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Feasibility of recovered toner powder as an integral pigment in concrete

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Colour is an important property in many construction materials with pigments, coatings and paints being used primarily for aesthetic, safety and restoration purposes. However, the use of integral pigments in materials such as mortar and concrete can significantly increase material costs. Recovered toner powder (RTP) from printer and photocopier cartridges has the potential to be a low-cost and sustainable alternative pigment. The aim of this research was to examine the feasibility of using cyan, yellow, magenta and black RTP to create a range of colour options for mortar and concrete, and thereafter assess the colour stability in outdoor, indoor, ultraviolet and wet/dry conditions using the colour change parameter ΔE. The work showed that the RTP as a pigment could be blended to make a range of primary and secondary colours and had good colour stability in all environments with minimal impact on selected properties of hardened concrete.

Notation

a^*	red/green of specimen as measured by chroma meter
b^*	yellow/blue of specimen as measured by chroma meter
C^*	saturation
h^*	hue
L^*	lightness of specimen as measured by chroma meter
ΔC^*	change in specimen colour saturation level
ΔE_{00}	change in perceived colour of specimen as measured by CIEDE2000 colour change model
ΔE_{76}	change in perceived colour of specimen as measured by CIE1976 colour change model
Δh^*	change in specimen colour hue

1. Introduction

Colour in construction materials is a property that is often taken for granted and in many cases where colour is required it is often provided through applications of coatings and paints or additional materials such as cladding. Although colour plays an important role in shaping the aesthetic qualities of structures, it is often used in many other ways, including providing safety hazard warnings and lane separation on highways, cycle paths and pedestrian walkways (Vera-Villarroel *et al.*, 2016), to enhance solar reflectance on buildings and roofs (Levinson *et al.*, 2010) and matching materials with original substrates, particularly in the repair of historically sensitive structures (Rodríguez-Gordillo *et al.*, 2007). These are all areas where integral pigments within the construction material itself is the preferred option.

In terms of mortar and concrete, integral pigments such as carbon black (Concrete Society, 2002), natural oxides (Cornell and Schwertmann, 2003) and synthetics such as phthalocyanine greens and blue (López *et al.*, 2016a) are often used and these can be influenced by the chemistry of the cement matrix (Jang *et al.*, 2014). Given the costs of the pigments required to influence the colour of cement-based materials, this can often result in a doubling of material costs compared with standard ready-mix concrete. Due to these high costs related to pigmenting concrete, the competitiveness of integral pigments compared with other means of producing coloured finishes in architectural concrete is reduced.

An alternative material being considered as a sustainable, low-cost integral pigment for concrete and mortar is recovered toner powder (RTP). Toner cartridge sales in the EU were 120 million units in 2016–2017 (Etira, 2017) and with as much as 8–10% of the toner left within spent cartridges, an estimated 12 000 t of waste toner was produced in the EU during that period (K. Moock, private communication, 2018). Toner powder is a highly engineered fine particulate material, typically polymer based with various other compounds such as iron oxide, amorphous silica and pigments. Being immiscible in water and a potential dust hazard, RTP is classified as a special waste by the Scottish Environment Protection Agency and a hazardous waste by the UK/EU (Sepa, 2018). The main disposal route is currently landfilling, which is extremely costly for special wastes, although some work has shown it to be beneficial as a filler material in asphalt (Khedaywi, 2014; Popa *et al.*, 2015).

The performance of integral pigments is not only judged by their impact on other concrete and mortar properties such as workability, setting time, strength and durability, but also by their ability to provide a repeatable, perceptible change in the colour of concrete surfaces (López *et al.*, 2016b). Common pigments often require the use of a white cement (typically a CEM II/A-L) to provide noticeable changes in colour and these have proven to be relatively stable in typical outdoor conditions (López *et al.*, 2016a). To assess the likely performance of alternative pigments in comparison with traditional materials, colour measurement is crucial and a number of measurement systems exist. However, the $L^*a^*b^*$ colour space as defined by the International Commission on Illumination (CIE), based on one channel for luminance (lightness) (L^*) and two colour channels (a^* and b^*), is still very popular and two colour-difference models (CIE1976 and CIEDE2000) are used within the construction industry for determining perception of differences (CIE, 2001, 2004; Robertson, 1977).

Research at the University of Dundee has been conducted to examine the potential of using RTP as an integral pigment in concrete with particular emphasis on colour production and performance in various weathering environments. The work presented here focuses on the feasibility of using RTP blends to create various colour combinations and the impact of environmental conditions, including ultraviolet (UV) exposure and wetting and drying, on the colour fastness of pigmented concrete.

2. Experimental programme

A feasibility study was undertaken in three main parts to determine whether RTP could be used as a sustainable durable pigment for concrete. The study focused on

(*a*) a colour development study on cement pastes to determine the ease with which primary and secondary colours could be produced using RTP as a pigment
(*b*) a concrete weathering study to examine the likely performance of the RTP (cyan, magenta, yellow and black) alongside a control (white cement) concrete
(*c*) a concrete surface study to examine the influence of controlled-permeability formwork (CPF) on RTP and non-RTP concrete properties.

2.1 Colour development study

To determine the ability of toner to blend and develop secondary colours, 100 mm dia. × 15 mm thick paste specimens were produced by replacing the control cement with RTP at different percentage levels (5, 10 and 20% by weight). Initially, primary colours (in printing terms) were produced (cyan, yellow and magenta) at the three toner levels and the impact on $L^*a^*b^*$ compared with the control white cement. A series of cement/RTP combinations was then cast and three secondary colours were produced (green, red and purple). The range of colours is shown in Figure 1. To produce the secondary colours, RTP was blended in equal parts prior to mixing (green = cyan + yellow, purple = magenta + cyan, red = magenta + yellow). Three disc specimens were produced and tested for each colour combination.

Figure 1. Paste specimens produced for the colour development study showing primary colours (cyan, magenta, yellow), secondary colours (purple, green, red), black, and control white (CEM II/A-L). A full-colour version of this figure can be found on the ICE Virtual Library (www.icevirtuallibrary.com)

2.2 Weathering study

Details of the five weathering environments (black-box control, outdoor exposure, wet/dry, UV exposure, indoor exposure) are given in Table 1. 300 mm × 300 mm × 50 mm concrete specimens and 100 mm cubes (wetting and drying environment only) were placed in different environments for a period of 8 weeks to determine the effects of temperature, relative humidity (RH), exposure to moisture and UV radiation. Colour coordinates were measured pre-weathering, and at periods of 1, 4 and 8 weeks exposure. Three slab specimens were produced for each weathering environment and six 100 mm cubes were used in the wetting/drying chamber.

2.3 Formwork surface study

Concrete prism specimens of 500 mm × 300 mm × 150 mm were cast with 100% CEM II/A-L and CEM II/A-L + 10% cyan RTP. CPF was used on one of the large specimen faces with the remaining large face being cast against conventional marine ply (impermeable membrane formwork (IMF)). The slab specimens were standard cured for 28 d and then four 100 mm cores were extracted and sliced (20 mm thick slices). This allowed a comparison of colour coordinates, capillary

Table 1. Details of weathering environments used

Environment	Conditions	Ambient conditions
Black box (control)	Samples were placed in a dark box with minimal intrusion from light	20 ± 2°C, 40–50% RH
Outdoor exposure	Samples exposed on the roof of the Fulton Building, University of Dundee, with full exposure to precipitation and UV (January–March)	8 ± 5°C, 80–90% RH
Wet/dry exposure	3 h cycles of wetting and drying. The water used was potable water	Wetting: 18 ± 2°C (mains water) Drying: 20 ± 2°C, 40–50% RH
UV exposure	Samples placed in an UV light box for accelerated degradation	40 ± 5°C, 40–50% RH 100 W UV bulb (mean distance 300 mm)
Indoor exposure	Indoor environment, samples placed in a laboratory environment with indirect exposure to sunlight	20 ± 2°C, 40–50% RH

Table 2. Physical and chemical characteristics of CEM II/A-L used

Property	
Blaine fineness: m^2/kg	480
Particle density: g/cm^3	3·05
Initial setting time: min.	155
Bulk oxide composition: %	
Calcium oxide	64·1
Silicon dioxide	15·9
Aluminium oxide	3·1
Ferric oxide	0·2
Magnesium oxide	2·8
Manganese oxide	0·1
Titanium dioxide	0·1
Potassium oxide	0·4
Sodium oxide	0·1
Phosphorus pentoxide	0·1
Sulfur trioxide	2·2

porosity, hardened density and surface strength (rebound hammer) to be made between RTP and non-RTP concrete cast against both IMF and CPF faces.

3. Materials and mix proportions

3.1 Portland–limestone cement

A commercially available Portland–limestone cement (CEM II/A-L) conforming to BS EN 197-1:2011 (BSI, 2011) was used as the control (white) cement to enhance the potential for pigmenting cement pastes and concretes. The chemical and physical characteristics are shown in Table 2 and the particle-size distribution in Figure 2.

3.2 Coarse and fine aggregates

Natural glacial gravel coarse aggregates were in two size fractions (4/10 and 10/20 mm) with glacial fine aggregates in a single size fraction (0/4 mm), all of which conformed to BS EN 12620:2013 (BSI, 2013a). The absorption values for the aggregates were 1·6% for 10/20, 1·8% for 4/10 and 0·8% for 0/4. All aggregates were air dried in the laboratory (50–60% RH, 20 ± 2°C) prior to use.

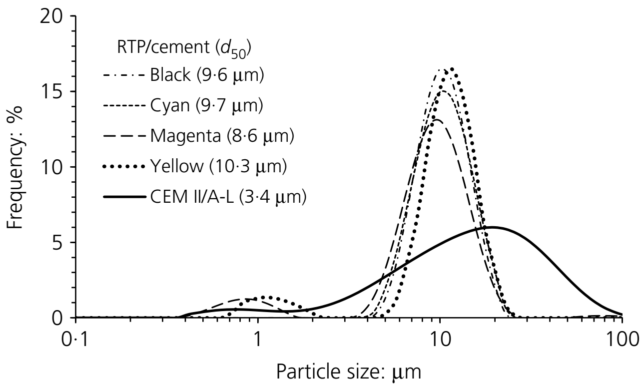

Figure 2. Particle-size distribution of cyan, magenta, yellow and black RTP and CEM II/A-L control cement

3.3 RTP

The chemical characteristics of toner are commercially sensitive, however, it typically consists of styrene-acrylate copolymer, polyester, magnetite, iron oxide, carbon black, propylene wax, ethylene/propylene resin, paraffin wax and chromium/azo dye complex (A. Watson, private communication, 2015). A supply of RTP was obtained from a local recycler who recovers toner powder from spent laser printer cartridges and photocopiers and separates the RTP into its original cyan, magenta, yellow and black colours.

The particle-size distribution of the four available RTPs (cyan, magenta, yellow, black) is shown in Figure 2, with all RTPs having particle sizes d_{50} of 8–10 µm. Figure 3 shows that the RTP particles (under 500 × magnification using scanning electron microscopy (SEM)) are mostly angular for cyan, magenta and yellow, however, the black RTP particles are spherical in shape due to differences in the manufacturing process (A. Watson, private communication, 2015).

3.4 Cement paste and concrete mix proportions, preparation and conditioning

The cement paste and concrete mix proportions are shown in Tables 3 and 4. The RTP was used as a cement replacement for

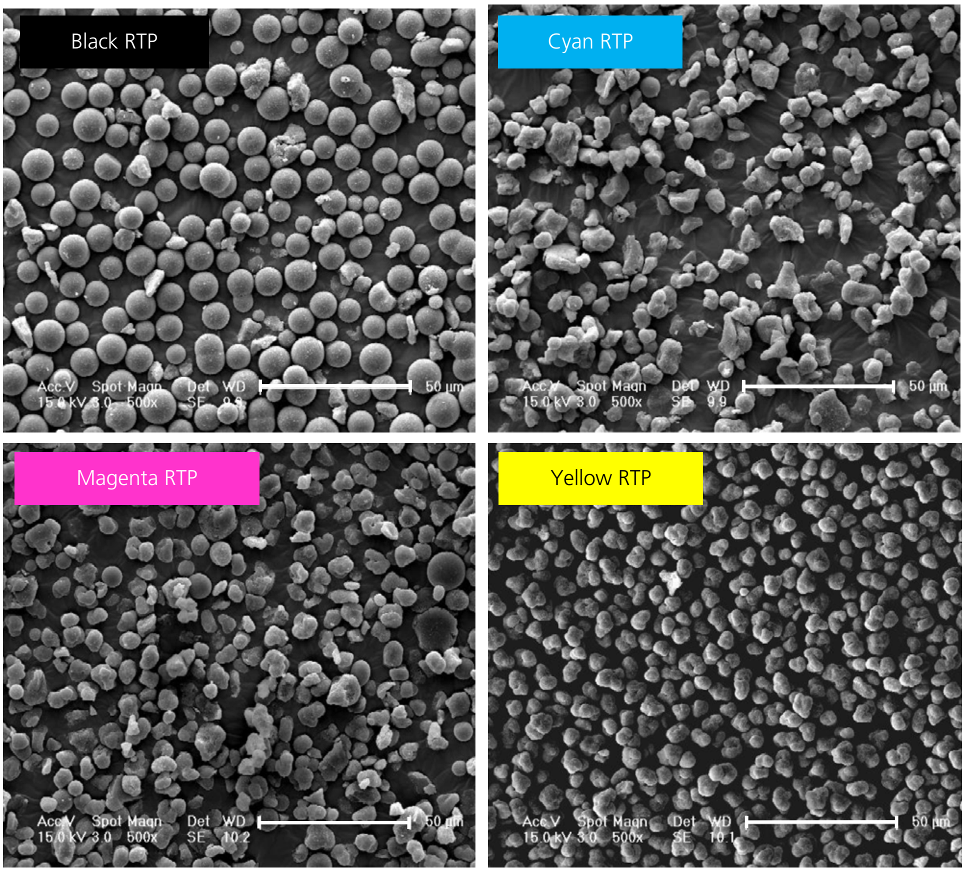

Figure 3. SEM images of RTP particles at 500× magnification (scale bar is 50 μm). A full-colour version of this figure can be found on the ICE Virtual Library (www.icevirtuallibrary.com)

Table 3. Mix proportions for cement pastes containing RTP for colour development study

RTP content: %[a]	Mix proportions: g CEM II/A-L	RTP[b]	Water	w/(c + RTP) ratio
0	150	0	75	0·5
5	142	8	75	0·5
10	135	15	75	0·5
20	120	30	74	0·5

[a] Replacement by weight of cement
[b] RTP content for binary combinations split evenly (e.g. green = cyan:yellow at 1:1 ratio)

both paste and concrete to enhance the sustainability and potentially reduce the cost of the mixes by reducing the CEM II/A-L content. While the water/(cement + RTP content) (w/(c + RTP)) ratio was constant (0·50 for paste, 0·51 for concrete), the water/CEM II/A-L content varied, which led to a variation in the 10 mm cube strength (tested to BS EN 12390-3:2009 (BSI, 2009a)), as shown in Table 4. This variation in water/CEM II/A-L ratio (0·54–0·64) was higher than that specified for typical structural concrete as coloured concretes are rarely used in structural elements with high loading requirements and, as such, strength was not the primary concern. Workability of the concretes was designed to an S2 slump class (60–90 mm) as per BS EN 206-1 (BSI, 2013b) and slump values are shown in Table 4. As the RTP displayed hydrophobic properties, a small amount (<0·5% by weight of RTP) of an admixture previously developed by the University of Dundee (patent no. GB2505342 (Intellectual Property Office, 2018)) was added, which allowed the RTP to be mixed into the pastes and concretes. Although the admixture contained surfactants, the water content was kept constant and hence the impact on workability was minimal.

Paste samples were prepared by mixing the cement paste, water and toner/admixture combinations in a paddle mixer for 1 min. Specimens were cast into 100 mm dia. ring moulds sitting on a glass surface to ensure a smooth finish on the bottom face of the test disc. They were cured in the mould for 24 h and then transferred to an air-curing chamber (20 ± 2°C, 50 ± 5% RH) for 7 d.

Table 4. Mix proportions and strength development for concrete containing RTP for weathering study (w/(c + RTP) = 0·51)

Mix	w/CEM II/A-L ratio	Mix proportions: kg/m³						RTP[a]	Slump: mm	Cube strength: MPa				
		Water	CEM II/A-L	RTP	0/4	4/10	10/20			3 d	7 d	28 d	Mean[b]	V: %[c]
Control	0·51	180	350	0	610	375	750	—	65	17·8	30·1	39·6	—	—
5% RTP[d]	0·54	180	333	17	600	370	735	C	70	16·6	27·3	36·0	35·5	2·9
								M	65	15·1	26·5	35·2		
								Y	75	15·4	24·2	34·3		
								K	70	17·3	27·5	36·8		
10% RTP[d]	0·57	180	315	35	600	370	735	C	75	14·6	23·7	30·4	27·5	8·2
								M	80	13·4	22·0	28·0		
								Y	85	11·5	18·9	24·9		
								K	80	12·2	19·5	27·1		
20% RTP[d]	0·64	180	280	70	600	370	735	C	90	10·3	17·1	22·8	21·5	6·2
								M	95	10·0	15·9	21·8		
								Y	85	9·4	14·5	19·6		
								K	85	10·5	17·5	21·5		

[a] C = cyan, M = magenta, Y = yellow, K = black
[b] Mean strength across cyan, magenta, yellow and black RTP concretes at 28 d
[c] Coefficient of variation across cyan, magenta, yellow and black RTP concrete strength at 28 d
[d] Replacement by weight of cement

Concrete was mixed using the standard procedure in BS 1881-125:2013 (BSI, 2013c) with the toner/admixture combination added at the same time as the cement. Specimens were removed from the moulds after 24 h and water-cured for 28 d. Prior to placing in the weathering environments, concrete samples were dried in laboratory air (20 ± 2°C, 50 ± 5% RH) for 48 h.

4. Test methodologies

4.1 Calorimetry of cement pastes

The influence of RTP on the hydration of CEM II/A-L was examined using isothermal calorimetry. Cement paste specimens (w/c ratio = 0·5) with an additional 10% RPT content were tested with RTPs premixed containing 0·35% admixture (by weight of toner) and then dried until constant mass at 50°C to remove moisture so that the w/c ratio was 0·5 for each calorimetry sample. Samples were monitored for a period of 48 h. Figures 4(a)–4(d) compare the thermal power (mW/g of CEM II/A-L) for cement plus 10% RTP of cyan, magenta, yellow and black. Immediately after mixing, the RTP pastes exhibited a slightly higher heat release throughout the 48 h test period but more so up until the end of the dormant period (as shown in the inset graphs in Figure 4). This may be due to toner particles providing additional nucleation sites or partially disrupting the initial semi-permeable layer formed on cement particles.

A general observation for all RTP colours was that the ettringite/monosulfate transition peak associated with CEM II/A-L (shown here at around 12 h) appeared marginally sooner with the addition of RTP; indeed, the calorimetry study showed that the RTP did not hinder the hydration reaction.

4.2 Colour measurement of cement pastes and concretes

Colour measurement can be carried out using various systems (e.g. CIE *Yxy*, CIE $L^*a^*b^*$, CIE $L^*C^*H^*$, colorimetric densities, Munsell notation). However, in the current study, the CIE $L^*a^*b^*$ was used as this is commonly accepted as the most complete colour system used to describe all the colours visible to the human eye (Habekost, 2013). CIE $L^*a^*b^*$ uses three parameters to plot a colour space, which can be organised in a cube form. The parameters each represent a different property of the colour being measured, with L^* representing changes in lightness or tone (0 = black to 100 = white), a^* representing red ($+a^*$) to green ($-a^*$) changes and b^* representing yellow ($+b^*$) to blue ($-b^*$). In theory, there is no maximum or minimum value for a^* or b^*; however, typical values range from −128 to + 127 (256 levels).

The use of $L^*a^*b^*$ also meant that other parameters such as colour saturation (C^*) and hue (h^*) could be calculated. This allowed determination of the impact of toner content and weathering effects on the intensity of colour (saturation) and the degree to which a stimulus can be described as similar to or different from stimuli that are described as red, green, blue and yellow (hue) (Fairchild, 2010).

To obtain $L^*a^*b^*$ values, a Minolta CR-210 chroma meter was used (under CIE standard illuminant D_{65}), with a standard (colorimetric) observer of 2° (CIE1931 calibration coordinates of $x = 0{\cdot}3158$, $y = 0{\cdot}3333$) on the surface of dry cement paste and concrete specimens.

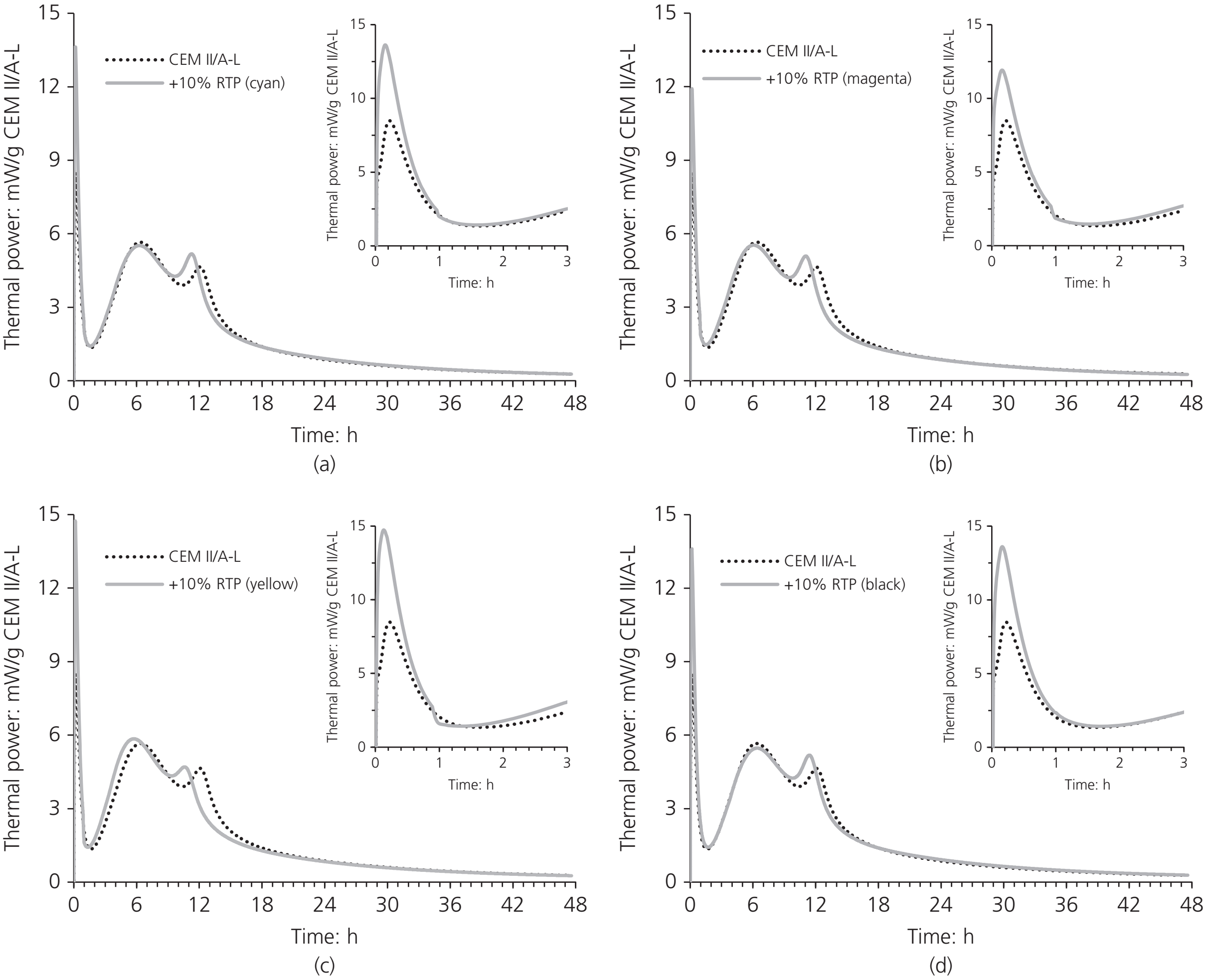

Figure 4. Isothermal calorimetry curves for cement pastes of CEM II/A-L plus 10% RTP of (a) cyan, (b) magenta, (c) yellow and (d) black. Inset graphs focus on early reactions up to 3 h from mixing

For the cement paste samples, three discs were tested and the average values calculated. For the concrete samples, two readings on a single face of three slabs were taken (six values in total) and a single reading from each of the six cubes (wetting and drying environment only) was taken. The averages of these readings are expressed in this paper. Across the paste samples tested, the largest coefficient of variation was 9% for $L^*a^*b^*$ readings. In both concrete slabs and cubes, the maximum coefficient of variation was found to be 12%.

Where necessary (in wetting/drying and outdoor environment weathering), prior to reading the colour coordinates, concrete specimens were dried for 24 h in laboratory air (20 ± 2°C, 50 ± 5% RH) to ensure the specimens were in a similar surface dry condition.

4.3 Measurement of colour changes: lightness, saturation and hue

Colour changes were compared by examining the changes in colour saturation (ΔC^*) and hue (Δh^*), which are functions of a^* and b^* values. C^* and h^* were calculated as using Equations 1 and 2.

$$1. \quad C^* = [(\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

$$2. \quad h^* = \arctan(b^*/a^*)$$

Changes in the visual perception of the colour, due to either varying RTP content, weathering exposure effects or formwork surface material were expressed as ΔE, based on either the CIE1976 or CIEDE2000 formulae. ΔE is taken as a measure of the perceived difference between colours (effectively the geometrical distance between their positions in the CIE $L^*a^*b^*$ colour space).

CIE1976 expresses the perceived colour change ΔE_{76} as

$$\Delta E_{76} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{3}$$

where ΔL^*, Δa^* and Δb^* are the differences in colour coordinates between two measurements and this is commonly used by industry as a conformity check for pigments (BSI, 2014).

A more recent approach, CIEDE2000, provides an improved colour-difference recognition, taking into account corrections for non-uniformity of the CIELAB space and parameters that account for illuminating and viewing conditions.

The CIEDE2000 ΔE_{00} is expressed as

$$\begin{aligned}\Delta E_{00} = \Bigg[&\left(\frac{\Delta L'}{K_L S_L}\right)^2 + \left(\frac{\Delta C'}{K_C S_C}\right)^2 + \left(\frac{\Delta H'}{K_H S_H}\right)^2 \\ &+ R_T\left(\frac{\Delta C'}{K_C S_C}\right)^2\left(\frac{\Delta H'}{K_H S_H}\right)^2\Bigg]^{1/2}\end{aligned} \tag{4}$$

where the $L^*a^*b^*$ values are transformed to corresponding $L'C'H'$ to correct for hue angle, chroma and lightness values. Also, weighting functions (S_L lightness difference, S_C chroma difference, S_H hue difference) deal with non-uniformity in the light space and the parametric K factors deal with illumination and viewing conditions (set as 1 as reference conditions were similar to those found in practice). The rotation term (R_T) accounts for interaction between chroma and hue differences.

While there are no guidelines on ΔE values for colour changes in concrete, it is commonly accepted that a ΔE of 1·0 is the lower limit of what is perceptible by the human eye and, in concrete, ΔE values of below 1·5 are commonly accepted as the limit of perception (Teichmann, 1990). In this study, ΔE values were classified as

<1·5 = no perceptible difference in colour
1·5–3·0 = slight difference in colour
3·0–6·0 = obvious difference in colour
>6·0 = large difference in colour

For the purpose of this study, the authors selected a ΔE of 3·0 as the upper threshold (for both ΔE_{76} and ΔE_{00}) for allowable changes in colour but changes were also compared with a ΔE of 1·5 in some cases to assess changes in terms of the upper and lower limits of slight differences in colour.

In addition, to examine the position of the pigmented paste samples in relation to the CIE1931 (CIE, 2004) chromaticity diagram, $L^*a^*b^*$ colour space values were converted to xyz colour spaces using the CIE XYZ tri-stimulus values. These is a device-independent colour representation, which effectively serves as a standard reference against which other colour spaces can be defined. Conversion from $L^*a^*b^*$ to XYZ was carried out using the inverse of

$$X = X_n f^{-1}\left(\frac{L^*+16}{116} + \frac{a^*}{500}\right) \tag{5}$$

$$Y = Y_n f^{-1}\left(\frac{L^*+16}{116}\right) \tag{6}$$

$$Z = Z_n f^{-1}\left(\frac{L^*+16}{116} + \frac{b^*}{200}\right) \tag{7}$$

where X_n, Y_n and Z_n are the tri-stimulus values of the reference white calibration sample (Fairchild, 2010).

x, y and z chromaticity values are then derived from the XYZ tri-stimulus values as

$$x = \frac{X}{X+Y+Z} \tag{8}$$

$$y = \frac{Y}{X+Y+Z} \tag{9}$$

$$z = \frac{Z}{X+Z+Z} = 1 - x - y \tag{10}$$

Thus, z is a function of x and y and can be ignored, allowing xy to be plotted (Fairchild, 2010).

4.4 Tests on concrete slices

To examine the influence of RTP and surface finish on the near-surface properties of concrete, a series of comparative tests was carried out on 100 mm dia. × 20 mm thick concrete slices. Surface hardness was tested to BS EN 12504-2:2012 (BSI, 2012) with six rebound readings taken per slice. Capillary porosity of the slice was tested to BS 1881-124:2015 (BSI, 2015) and hardened density to BS EN 12390-7:2009 (BSI, 2009b).

Table 5. Colour coordinates ($L^*a^*b^*$), colour saturation (C^*) and hue (h^*) and change between 5 and 20% RTP content

RTP recipe: % by weight of cement		Colour coordinates, saturation and hue					Change, with respect to 5%		
		L^*	a^*	b^*	C^*	h^*	$\Delta C^*_{5\%}$	$\Delta h^*_{5\%}$	$\Delta E_{76,5\%}$
Control (0%)		89·05	−0·96	5·97	6·05	−1·41	—	—	—
Cyan	5	72·56	−3·30	−14·02	14·40	1·34	—	—	—
	10	66·15	−4·47	−21·86	22·31	1·37	7·91	0·03	10·2
	20	56·50	−1·88	−32·85	32·90	1·51	18·50	0·17	24·8
Magenta	5	73·10	19·50	−4·68	20·05	−0·24	—	—	—
	10	56·30	30·19	−6·86	30·96	−0·22	10·91	0·01	20·0
	20	46·66	43·03	−8·08	43·78	−0·19	23·73	0·05	35·6
Yellow	5	76·35	−4·25	28·39	28·71	−1·42	—	—	—
	10	70·35	−3·05	31·45	31·60	−1·47	2·89	−0·05	6·8
	20	69·73	−5·35	31·20	31·66	−1·40	2·95	0·02	7·3
Black	5	60·00	0·40	1·71	1·75	1·34	—	—	—
	10	50·05	0·49	1·62	1·67	1·27	−0·33	−0·18	17·0
	20	43·00	0·57	1·30	1·42	1·16	−0·07	−0·07	10·0
Purple[a]	5	71·97	9·38	−7·68	12·12	−0·69	—	—	—
	10	59·02	8·91	−17·92	20·01	−1·11	7·89	−0·42	16·5
	20	50·83	11·61	−22·42	25·25	−1·09	13·12	−0·41	25·9
Green[a]	5	68·55	−7·52	5·90	9·56	−0·67	—	—	—
	10	66·33	−8·65	4·67	9·83	−0·50	0·27	0·17	2·8
	20	57·52	−11·73	6·64	13·48	−0·52	3·92	0·15	11·8
Red[a]	5	68·40	9·38	8·00	12·33	0·71	—	—	—
	10	62·51	13·18	10·71	16·98	0·68	4·65	−0·02	7·5
	20	54·59	18·52	13·21	22·75	0·62	10·42	−0·09	17·4

[a] Secondary colours created through 1:1 binary combinations of RTP: purple = cyan + magenta, green = cyan + yellow, red = magenta + yellow

5. Colour development study: results

Table 5 compares the $L^*a^*b^*$ values of the paste discs along with colour saturation (C^* and ΔC^*) and hue (h^* and Δh^*). The data show that adding small amounts of toner into the mixture (5%) was enough to change the h^* value in all colour combinations except when using yellow RTP. Increasing the level of RTP content from 5 to 20% led to a notable reduction in the L^* value, indicating that these samples absorbed more light. As the RTP content increased, the colour saturation also increased (ΔC^*) with magenta and cyan RTP; however, ΔC^* was much lower when using yellow RTP. The influence of using yellow RTP was also seen in the change in colour space (ΔE_{76}), with significant colour change in magenta and cyan toner compared with yellow toner, indicating that higher levels of yellow toner may be needed to produce colour changes in CEM II/A-L cements. This influence of using yellow toner on saturation and perceived colour change was also seen in green and red combinations with the colour saturation change being less than that of combinations where yellow was not used.

The work on paste showed that RTP has the potential to produce a range of colours as both a single pigment and as a blended pigment with relatively low percentage values (10%) replacement of CEM II/A-L by toner making a perceivable difference – that is, $\Delta E_{76} > 3{\cdot}0$.

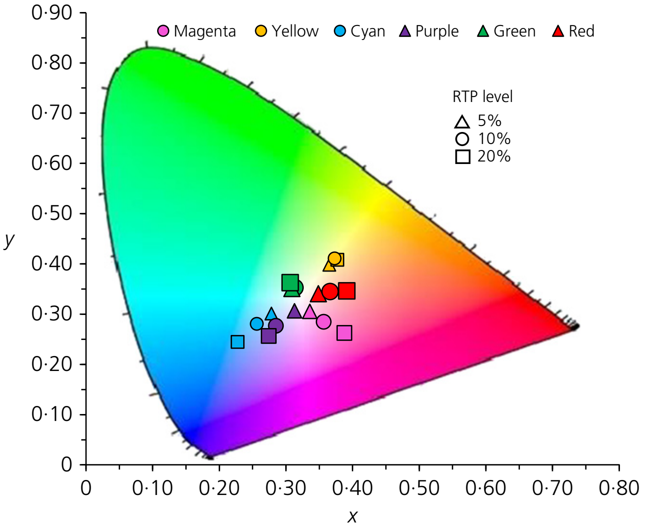

Figure 5. Comparison of colour coordinates on CIE1931 colour space chart for the colour development study. A full-colour version of this figure can be found on the ICE Virtual Library (www.icevirtuallibrary.com)

Figure 5 shows the single and blended colours of the samples plotted on the CIE1931 colour space chart. The figure confirms that there was a significant shift in the colour space

Table 6. Lightness (L^*), saturation (C^*) and hue (h^*) for control and RTP pigmented concrete (20% RTP content) measured up to 8 weeks exposure in various weathering conditions

		Pre-exposure			1 week			4 weeks			8 weeks		
RTP concrete	**Weathering environment**	L^*	C^*	h^*	L^*	C^*	h^*	L^*	C^*	h^*	L^*	C^*	h^*
CEM II/A-L control, (no RTP)	Black box	62·82	8·22	1·32	62·81	8·22	1·32	62·81	8·22	1·27	62·70	8·68	1·29
	Outdoor	66·18	7·60	1·34	66·18	7·60	1·34	67·12	7·81	1·32	66·21	7·85	1·30
	Wet/dry	73·99	7·45	1·40	73·91	7·46	1·41	72·69	7·59	1·42	72·10	7·39	1·41
	UV box	69·25	7·73	1·35	69·28	7·75	1·35	70·59	8·00	1·33	70·47	7·89	1·33
	Indoor	69·37	7·58	1·34	69·37	7·59	1·34	71·20	7·41	1·33	71·30	7·35	1·32
Cyan	Black box	52·40	19·42	1·35	52·38	19·41	1·35	52·30	20·08	1·35	51·55	19·08	1·33
	Outdoor	51·10	19·96	1·34	51·11	19·96	1·34	49·00	19·10	1·32	49·00	18·76	1·33
	Wet/dry	54·20	20·32	1·32	54·13	20·31	1·32	55·32	20·54	1·32	56·32	19·68	1·29
	UV box	52·10	19·92	1·32	52·04	19·92	1·32	52·44	19·15	1·28	51·70	19·07	1·27
	Indoor	51·10	19·99	1·36	51·02	19·98	1·36	52·00	19·89	1·31	52·00	19·76	1·29
Magenta	Black box	48·66	28·77	−0·21	48·66	28·77	−0·21	48·44	29·91	−0·20	48·81	30·18	−0·18
	Outdoor	51·23	24·14	−0·24	51·22	24·12	−0·24	52·85	25·24	−0·21	52·20	25·03	−0·21
	Wet/dry	57·14	25·15	−0·23	57·13	25·16	−0·23	55·60	25·85	−0·21	55·30	25·85	−0·19
	UV box	50·23	28·86	−0·23	50·22	28·78	−0·23	51·10	28·87	−0·20	51·20	28·28	−0·18
	Indoor	51·99	30·08	−0·24	51·91	30·01	−0·24	52·60	29·50	−0·23	52·99	29·48	−0·23
Yellow	Black box	59·30	20·95	−1·37	59·25	20·94	−1·37	60·64	22·08	−1·37	60·47	22·25	−1·37
	Outdoor	63·90	24·29	−1·37	63·91	24·28	−1·37	62·36	22·67	−1·37	62·50	22·31	−1·36
	Wet/dry	64·20	21·21	−1·36	64·17	21·21	−1·36	62·27	19·85	−1·41	62·20	19·85	−1·41
	UV box	64·50	24·74	−1·43	64·56	24·73	−1·43	65·39	24·38	−1·43	62·20	23·69	−1·42
	Indoor	64·20	25·88	−1·42	64·13	25·88	−1·42	63·72	25·38	−1·40	62·50	25·25	−1·40
Black	Black box	43·00	1·42	−1·16	43·00	1·37	−1·13	42·00	1·17	−0·99	42·00	1·12	−1·07
	Outdoor	42·82	1·48	−1·15	42·88	1·49	−1·15	41·69	0·72	−0·66	42·50	0·69	−0·62
	Wet/dry	45·02	1·20	−1·56	45·00	1·20	−1·56	42·20	0·36	−1·35	42·80	0·22	−1·34
	UV box	42·60	1·44	−1·22	42·57	1·47	−1·22	45·01	0·97	−1·20	44·40	0·60	−1·14
	Indoor	42·32	1·65	−1·27	42·29	1·67	−1·27	44·41	1·21	−1·41	44·00	1·00	−1·21

when using cyan- and magenta-based toner as a pigment with changes seen in both x and y coordinates for cyan, magenta, purple (cyan + magenta) and red (magenta + yellow). The change in coordinates was much lower when using the yellow toner as the base pigment with small shifts in x and y coordinates for yellow and green (yellow + cyan), indicating that higher percentages of yellow toner would be required to make meaningful changes to deeper greens and yellows when using a CEM II/A-L cement.

6. Colour weathering resistance study: results

Table 6 shows the lightness (L^*), colour saturation (C^*) and hue (h^*) for concrete samples in the colour weathering study. Samples were tested pre-exposure and after 1, 4 and 8 weeks. Pre-exposure colour coordinates for samples within colour bandings were deemed to be similar, with variations for $L^*a^*b^*$ being less than 10%. This level of variability was deemed to be consistent with the natural colour variability of concrete.

Figures 6 and 7 compare the colour differences (ΔE_{76} and ΔE_{00}, respectively) of all specimens from pre-exposure to 8 weeks exposure. Figures 8 and 9 show the change in colour saturation (ΔC^*) and hue (h^*), respectively. Figures 6 and 7 show that, across all colours, although there was a small shift in colour coordinates within the black-box control series, in all cases $\Delta E_{76} < 3{\cdot}0$, as was ΔE_{00}. This indicated that although there were changes in the $L^*a^*b^*$ values, there was no significant noticeable difference in colour within the control series at 8 weeks.

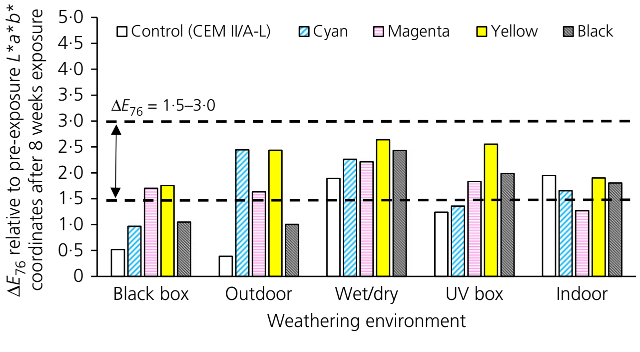

Figure 6. Change in colour space (ΔE_{76}) compared with pre-exposure for various RTP concretes after 8 weeks exposure in various weathering environments. A full-colour version of this figure can be found on the ICE Virtual Library (www.icevirtuallibrary.com)

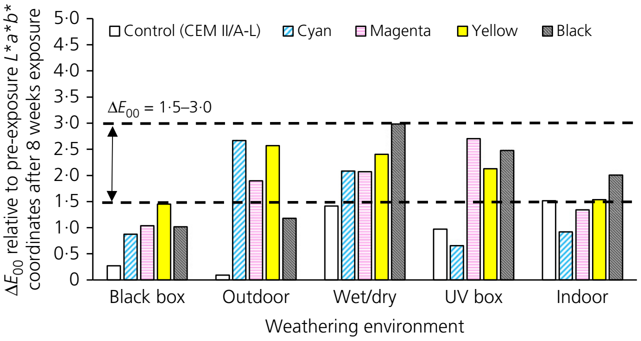

Figure 7. Change in colour space (ΔE_{00}) compared with pre-exposure for various RTP concretes after 8 weeks exposure in various weathering environments. A full-colour version of this figure can be found on the ICE Virtual Library (www.icevirtuallibrary.com)

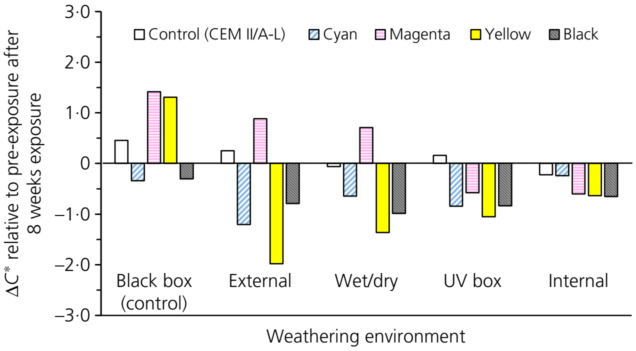

Figure 8. Change in colour saturation (ΔC^*) compared with pre-exposure for RTP concretes after 8 weeks exposure in weathering environments. A full-colour version of this figure can be found on the ICE Virtual Library (www.icevirtuallibrary.com)

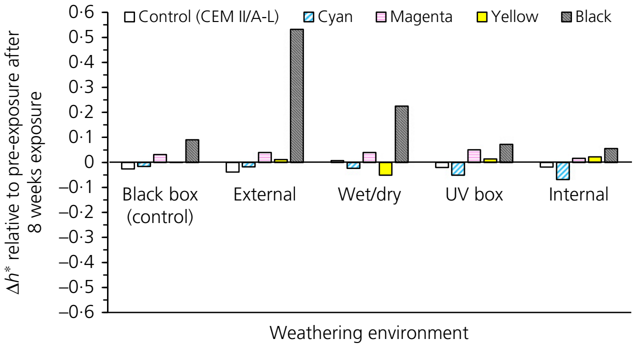

Figure 9. Change in colour hue (Δh^*) compared with pre-exposure for RTP concretes after 8 weeks exposure in weathering environments. A full-colour version of this figure can be found on the ICE Virtual Library (www.icevirtuallibrary.com)

6.1 Outdoor weathering environment

Measurement of colour coordinates after up to eight weeks in the outdoor weathering series showed that cyan and yellow toner concretes produced ΔE_{76} and ΔE_{76} in the region of 2·5 in both cases. This change was the largest of the colour series subset, with magenta next and then black (ΔE_{76}, ΔE_{00} both <1·5).

In terms of colour saturation, a similar trend was seen with yellow and cyan RTP exhibiting a greater reduction in colour saturation at 8 weeks compared with the other colours. For all colours, the hue was largely unchanged at 8 weeks, apart from black toner, which showed a movement of +0·55 units. This, in part, is related to the fact that the L^* value of the black RTP specimens varied between 42 and 45 units, indicating that there was some influence from the a^* and b^* parameters causing a change to the ΔE_{76} and ΔE_{00} values as lightness (L^*) remained largely unchanged after 8 weeks. Although there were changes in the measured colour space in the outdoor weathering series, the maximum ΔE_{76} and ΔE_{00} values were <3·0 units.

6.2 Wet/dry weathering environment

Wetting and drying of the RTP concrete specimens (100 mm cubes) showed an increase in change in colour space coordinates after 8 weeks (~56 cycles of wetting/drying). This was seen across all colours, including the control white CEM II/A-L specimen. ΔE_{76} and ΔE_{00} were around 2·0 units for cyan and magenta, with yellow increasing to $\Delta E_{76} = 2{\cdot}5$ and $\Delta E_{00} = 2{\cdot}3$ units. Black RTP performed better when considered under the ΔE_{76} compared with ΔE_{00}, which was close to the acceptable limit of 3·0 units. As was seen with the outdoor weathering, there was a loss in colour saturation in cyan, yellow and black toner and the hue of all colours other than black remained unchanged.

Once testing had been completed, the specimen surfaces were inspected for signs of any leaching/loss of toner from the concrete; however, there was no evidence to suggest that this was happening. In most cases, the lightness of the specimens decreased, which suggests that even though they were surface dried for 48 h before testing for colour coordinates, the residual moisture within the surface zone may well have been contributing to the loss in lightness measured.

6.3 UV box weathering environment

The UV box specimens showed an increase in ΔE_{76} and ΔE_{00} in all specimens, including the white control CEM II/A-L specimen. Concrete with yellow RTP showed the highest ΔE_{76} value, however magenta RTP was highest when using the ΔE_{00} index. Again, all RTP specimens showed a change in colour <3·0 units. The RTP specimens performed well in terms of colour saturation, with all exhibiting a small loss in

Table 7. Comparison of hardened concrete properties of CEM II/A-L and 10% cyan RTP concrete cast against IMF and CPF

	CEM II/A-L control		10% cyan RTP	
Property	**IMF**	**CPF**	**IMF**	**CPF**
Colour coordinates				
L^*	65·00	60·06	60·00	56·65
a^*	2·64	2·92	−4·20	−4·00
b^*	9·12	7·10	−10·05	−10·80
$\Delta E_{76,\ \mathrm{IMF\text{-}CPF}}$	5·35		3·44	
Capillary porosity: %	6·1	5·4	7·6	6·1
Hardened density: kg/m^3	2365	2375	2270	2315
Surface hardness: rebound number	36	45	35	43

C^* (<1·0 unit) at 8 weeks and hue was unaffected (changes of <0·1 unit), indicating a good level of UV resistance.

6.4 Indoor weathering environment

RTP concretes exposed to the indoor environmental conditions also performed well with magnitudes of ΔE slightly marginally higher than those experienced in the black-box control conditions. Both ΔE_{76} and ΔE_{00} were <2·0 units for all colours with no definitive ranking of colour change for RTP concretes. There were marginal reductions in colour saturation at 8 weeks (all <1·0 unit) and, as with other environments, hue was largely unchanged.

7. Influence of RTP and formwork surface on concrete properties

Table 7 shows the influence of the formwork face on the colour coordinates, capillary porosity, hardened density and surface hardness of toner (10% cyan) and non-toner concretes cast against both IMF and CPF. Table 4 gives details of the compressive strength at 28 d for the control and 10% toner concretes.

There was a difference in strength of approximately 12 MPa, which can be explained by the fact that the toner replaced the CEM II/A-L and thus the effective w/c ratio increased (from 0·51–0·57). In addition, as the toner contained an admixture (part of which contains a surfactant), it is likely that the air content of the concrete also increased, contributing to a reduction in compressive strength. This was further confirmed by the increase in capillary porosity seen between the two concretes, with the toner concrete exhibiting a marginal increase in capillary porosity and a marginal reduction in hardened density. The reduction in density can be attributed to the fact that the toner powder is a lower density material than CEM II/A-L.

The influence of using CPF on both the RTP and non-RTP concretes was apparent, with CPF increasing the hardened density, reducing capillary porosity and improving the surface hardness of the concrete compared with the use of IMF. CPF also influenced the colour coordinates of the concrete, the main impact being on the contrast (L^* value) although this influence was lower in the toner concrete with a $\Delta E_{76,\mathrm{IMF/CPF}} = 3{\cdot}44$ compared with $\Delta E_{76,\mathrm{IMF/CPF}} = 5{\cdot}35$ for non-toner concrete.

8. Discussion and conclusions

The aims of this study were to assess the feasibility of using powder recovered from toner printer cartridges as a viable pigment in concrete, determine the ease of creating primary and secondary colours and assess the performance of concrete in typical weathering environments. The work showed that, with the addition of a patented admixture developed by the authors, it is possible to use 5–10% RTP as a cement replacement to alter the colour of cement pastes and concretes using cyan, magenta and black toner. When considering yellow toner, higher percentages may be required (10–20%) as the pigment within the waste toner is not as effective at influencing the colour of cement paste and concrete even when using white cement (CEM II/A-L). This was also the case when blending the yellow RTP with cyan to form green, further indicating the need for increased quantities of yellow RTP to be effective.

The change in colour of both the cement pastes and concretes was more apparent using cyan, magenta and black toner, as these colours typically have significantly different $L^*a^*b^*$ values from the control white cement and the visual impact is thus easier to discern.

The performance of the RTP concrete in weathering environments was very positive with very small changes in colour coordinates measured after 8 weeks across a range of conditions. In all cases, both the ΔE_{76} and ΔE_{00} values were <3·0 units, indicating that changes in colour were small. This was particularly promising in accelerated UV conditions. Similar performance was seen in terms of colour saturation and hue, which remained relatively stable over the test period. In a wetting/drying environment, some loss of lightness was seen, however, it is believed that this was due to the residual moisture being present in the test specimens rather than a true reduction in L^* value.

The impact on other concrete properties was also minimal, with small changes to near-surface capillary porosity and density due to the fact that the toner powder is less dense than the cement it was replacing and the fact that the patented admixture contained a surfactant, which may influence the air content of the concrete. While some reductions in strength were seen, this was due to the fact that RTP was used to replace the CEM II/A-L; however, calorimetry showed that when used as an addition rather than a replacement, the RTP did not affect the rate of hydration.

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