SrO	TiO_2	LOI 1000
OPC	3.99	-	60.77	-	4.06	0.96	0.59	-	0.03	-	2.2	20.07	-	-	2.83
TW	<0.01	<0.01	<0.01	0.04	4.98	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.27	<0.01	0.03	92.97

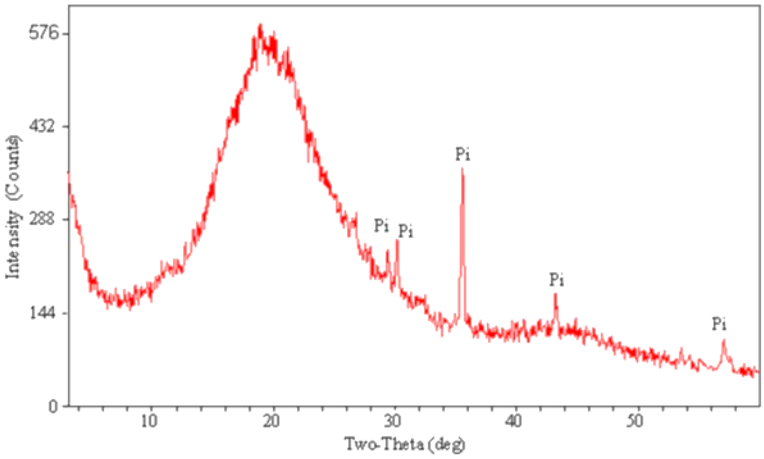

Figure 2. XRD pattern of TW.

TW shows a low silica and alumina content. It does not necessarily indicate a potential pozzolanic reactivity of the toner. As the loss of ignition (LOI) measures the mass reduction during calcination at 1000 °C, it serves to quantify the elements that volatilize at or below this temperature. On the other hand, a high LOI can be correlated with the presence of graphite and organic compounds, as evidenced by XRD analysis.

Based on the chemical analysis, it is observed that the TW does not contain silica or aluminum, which aligns with what is established in [30,31]. Therefore, the hypothesis could be raised that this material does not possess pozzolanic properties. Additionally, given the high LOI, indicating a significant presence of organic compounds, it might require more water and potentially affect the setting times.

2.2. Cement Pastes

The pozzolanic activity of blended cement was determined by the Frattini test, according to EN 196-5 [32]. A total of 20 g of blended cement was mixed with 100 mL of boiled distilled water. The water-to-binder (w/b) ratio used was 0.50. After preparation, samples were left for 7 and 28 days in a sealed plastic container at 40 °C. The blended cement is considered pozzolanic when the calcium hydroxide concentration in the sample solution is located below the solubility isotherm of calcium hydroxide.

The flow properties of cement paste were assessed using a mini-slump test [33]. Distilled water was utilized to formulate the cement pastes with a w/b ratio of 0.50. Following mixing, the cement paste was poured into a cone placed on a glass plate. The cone was incrementally raised to allow the paste to spread across the glass surface. After a minute, two perpendicular spreading diameters of the paste were measured, and their mean was computed. The remaining paste in the containers was re-mixed every 5 min, and its flow characteristics were evaluated at intervals of 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 60, 120, and 180 min.

The rate of heat evolution and the total heat released during hydration were determined under constant temperature conditions at 20 °C using a conduction calorimeter. A mixture with 20 g of cementitious material was homogenized in a small plastic bag with a w/b ratio of 0.50. The bag containing the cementitious material and mixing water was introduced into the calorimeter until thermal stabilization was achieved. Subsequently, the cement was manually mixed with 10 g of water for 30 s. The bag was sealed, placed securely in the calorimeter cup, and measurements commenced immediately. The heat evolution rate of the cement pastes was monitored over a period of 48 h.

Then, the amount of water required for normal consistency (ASTM C187 [34]) and the initial and final setting times (ASTM C191 [35]) were determined.

2.3. Cement Mortars

Then, mortars were proportioned with a w/b = 0.50 and binder/sand = 0.33. Three sets of three prismatic specimens of 4 × 4 × 16 cm were molded for each of the blended cements studied and three sets for the reference sample, according to ASTM C109/C109M [36]. Mortars were made with 1350 g of graded standard sand (ASTM C778 [37]), 450 g of binder, and 225 g of distilled water. Compressive strength was determined at 7, 28, and 56 days.

The pozzolanic activity index (PAI) was determined. This index indicates the pozzolanic reactivity and potential contribution of the material to the overall strength development of mixes. PAI represents the relative strength contribution of the pozzolan compared to the reference cement. Therefore, a higher activity index indicates greater pozzolanic reactivity and potential for enhancing the mixtures' properties. The UNE-EN 450-1 standard [38], specified for fly ashes with a 25% substitution of PC, proposes that a mineral addition is considered a pozzolan when the PAI is greater than 75% at 28 days and 85% at 90 days.

Since TW can be considered a hazardous waste, the mobility of contaminants was studied. Leaching in construction materials is not standardized. Therefore, the NEN 7345: 19944 [39] standard for waste acceptance in landfills was followed. A liquid/solid

(L/S) ratio of 2 was used, and the leachate was analyzed after 56 days using an Induced Plasma Atomic Emission Spectrometry (ICP-OES) performed with simultaneous Shimadzu model 9000 equipment in an external laboratory. Each sample was subjected to an atomic emission spectrometry reading, which was then divided into three sub-measurements or integrations, each lasting 15 s. Subsequently, the software calculates the average of these three integrations and records it in the results spreadsheet. The error between the sub-readings is less than 1.1%.

2.4. Embodied CO_2 of Mortars

Finally, a life cycle assessment (LCA) was carried out to determine the embodied CO_2 (ECO_2) per m^3 of mortar, following the guidelines of ISO 14040 [40]. The aim of the LCA is to determine the CO_2 equivalent emissions per m^3 of mortar. The functional unit was set up to examine the sustainability of mortars with and without TW. The LCA was carried out from cradle to gate. Therefore, casting, use, demolition, recycling, and final disposal of mortars were not taken into account.

ECO_2 considers the production processes of the OPC and its transport from Olavarría (Buenos Aires, Argentina) to Bahía Blanca (Buenos Aires, Argentina), adopting a transport distance of 298 km using trucks, the production of natural quartzite sand, the transport of TW from the print shops to the ready-mix concrete plants, considering an average transport distance of 9 km, and the water treatment to produce tap water. Data were obtained by literature compilation. At this stage of the research, the removal of TW from the cartridges is performed manually; thus, other ECO_2 related to this material are not considered. ECO_2 from toner production is likewise neglected since it is a waste from another industry. The study will be carried out from "cradle to gate". The life cycle impact assessment (LCIA) was conducted considering one impact category: ECO_2 per m^3 of mortar. The ECO_2 of the component materials and the one due to transport are shown in Table 2.

Table 2. Embodied CO_2 of each mortar component material and its transport.

Material/Transport	ECO_2
Ordinary Portland Cement, kg/t of cement [41]	896
Natural quartzite sand, kg/t of sand [41]	14
Tap water, kg/t of water [42]	9
Truck transport, kg/t km [43]	0.124

3. Results

3.1. Cement Pastes

3.1.1. Frattini Test

Figure 3 shows the results of the Frattini test from three different measurements of T0, T2.5, T5, T10, and T15 samples. The results are plotted as points in the calcium oxide (CaO) vs. hydroxide (OH-). For OH, the variation in the method is ±0.75 mmol/L, and for CaO, it is ±0.5 mmol/L. At 7 and 28 days, all samples are located above the solubility isotherm, indicating that TW does not consume the calcium hydroxide (CH) released by the OPC. This behavior is not observed in samples T2.5-28d and T5-28d; however, they fall within the error range of the method. Therefore, it is confirmed that TW does not exhibit pozzolanic activity according to the Frattini test.

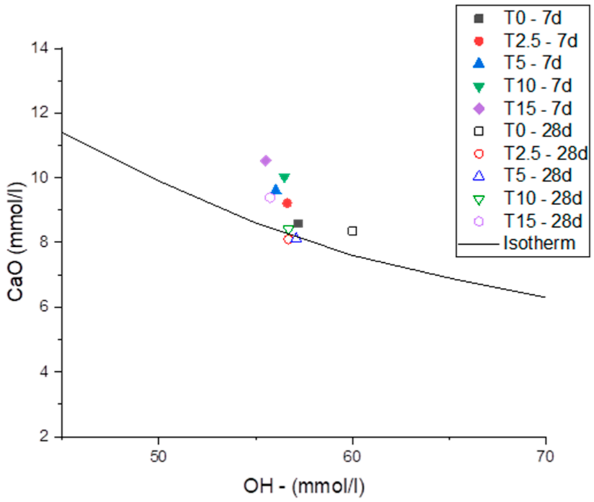

Figure 3. Frattini test of pastes with different TW replacements.

3.1.2. Mini-Slump

Figure 4 shows the flow (as the extended diameter) of the blended cement pastes and the reference cement paste expressed in %, at 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 60, 120, and 180 min after mixing.

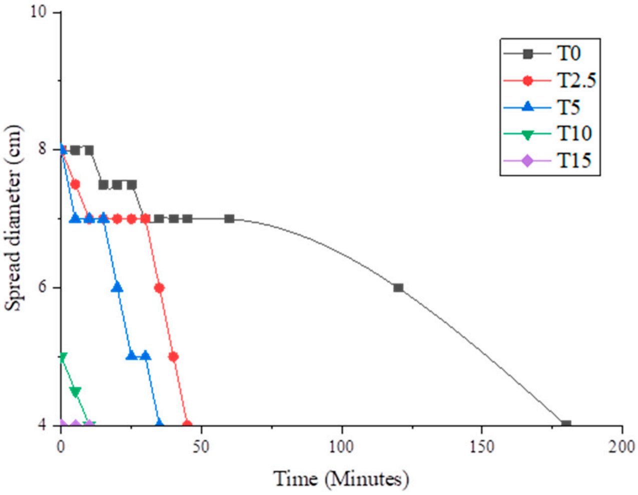

Figure 4. Mini-slump test of pastes with different TW replacements.

The extended diameter of T15 could not be determined due to its limited flowability. For T2.5, T5, and T10, the test ended at 45, 35, and 10 min, respectively.

For blended cement pastes, the flowability is lower than that of the reference paste (T0) at all times studied. TW is replaced by weight, and it has a density 2.81 times lower than that of the cement; therefore, TW occupies a greater volume compared to the cement. Consequently, the surface area to be wetted is significantly larger, and the amount of water available to mobilize the cement paste is reduced.

This decrease may be attributed to the carbon content present in the residue. Graphite (carbon) is a solid material that, in significant amounts, can act as a flowability reducer in cementitious matrices. If added in excessive quantities, the mixture becomes less manageable due to the hydrophilic properties of graphite [44]. The flowability value decreased as the toner powder content increased, which is similar to the case when it has been replaced in asphalts [45]. This could also be explained because the initial w/b ratio used to prepare the samples can be slightly reduced when more TW is added, mainly because the TW can compete with cement for water, consequently decreasing the quantity of water utilized for OPC hydration [46].

3.1.3. Calorimetry

Figure 5 shows the results of the heat evolution rate (mW/g) and cumulative heat released (J/g) for all samples. The heat release rate curves are similar for the number of maxima observed, each presenting six singular points: first, second, and third maximums (1M, 2M, and 3M) and first, second, and third minimums (1m, 2m, and 3m). The 1M value is not considered due to the processing characteristics of the paste. Once the temperature has stabilized, the materials are mixed manually outside the equipment.

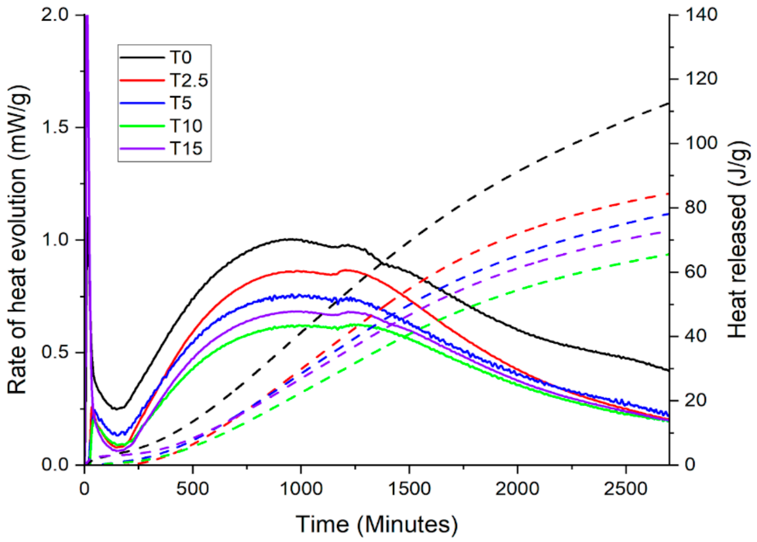

Figure 5. Calorimetry of pastes with different TW replacements.

The samples show the formation of a first stage with a significant heat release rate as a result of the first hydrolysis of the cement components, which subsequently reduces to register the 1m. For the standard sample, the initial minimum was measured at a rate of 0.24 mW/g for about 150 min.

Ettringite deposition on the cement grains slows the hydration process, so the dormant period is characterized by a low rate of heat release. The pastes remain malleable and workable during this time. Next, the hydration reactions accelerate as a consequence of the C-S-H gel formation, registering the 2M in the curve and causing the pastes to set. The maximum was attained in 980 min for the standard sample. The 2M shows a noticeable drop in the pastes' heat release rate with toner, which supports the cement's dilution.

The hydration reactions slowed down after the 2M, which led to a reduced rate of heat release. The conversion of ettringite into hydrated calcium monosulfoaluminate is represented by the 3M. Then, 3m is finally produced when the rate of heat emission slows down. The 3M does not show up if the cement has little or no tricalcium aluminate (C_3A) content. The test was considered completed after 48 h. Lastly, because the total heat values of the samples were lower than the norm, the results demonstrate the diluent impact of the PC caused by the addition of toner.

The incorporation of TW into pastes reduces the cement content, thus increasing the effective water-to-cement ratio and decreasing the available particles for hydration. Consequently, with less cement present, there is reduced heat generation (dotted lines) as TW acts as a dissipative focal point. This effect could be useful in situations where it is essential to control the heat released by the cement hydration reactions in order to minimize the risks of thermal cracking, for example, in massive concrete.

3.1.4. Normal Consistency Paste

Table 3 details the water requirement (expressed as % by weight of binder) to obtain pastes of normal consistency. During the mixing of the blended cement pastes, black bubbles were observed due to the presence of TW in the cement mixes.

Table 3. Water requirement for cement pastes with different TW replacements.

Sample	TW Replacement Level (%)	Water Requirement (%)
T0	0	25
T2.5	2.5	25.6
T5	5	26
T10	10	29
T15	15	33

As was observed for flowability, the higher the replacement level of cement by TW, the higher the water requirement. This is also attributed to the larger surface area to be wetted and the lower availability of mixing water.

3.1.5. Setting Times

When a hydraulic binder is mixed with water to obtain a paste of normal consistency [47], it successively presents two different events that develop over time: (a) a sudden increase in viscosity followed by a rise in temperature of the paste (beginning of setting), and (b) a progressive and regular transformation of the paste into a rigid block (end of setting).

Table 4 shows the initial and final setting times of the pastes. It shows that the replacement of cement by TW accelerated the initial setting time and delayed the final setting time, compared to the reference sample. The maximum difference in the initial setting time was observed in T2.5 and T5 compared to T0 (18% shorter). For the final setting time, the maximum difference compared with T0 was found in T2.5 (9% longer). However, from a practical point of view, these differences (10 to 20 min) do not represent a major concern for use in mortars and concretes in building applications.

Table 4. Setting times of cement pastes with different TW replacements.

Sample	Setting Times (min)		Setting Duration (min)
	Initial	Final	
T0	130	210	80
T2.5	110	230	120
T5	110	225	115
T10	115	225	110
T15	115	210	95

On the other hand, the higher the cement replacement by TW, the faster the final setting. It is attributed to the stimulating effect on cement hydration due to the presence of the small particles of TW.

3.2. Cement Mortars

Figure 6 (left) shows the visual appearance of mortars with different TW replacement levels. It shows that the higher the cement replacement by TW, the darker the color of the mortar. Figure 6 (right) shows the compressive strength of mortars from 7 to 56 days and the standard deviation.

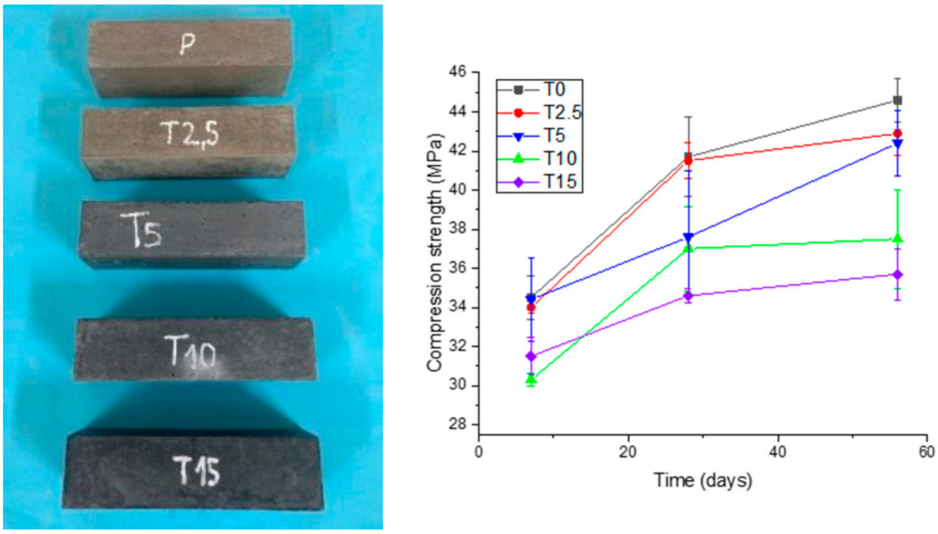

Figure 6. Mortars with different TW replacements (**left**) and compressive strength values (**right**).

Compressive strength decreased as the percentage substitution of OPC by TW increased. For all ages studied, this loss is not very significant. with additions of up to 5% of toner, while for higher doses, 10% and 15% of toner, the loss is in the order of 11% and 17% at 28 days and 15% and 20% at 56 days, respectively. Also, it is observed that at 56 days of age, the difference in standard deviation between T2.5 and T5 is not significant. However, for T10 and T15, there is a large difference.

A filler effect is attributed to the TW particles being located between the cement grains, which increases their contact area with water and leads to a faster initial hydration rate [48]. As a result, the initial compressive strength increased due to this physical effect [49,50]. In the mortar studied, TW stimulates the early hydration of T2.5 and T5. However, for T10 and T15, a dilution effect is detected, and it is higher than the filler effect, showing an evident decrease in compressive strength.

At 28 and 56 days, the dilution effect is observed in all mortars since TW does not exhibit pozzolanic activity, so its presence does not contribute to strength.

Table 5 presents the PAI results for all samples. While all mixes exceed the limit value at 28 days (0.75), the stimulating effect at early ages is also observed at T2.5 and T5, with a noticeable drop in strength greater than the replacement percentage at T10 and T15. As the amount of TW increases, the quantity of OPC decreases, consequently leading to an increase in the effective w/b ratio [51]. For the same degree of hydration of the cementitious material, this dilution effect implies a lower volume of hydrated cement products.

Table 5. PAI index of cement mortars with different TW replacements.

Age (Days)	T2.5	T5	T10	T15	PAI Limit
7	0.986	0.997	0.878	0.913	0.75
28	0.995	0.947	0.887	0.830	
56	0.962	0.951	0.852	0.800	
90	UD*	UD*	UD*	UD*	0.85

UD*: undetermined.

Table 6 shows the results of the leaching test at 56 days. On a 71-element scan in qualitative mode, only significant emission signals were detected for aluminum, calcium, potassium, sodium, sulfur, and silicon. Those elements are part of the chemical composition of the cement and not the TW, so no leaching of elements hazardous to human health is observed. On the other hand, all values detected are lower than the permitted limits established by National Argentine Law No. 24,051 [52] for rainwater discharges.

Table 6. Elements detected in the spectrometry of the curing water of mortars with different TW replacements after 56 days.

(mg/L)	T0	T2.5	T5	T10	T15	Limits [52]
Al	4.2	<0.19	-	<0.19	-	15
B	0.05	0.17	0.05	0.09	0.05	2
Ba	0.01	0.01	0.01	0.05	0.02	2
Ca	0.34	0.74	0.40	0.69	1.10	Unspecified
Cr	0.01	0.01	0.01	0.01	0.02	2
Cu	0.02	0.02	0.02	0.02	0.02	2
Fe	<0.01	0.01	0.01	<0.01	0.03	2
K	94	72	99	100	88	Unspecified
Li	0.13	0.07	0.10	0.09	0.17	Unspecified
Mg	0.02	0.05	0.02	0.05	0.05	Unspecified
Na	48	28	43	45	79	Unspecified
S	11	9	7.2	3.6	11	Unspecified
Si	20	18	13	15	23	Unspecified
Sr	0.01	0.02	0.01	0.06	0.03	Unspecified
Zn	<0.01	<0.01	<0.01	<0.01	0.08	2

Given the absence of positive pozzolanic reactivity in the TW (observed in the Frattini test), it is logical to note a higher calcium content in samples with the waste, as the TW did not capture this element. Additionally, the iron from the toner remained retained in the cementitious mixtures. The objective of this test is to assess whether the leached components are contaminants and if they comply with current regulations.

3.3. Embodied CO_2 of Cement Mortars with TW

Table 7 presents the ECO_2 of the component materials of cement mortars. It is observed that, for T0, about 95% of the ECO_2 of the mortar is due to the production and transport of the OPC. On the other hand, when the replacement of OPC by TW is increased, the ECO_2 of the mortars decreases, reaching a 14.3% reduction for T15. This indicates that the use of TW as a replacement for OPC appears as an interesting alternative regarding environmental performance since it allows revalorizing waste that can affect human health as well as reducing the CO_2 emissions of construction materials.

Table 7. ECO_2 of the component materials of cement mortars with different TW replacements.

Sample	ECO_2 per m^3 of Mortar (kg of CO_2 Equivalent/m^3)					
	OPC	Sand	Tap Water	TW	Total	Reduction (%)
T_0	466.5	21.0	2.3	0.00	489.7	-
$T_{2.5}$	454.8	21.0	2.3	0.01	478.1	2.4
T_5	443.2	21.0	2.3	0.03	466.4	4.8
T_{10}	419.8	21.0	2.3	0.06	443.1	9.5
T_{15}	396.5	21.0	2.3	0.08	419.8	14.3

4. Discussion

The properties of the examined cementitious mixes are influenced by TW substitution. TW is shown to have no pozzolanic activity in the Fratini test, which suggests that calcium silicate formation is absent and that the material is unable to react with the calcium hydroxide generated during cement hydration. Likewise, the calorimetric curves indicate that the samples containing TW do not exhibit acceleration in the hydration process when compared to the standard sample (T0). The impact of additives on cement hydration has been established [53]. T2.5 and T5 do not show significant variation in heat release during the dissolution of the crystalline phases of cement in comparison to the standard reference sample. At 7 days, T10 exhibits a higher number of nucleation sites, which could be attributed to the packing effect, which stimulates a response adequate to surpass heat generation in comparison to the T15 sample. Additionally, the incorporation of 15% TW may exceed the maximum packing limit, which could result in the separation of particles from the cementitious material. These chemical reactions exert an influence on strength development at various ages studied, as evidenced by the relationship between the area under the calorimetric curve, the total heat released, and, generally, the extent of strength development. The decline in strength is attributable to the dilution effect resulting from the replacement of cement with TW. However, a stimulation effect was observed for T2.5 and T5, as PAI was close to 1. The filler effect induces an alteration in the initial porosity of the mixture by the fine particles of TW filling the interstitial spaces between the cement grains [54]. Consequently, there is a potential for a slight increase in strength, particularly at early ages [53]. At low replacement levels, heterogeneous nucleation enhances the reactivity of the cementitious material [55]. This phenomenon is evident in the strength development observed in the samples at 7 days, as the TW has an insignificant impact on the standard mix.

As previously stated, TW has small-sized particles that exhibit a pronounced affinity for water. The incorporation of TW increases the amount of water required to attain the normal consistency of the paste. It could be attributed to the toner′s density, which is approximately three times lower than OPC, leading to a larger surface area to be wetted and reducing the availability of mixing water. The same effect is evident in the paste flowability, as indicated by the mini-slump test. In the case of T15, the extended diameter could not be determined due to its limited workability. Particularly, in the initial phase immediately following mixing, the fluidity index of the various pastes decreases compared to the standard (T0) as TW substitution increases.

As regards the setting characteristics, an increase in the substitution percentage correlates with a decrease in setting time. This reduction is linked to the reduced size and increased quantity of TW particles in the pastes, leading to accelerated drying. This trend is further evident in the calorimetric curves, specifically at the start and maximum peak of heat release during hydration. It is essential to highlight that the setting times were measured using the w/b ratio obtained from the normal consistency paste, while a constant ratio of 0.5 was employed for the calorimetric curves. Consequently, slight variations between the results may exist.

In summary, no appreciable differences are visually observed in terms of sample color, water demand to obtain a normal consistency paste, flowability, setting time, and compressive strength for T2.5 and T5 compared to T0. In contrast, a significant influence on the examined properties was observed for T10 and T15 compared to T0. It is evident that the lower density of TW worsens the flowability, and the dilution effect is stronger, negatively affecting the compressive strength when a higher volume of TW is included.

The results of the LCA show that the adoption of TW has a favorable effect on ECO_2. For this reason, the incorporation of TW could be a sustainable alternative for its final disposal, since both the production and transportation of cement produce fewer emissions.

5. Conclusions

This paper aims to find a better solution to the final disposal of hazardous waste such as toner, to valorize e-wastes, and to explore the use of black toner waste (TW) as a supplementary cementitious material replacement in cement pastes and mortars. For this purpose, Portland cement pastes and mortars were studied, and the life cycle assessment of the blended cement was evaluated, drawing the following conclusions:

- TW does not show pozzolanic activity according to the Frattini test.
- According to calorimetry, the replacement of Portland cement by TW produces a noticeable dilution effect. Both the heat evolution rate and cumulative heat released over the first 48 h decrease as the percentage of replacement of Portland cement by TW increases. However, variations in setting times generated by the incorporation of the residue in cement mixes are not relevant.
- The presence of TW reduces the flowability of the mixes.

- The replacement of Portland cement by TW does not significantly affect the compressive strength at early ages. However, the dilution effect becomes more pronounced at later ages. On the other hand, the decrease in compressive strength is not very relevant up to replacements of 5% by TW. T15 showed the greatest reduction in compressive strength at 56 days.
- All hazardous substances result below the legal limits in the leaching test.
- The replacement of TW for Portland cement is an interesting alternative regarding environmental performance since it allows revalorizing a waste that can affect human health as well as reducing the CO_2 emissions of construction materials. The use of TW in cement mixes could contribute to the reduction of up to 14.3% of CO_2 emissions with a cement replacement of 15% in cement-based materials.

To summarize, toner waste originated in a local industry can be immobilized in a cementitious matrix as it does not cause leaching above the established limits and contributes to the reduction of CO_2 emissions in cement-based materials. Taken together, these results suggest the incorporation of toner in percentages up to 15% in cement mixes is a feasible alternative for the final disposal of this potentially hazardous waste.

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