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Carbon dioxide emissions and heavy metal contamination analysis of stone mastic asphalt mixtures produced with high rates of different waste materials

Sara R.M. Fernandes, Hugo M.R.D. Silva*, Joel R.M. Oliveira

CTAC, Centre for Territory, Environment, and Construction, University of Minho, 4800-058, Guimarães, Portugal

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The incorporation of waste materials in asphalt mixtures has driven several studies mainly focused on improving their mechanical performance while minimizing the use of virgin materials. However, these could only be considered cleaner solutions for road paving works if their production and application do not present additional risks for human health and the environment. Therefore, this study aims at assessing the carbon dioxide emissions and possible leachates of stone mastic asphalt mixtures produced with high rates of different waste materials for binder modification or material recycling. Thus, a chemical analysis of eluates that were in contact with those mixtures and an estimation of the carbon dioxide emissions associated with their production and transportation were carried out under different scenarios. In conclusion, these mixtures comply with the established specifications for hazardous leachates. The addition of waste materials to these mixtures decreases carbon dioxide emissions, especially for recycled stone mastic asphalt mixtures with 50% reclaimed asphalt pavement material and bitumens modified with waste materials. Thus, the studied mixtures are innovative solutions for future use in pavement maintenance and rehabilitation operations, in line with the circular economy concept.

1. Introduction

The incorporation of different waste materials in asphalt mixtures should be evaluated to assess the actual global warming and water contamination preventive effects of this solution. In the present work, carbon dioxide emissions and heavy metal contamination analyses of Stone Mastic Asphalt (SMA) mixtures incorporating high rates of wastes materials were carried out to validate waste material incorporation as a clean production process, i.e., with lower levels of CO_2-equivalent emissions and, simultaneously, without producing leachates that are considered harmful for human health and the environment. Thus, five waste materials were selected to carry out this analysis, namely reclaimed asphalt pavement (RAP), waste engine oil, recycled engine oil bottoms, waste polyethylene and crumb rubber recycled from used tires. RAP was incorporated in a much high amount, but only in some of the studied mixtures, since the recycling with 50% RAP is not technologically available in many asphalt plants. The other wastes were incorporated in smaller amounts, but they are substituting/modifying the asphalt binder, which is the most expensive component of asphalt mixtures.

According to Yang et al. (2015), the paving industry has a high impact on the environment due to the generation of greenhouse gases, namely the carbon dioxide emissions (or the global warming potential obtained by converting the amount of other greenhouse gases in CO_2-equivalent emissions). The high demand of different natural resources together with the increase in pollutant emissions could become unsustainable for the future generations (Castellano et al., 2014), highlighting the need to adopt more sustainable strategies and practices for the paving industry that combine the technical requirements of paving materials with the reduction of its environmental impact (Wang et al., 2018).

Steel slag was used as a partial substitute of aggregates in asphalt mixtures, in the works of Wu et al. (2007) and Pasetto et al. (2017), to reduce the environmental impact of their extraction for paving operations. The study of other by-products prompted the development of additional sustainable mixtures, as those shown in the work of Almeida et al. (2007), with

* Corresponding author.
E-mail addresses: id4966@alunos.uminho.pt (S.R.M. Fernandes), hugo@civil.uminho.pt (H.M.R.D. Silva), joliveira@civil.uminho.pt (J.R.M. Oliveira).

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carbonated stone slurry use as sand substitute in cement concrete production, or in the work of Pérez and Pasandín (2017), with recycled concrete aggregates and crumb rubber incorporation in hot mix asphalt production.

Several studies have supported the use of waste materials in asphalt mixtures, namely, as a partial substitute of virgin bitumen (Fernandes et al., 2017a, 2017b, 2018) or rejuvenating agent (Jia et al., 2014; Kamaruddin et al., 2014), as bitumen modifier (Costa et al., 2017a; Liang et al., 2015; Lo Presti et al., 2014) and also as partial substitute of aggregates (Costa et al., 2017b; Ranieri et al., 2017; Wu et al., 2007). According to the results presented in the mentioned works, these asphalt mixtures with waste materials present a mechanical performance similar to or better than that of conventional asphalt mixtures, attesting the potential of these alternative solutions.

Waste engine oils and recycled engine oil bottoms are examples of rejuvenating agents or partial substitutes of bitumen (Romera et al., 2006). According to Silva et al. (2012) and Qurashi and Swamy (2018), waste engine oil decreases mixing and compaction temperatures, as well as softening point temperature, while it increases bitumen penetration. Additionally, recycled engine oil bottoms are used in countries with a cold climate to decrease the lower temperature of the bitumen performance grade with the aim of reducing the low-temperature cracking phenomenon (Institute, 2016; Li et al., 2017). Moreover, both waste engine oil products can be partial substitutes of bitumen, together with waste or virgin polymers, showing a performance better than that of a conventional bitumen or commercial modified binders (Fernandes et al., 2018).

Some polymer wastes, like plastics (Kalantar et al., 2012; Leng et al., 2018b) and crumb rubber (Saberi.K et al., 2017), have been added to the bitumen to improve its properties and, as a result, increase the performance of the resulting asphalt mixtures. Polymer modified bitumens typically increase fatigue cracking and rutting resistance of asphalt mixtures, allowing a reduction on flexible pavement thicknesses and life-cycle costs (Becker et al., 2001). Moreover, waste and virgin polymers present similar behavior when added to the bitumen, while the former results in a lower cost, becoming the most economical and environmentally friendly option (Fuentes-Audén et al., 2008; González et al., 2012).

Reclaimed asphalt pavements (RAP) from end-of-life roads can also be used to decrease the quantities of new aggregates and bitumen used in the production of asphalt mixtures, as well as landfill volumes (Dinis-Almeida et al., 2016). The recycling of asphalt mixtures could also be an attractive solution, both in technical (Noferini et al., 2017; Palha et al., 2013) and economical (Singh et al., 2017) terms, namely when comparing it to the traditional asphalt pavement overlay since cracking problems, roughness, and other distresses can be solved with this cleaner production process (Kim et al., 2018).

Therefore, incorporation of waste materials (e.g., reclaimed asphalt pavement, waste crumb rubber, among others) in the production of asphalt mixtures allow reducing the extraction of natural resources and the landfill of waste materials. However, sometimes extra heating and consequent higher energy consumption are required, increasing production costs (Thives and Ghisi, 2017). Thus, environmental analysis or life-cycle assessment (LCA) of solutions with the incorporation of alternative production techniques or RAP materials (Leng et al., 2018a; Vidal et al., 2013) should be performed to confirm the advantages of such solutions. Furthermore, during its service life RAP material is subjected to contamination by traffic that could result in leachates with high concentrations of heavy metals (Ramísio, 2007).

2. Methodology

Allied to the mechanical performance of an asphalt mixture with waste materials, it is also crucial to assess its carbon dioxide emissions and possible heavy metal contamination. The asphalt mixtures evaluated in this study comprise the use of wastes materials as binder modifiers or aggregate and bitumen substitutes, by using RAP. However, this could lead to risks for human health and natural ecosystems, and an increase in carbon dioxide (CO_2) emissions.

Therefore, these asphalt mixtures with high rates of waste materials were evaluated to determine the presence of heavy metals in their leachates, according to EN-12457-4, and also to estimate carbon dioxide emissions during the production stages. Those phases included obtaining raw and recycled materials, their transport to the asphalt plant, production in plant and transport of asphalt mixture to the construction site.

2.1. Evaluation of leachates from SMA mixtures with high rates of waste materials

The leaching test allows evaluating the asphalt mixtures ecotoxicity through the analysis of their eluates. The use of waste materials in asphalt mixtures could potentially increase the leachates toxicity and contaminate watercourses and harm human health.

According to EN 12457-4, the laboratory leaching test consists of drying the tested material to constant weight, to guarantee the absence of water. Then, a sample of each asphalt mixture with approximately 90 g, with a maximum dimension of 10 mm, is inserted in a closed container with 900 ml of distilled water. This container is agitated for 24 h. After that time, it is necessary to wait until the suspended solids settle and, after that, a filtration process should be carried out, with a membrane filter and a vacuum or pressure filtration device, to separate solids from the liquid (also known as eluate).

The eluate is analyzed using chemical analysis in an Atomic Absorption Spectroscopy apparatus to identify and quantify the heavy metals and compare them with the relevant Specifications. In the present work, they were compared with the values specified in the Portuguese Decree-law no. 183/2009, Annex IV, Part B, which stablishes the legal system on the landfill of waste. This Decree-law transposes into national law the European Council Directive no. 1999/31/CE, amended by Regulation no. 1882/2003 of the European Parliament and of the Council, and implements the Council Decision no. 2003/33/CE.

The heavy metals evaluated in this study (and specified in the mentioned Portuguese Decree-law) are the following: cadmium, chromium, copper, nickel, lead and zinc. These heavy metals can be part of the runoff that has been in contact with the road pavement, namely due to traveling vehicles (Ramísio, 2007). Thus, to guarantee an adequate leaching performance, the asphalt mixtures with high rates of wastes materials should present concentration values of these heavy metals lower than those established by the previously mentioned Decree-law.

2.2. Estimation of CO_2 emissions

In this study, a four-stage model was considered to estimate the CO2-equivalent emissions analyses. The first stage comprises material production, which includes the raw materials and the possible processing needed to obtain the recycled materials. The second stage covers material transportation from the suppliers or their extraction site to the asphalt plant. The third stage concerns asphalt mixtures production, considering the different mixing temperatures of each mixture. The last one includes the mixture transport from the asphalt plant to the construction site. Fig. 1 presents those four stages and the system boundary.

According to the different stages defined in Fig. 1, the emissions resulting from the processes used to obtain 1 kg of an asphalt mixture can be estimated using Equation (1).

$$CO_2\ Emissions = CO_2\ (P_{mat}) + CO_2\ (T_{mat}) + CO_2\ (P_{mix}) + CO_2\ (T_{mix}) \quad (1)$$

where $CO_2\ (P_{mat})$ are the total CO_2-equivalent emissions of the different materials used to produce 1 kg of asphalt mixture (kg CO_2-equiv./kg); $CO_2\ (T_{mat})$ are the total CO_2-equivalent emissions of transporting the different materials used to produce 1 kg of asphalt mixture from their supplier or extraction site to the asphalt plant (kg CO_2-equiv./kg); $CO_2\ (P_{mix})$ are the total CO_2-equivalent emissions resulting from the production of 1 kg of asphalt mixture (kg CO_2-equiv./kg); $CO_2\ (T_{mix})$ are the total CO_2-equivalent emissions of transporting 1 kg of the asphalt mixture from the plant to the construction site (kg CO_2-equiv./kg).

The different components ($CO_2\ (P_{mat})$, $CO_2\ (P_{mix})$, $CO_2\ (T_{mat})$ and $CO_2\ (T_{mix})$) necessary to obtain the total emissions of an asphalt mixture will be explained in the following sections. Since it was not possible to obtain the unitary values from experimental/field measurements, they were estimated based on relevant literature that used scenarios most closely related to this work.

2.2.1. Material production (stage I)

Table 1 presents the amount of CO2-equivalent per unit mass of material (kg CO2-equiv./kg), resulting from the extraction or production of the several materials (M) for the studied asphalt mixtures.

The emissions from waste engine oil and recycled engine oil bottoms production were assumed as zero since both are waste materials and do not need to undergo some treatment before being used in the bitumen modification. The HDPE kg CO2-equiv./kg value was assumed to be similar to that of CR because both waste materials result from separation and grinding processes. The emissions of SBS (kg CO2 equiv./kg value) were assumed to be the difference between the emissions of the modified and conventional bitumen mentioned in Mukherjee (2016) work. The same amount of emissions was considered for the fibers of the present study since both are virgin polymers.

Table 1
Values of kg CO_2-equiv./kg for different materials extraction/production.

Materials	kg CO_2-equiv./kg
Aggregates	0.00260 (White et al., 2010)
Bitumen	0.42600 (White et al., 2010)
Modified bitumen	0.49481 (Mukherjee, 2016)
Polymers:	
CR	0.01260 (White et al., 2010)
HDPE	0,01260
SBS	0.10461 (Mukherjee, 2016)
Fibers	0.10461
Reclaimed asphalt pavement	0.00013 (Valle et al., 2017)

The CO_2-equivalent emissions (in kg CO_2-equiv./kg) of the several materials ($CO_2\ (P_{mat})$) used in the production of asphalt mixtures were estimated using Equation (2). This calculation procedure is suitable for all type of asphalt mixtures.

$$CO_2\ (P_{mat}) = \sum \%\ material_i\ in\ the\ asphalt\ mixture \times CO_2 (P_{M_i}) \quad (2)$$

where $CO_2\ (P_{mat})$ are the total CO_2-equivalent emissions of the different materials used to produce 1 kg of asphalt mixture (kg CO_2-equiv./kg); $CO_2 (P_{M_i})$ is the CO_2-equivalent value of producing each material i (in kg CO_2-equiv./kg).

2.2.2. Mixture production (stage III)

Table 2 shows the CO_2-equivalent values considered for different types of asphalt mixtures ($CO_2\ (P_{mix})$). In this table, the

Table 2
Values of kg CO_2-equiv./kg to produce different asphalt mixtures.

Mixtures	kg CO_2-equiv./kg
Conventional asphalt mixture	0.0663 (White et al., 2010)
Asphalt rubber mixtures	0.0723 (White et al., 2010)
Recycled asphalt mixtures with:	
Conventional bitumen	0.0746
Bitumen modified with HDPE or SBS	0.0844
Bitumen modified with CR	0.0803

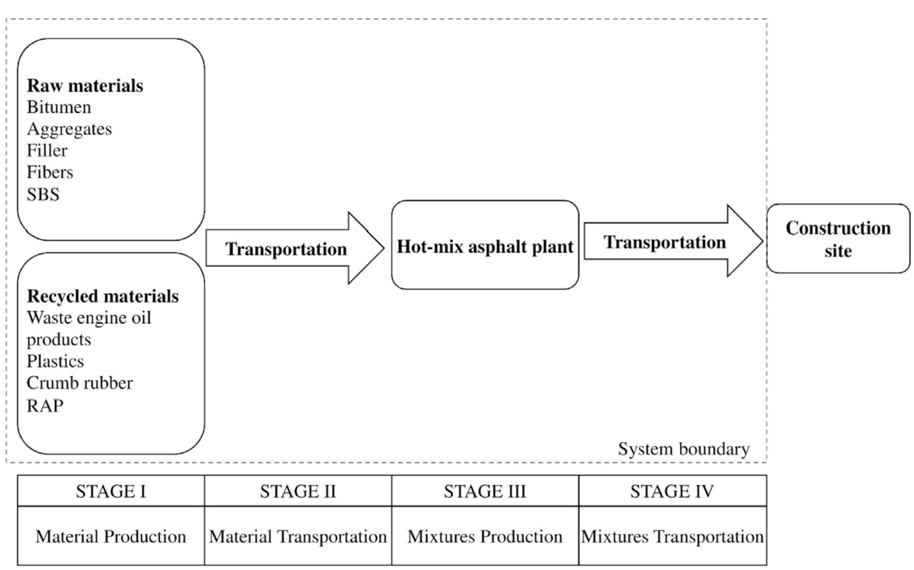

Fig. 1. Stages and system boundary of the CO_2 emissions estimation.

emissions related to the production of asphalt mixtures with waste materials were considered similar to those of the asphalt rubber mixtures presented by White et al. (2010).

In the case of recycled mixtures (with RAP material), the CO_2-equivalent values are an extrapolation of the values presented in the literature for different production temperatures, due to the overheating of 75% of the aggregates required to compensate 25% of RAP material introduced at room temperature. Moreover, the CO_2-equivalent values assumed for the recycled asphalt mixtures were only multiplied by the amount of material effectively heated, i.e., the new aggregates and the coarse fraction of the RAP material.

2.2.3. Materials and mixtures transportation (stage II and IV)

It is necessary to define the distances (d_i) from the suppliers or extraction site to the asphalt plant to estimate the emission values of transporting the different materials to be applied in asphalt mixtures ($CO_2(T)$), which, according to White et al. (2010), should be 0.0002821 kg CO_2-equiv./kg·km. Thus, the emission from materials transportation could be obtained by Equation (3):

$$CO_2\ (T_{mat}) = \sum \%\ material_i\ in\ the\ asphalt\ mixture\ \times CO_2(T) \times d_i \tag{3}$$

where $CO_2\ (T_{mat})$ is the total CO_2-equivalent value of the different materials transportation (kg CO_2-equiv./kg); $CO_2(T)$ is the CO_2-equivalent value for transporting 1 kg of material through 1 km (kg CO_2-equiv./kg km); d_i is the distance traveled for transporting each material i to the asphalt plant (km).

Lastly, the emissions related to the transportation of the asphalt mixtures from the plant to the construction site ($CO_2\ (T_{mix})$) were obtained by multiplying the CO_2-equivalent value of the transportation ($CO_2(T)$) by the distance between the asphalt plant and the construction site, as presented in Equation (4).

$$CO_2\ (T_{mix}) = CO_2(T) \times d_{\ plant\ to\ site} \tag{4}$$

where $CO_2\ (T_{mix})$ are the total CO_2-equivalent emissions of the transportation from the asphalt plant to the construction site (kg CO_2-equiv./kg); $CO_2(T)$ is the CO_2-equivalent value for transporting 1 kg of asphalt mixture through 1 km (kg CO_2-equiv./kg km); $d_{\ plant\ to\ site}$ is the distance from the asphalt plant to the construction site (km).

The distances between suppliers or extraction site of the material and the asphalt plant, as well as, the distance from the asphalt plant to the construction site will be explained in detail later, according to the different scenarios considered in the case study.

3. Case study

3.1. Characteristics of studied SMA mixtures

The use of high amounts and waste materials in new asphalt mixtures brings some environmental advantages such as the decrease in the consumption of natural raw materials and landfill volumes required for those wastes. However, it is important to evaluate other possible short-term effects of using waste materials in asphalt mixtures, like those associated with the production of toxic leachates or carbon dioxide emissions, to include that information in the evaluation of that solution.

The mechanical performance of new solutions for SMA mixtures with different waste materials was previously presented (Fernandes et al., 2017b, 2018), namely by incorporating waste engine oil (EO), recycled engine oil bottoms (RB), waste polyethylene (HDPE) and crumb rubber (CR). Furthermore, Fernandes (2018) evaluated the mechanical performance of recycled SMA mixtures with 50% reclaimed asphalt pavements (RAP) and with asphalt binders modified with the previously mentioned waste materials. All those SMA mixtures with high rates of waste materials, with or without RAP material, presented an excellent mechanical behavior, and at this stage, it is essential to assess their leaching and CO_2 emissions.

Thus, two control SMA mixtures and six SMA mixtures with bitumens modified with different waste materials were initially evaluated in this work, namely:

- SMA-BF0.3 (control SMA with conventional bitumen B35/50 and 0.3% fibers);
- SMA-PMB45/80 (control SMA with commercial modified bitumen PMB45/80-60);
- SMA-EO10H6 (SMA with bitumen modified with 10% EO and 6% HDPE);
- SMA-EO10S5 (SMA with bitumen modified with 10% EO and 5% SBS);
- SMA-EO7.5R20 (SMA with bitumen modified with 7.5% EO and 20% CR);
- SMA-RB15H6 (SMA with bitumen modified with 15% RB and 6% HDPE);
- SMA-RB15S5 (SMA with bitumen modified with 15% RB and 5% SBS);
- SMA-RB15R20 (SMA with bitumen modified with 15% RB and 20% CR).

Seven recycled SMA mixtures with 50% of RAP material (one for control and six with bitumens modified with waste materials) were also evaluated in this work, namely:

- SMA-RBF0.3 (control recycled SMA with conventional bitumen B160/220 and 0.3% fibers);
- SMA-REO15H6 (recycled SMA with bitumen modified with 15% EO and 6% HDPE);
- SMA-REO15S5 (recycled SMA with bitumen modified with 15% EO and 5% SBS);
- SMA-REO15R20 (recycled SMA with bitumen modified with 15% EO and 20% CR);
- SMA-RRB17.5H6 (recycled SMA with bitumen modified with 17.5% RB and 6% HDPE);
- SMA-RRB17.5S5 (recycled SMA with bitumen modified with 17.5% RB and 5% SBS);
- SMA-RRB22.5R20 (recycled SMA with bitumen modified with 22.5% RB and 20% CR).

The quantities of each material used to produce the different SMA mixtures are presented in Table 3 and Table 4, respectively for SMA mixtures without RAP and with RAP (recycled SMA mixtures). These values are essential to estimate the amount of CO_2 emissions

Table 3
Amount of each material used in SMAs (% by mass of mixture).

Mixture	Aggregates	Bitumen	Polymer	EO or RB	Fibers
SMA-BF0.3	94.20	5.50	0.00	0.00	0.30
SMA-PMB45/80	94.20	5.80	0.00	0.00	0.00
SMA-EO10H6	94.20	4.87	0.35	0.58	0.00
SMA-EO10S5	94.20	4.93	0.29	0.58	0.00
SMA-EO7.5R20	94.20	4.20	1.16	0.44	0.00
SMA-RB15H6	94.20	4.58	0.35	0.87	0.00
SMA-RB15S5	94.20	4.78	0.29	0.73	0.00
SMA-RB15R20	94.20	3.77	1.16	0.87	0.00

Table 4
Amount of each material used in recycled SMAs (% by mass of mixture).

Mixture	Aggregates	Bitumen	Polymer	EO or RB	Fibers	RAP
SMA-RBF0.3	47.10	3.20	0.00	0.00	0.30	49.40
SMA-REO15H6	47.10	2.76	0.21	0.53	0.00	49.40
SMA-REO15S5	47.10	2.79	0.18	0.53	0.00	49.40
SMA-REO15R20	47.10	2.27	0.70	0.53	0.00	49.40
SMA-RRB17.5H6	47.10	2.68	0.21	0.61	0.00	49.40
SMA-RRB17.5S5	47.10	2.71	0.18	0.61	0.00	49.40
SMA-RRB22.5R20	47.10	2.01	0.70	0.79	0.00	49.40

associated with the materials used to produce 1 kg of each SMA mixture.

Although SMA mixtures without RAP are only incorporating small amounts of waste materials for bitumen modification, those wastes are substituting the most valuable resource used in asphalt mixture, i.e., bitumen. Nevertheless, it becomes evident that recycled SMA mixtures are composed by much higher rates of waste materials incorporation because they comprise 50% RAP material and a bitumen modified with different waste materials (EO or RB and waste polymers). Thus, recycled SMA mixtures should have a higher impact on the minimization of raw materials extraction and reduction of landfill volumes. However, the use of RAP material in recycled SMA mixtures should not increase CO_2 emissions (e.g., due to the transportation of RAP material and the material overheat during production) or SMA leachates toxicity before being confirmed as an adequate solution for road pavements.

3.2. Different scenarios considered in this study

Considering different possibilities for the source of the materials and the asphalt plant and construction site locations, three distinct scenarios (Table 5) were used to study their influence on the CO_2-equivalent emissions during transportation for the several SMA mixtures evaluated in this work.

The first scenario (base scenario) represents the dominant construction sites in Portugal, mainly on the Portuguese coast nearby Lisbon and Oporto (places with higher population density). The facilities of the bitumen, polymers, and fibers suppliers are on industrial areas or suburbs of the abovementioned municipalities, at an average of 50 km from the major construction sites. Quarries are also set at the same distance, while asphalt plants are in between, but outside the urban perimeter. Thus, the distance between the construction site (mainly within the urban areas) and the asphalt plant is typically 30 km. RAP material, extracted from the construction site and transported to the asphalt plant, is necessarily at the same distance. The difference between quarries and asphalt plants sites (20 km) is the transportation distance for the aggregates.

The scenario II is slightly more optimistic and represents some specific cases observed in Portugal when the asphalt plant facility is in the quarry. In this case, the distance between the aggregates and the asphalt plant is zero, while maintaining the additional conditions. In the last scenario (III), the base scenario (I) distances were increased three times to assess more adverse situations of construction sites in isolated areas, representing Portuguese interior regions with lower population densities.

These scenarios will be used to analyze which is the stage with higher impact on the total CO_2-equivalent emissions and the relative influence of the emissions during the transportation phase.

Table 5
Different scenarios considered for transportation distances (km) of each material from their source to the asphalt plant and from the asphalt plant to the construction site.

Scenario	Scenario I	Scenario II	Scenario III
Aggregates	20	0	60
Bitumen	50	50	150
Polymers	50	50	150
Fibers	50	50	150
RAP material	30	30	90
Construction site	30	30	90

4. Results and analysis

4.1. Evaluation of leachates from different SMA mixtures

The leachates from eluates of SMA mixtures without RAP material were initially assessed according to EN 12457-4 standard, and the results are presented in Table 6.

All the SMA mixtures without RAP fulfill the specification limits established by the Portuguese Decree-Law no. 183/2009 for several heavy metals evaluated in this work. The less than sign (<) presented in leachates results means that the apparatus used is not capable of measuring the heavy metals presence with more precision since the measured values are lower than the quantification limit of this parameter when carried out by this method.

When compared to the mixtures with binders modified with waste materials, the control mixture with commercial modified bitumen (SMA PMB45/80) has higher zinc concentration values. The SMA mixtures with RB (recycled engine oil bottoms) and polymers generally present slightly higher concentration of heavy metals (copper and zinc) than the corresponding SMAs with EO (waste engine oil). RB is a waste material obtained from column distillation of EO, and the previous result was anticipated. In fact, the low impact of RB use in the heavy metal concentrations should be more emphasized. Nevertheless, the increase of heavy metal concentrations could be mainly related to the use of RB instead of EO, because there are higher concentrations of heavy metals in RB than in EO (Fernandes et al., 2018), and to the higher amount of RB used in SMA mixtures compared to the amount of EO.

The recycled SMA mixtures include RAP material derived from distressed or end-of-life road pavements. Thus, RAP material may probably present higher concentrations of heavy metal due to the contamination caused by vehicles during the pavement service life. Nevertheless, according to the leaching test results presented in Table 7, the RAP material used in this work fulfills the legal limits required for heavy metals presence.

The heavy metal concentration values of RAP material are higher than those previously presented for both control mixtures without RAP material (SMA-B0.3F and SMA-PMB45/80), especially for nickel and zinc. These results confirm RAP material contamination caused by tires and brake pads abrasion, as well as the accumulation of fuel and engine oil in the pavement surface. Thus, taking into account the high rates of RAP material incorporation in recycled SMA mixtures, the leachates from those mixtures must be assessed.

Table 8 presents the leaching test results from eluates of the recycled SMA mixtures. All mixtures fulfill the standards established by the Portuguese Decree-Law no. 183/2009 for the studied heavy metals, despite the higher amount of waste materials used in this case. Moreover, the recycled SMA mixtures with binders modified with waste materials generally present higher copper and zinc concentrations than those of the control mixture (SMA-RB0.3F), mainly due to the additional waste incorporation in these mixtures.

Although recycled SMA mixtures use high rates of waste materials (RB, EO, waste polymers, and RAP material), their eluates present less nickel and zinc than the RAP material. The use of new materials in those recycled SMA mixtures (with lower

Table 6
Amount of heavy metals in eluates from SMA mixtures without RAP.

Heavy metal	Limits (mg/kg)	Control mixtures		Mixtures with binders modified with waste materials					
		B0.3F	PMB45/80	EO10H6	EO10S5	EO7.5R20	RB15H6	RB12.5S5	RB15R20
Cadmium	0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Chromium	0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Copper	2.00	<0.25	<0.25	<0.25	<0.25	<0.25	0.31	0.25	<0.25
Nickel	0.40	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30
Lead	0.50	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30
Zinc	4.00	0.43	0.57	0.14	0.49	0.24	0.17	0.29	0.45

Table 7
Amount of heavy metals in eluates from RAP material.

Heavy metal	Limits (mg/kg)	RAP material
Cadmium	0.04	<0.04
Chromium	0.50	<0.50
Copper	2.00	<0.25
Nickel	0.40	0.30
Lead	0.50	<0.30
Zinc	4.00	0.79

concentrations of heavy metals) can partially justify this positive effect (reduction of heavy metal concentration). Furthermore, the new bitumen used in the recycled SMA mixture may be able to involve the RAP particles, encapsulating the heavy metals inside.

In conclusion, all SMA mixtures studied in this work, with several types of waste materials, do not present risks both for human health and for the environment, because they fulfill the maximum limits required for the heavy metals studied, according to the applicable law.

4.2. Estimation of CO_2 emissions resulting from the processes used to obtain the different SMA mixtures

Bearing in mind the amount of each material used to produce each SMA mixture, Fig. 2 shows the CO_2-equivalent emission values of the studied SMA mixtures produced with control bitumens and binders modified with wastes materials, according to Scenario I (considered as the base scenario), and scenarios II and III (blue and red error bar, respectively). These results allow understanding the effect of the different CO_2 emissions stages of each mixture. The same kind of analysis is applicable for different asphalt mixtures, just varying stages I and II due to the change in the amount of each material.

From Fig. 2, it is possible to see that the asphalt mixture produced with PMB-45/80 binder presents the highest CO_2-equivalent emissions (0.118 kg CO_2-equiv./kg), which could be related to the higher emissions of the modified bitumen production when compared to the conventional B35/50 bitumen.

On the other hand, the asphalt mixtures produced with bitumen modified with CR show CO_2-equivalent values (0.105 kg CO_2-equiv./

Table 8
Amount of heavy metals in eluates from recycled SMA mixtures with 50% RAP.

Heavy metal	Limits (mg/kg)	Control mix	Mixtures with binders modified with waste materials					
		RB0.3F	REO15H6	REO15S5	REO15R20	RRB17.5H6	RRB17.5S5	RRB22.5R20
Cadmium	0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Chromium	0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Copper	2.00	0.26	<0.25	0.31	0.27	0.42	0.40	<0.25
Nickel	0.40	<0.30	<0.30	<0.30	0.40	<0.30	<0.30	<0.30
Lead	0.50	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30
Zinc	4.00	0.37	0.41	0.39	0.66	0.45	0.40	0.51

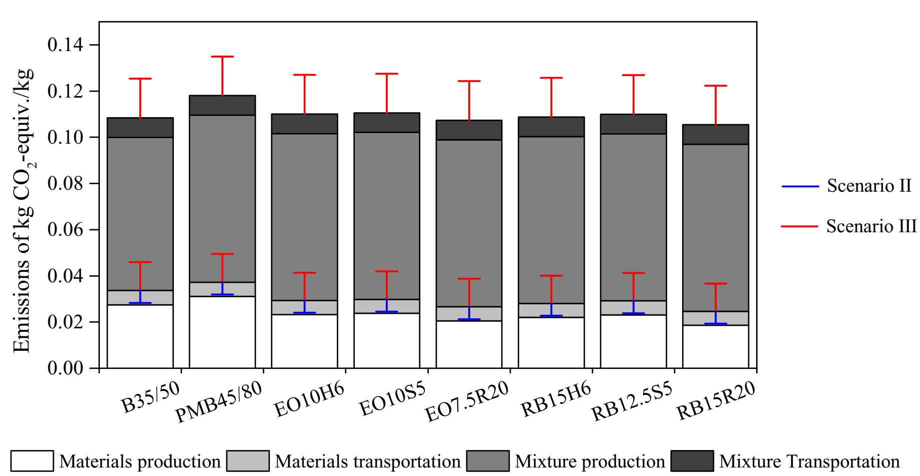

Fig. 2. CO_2-equivalent emissions of the different SMA asphalt mixtures and the different scenarios.

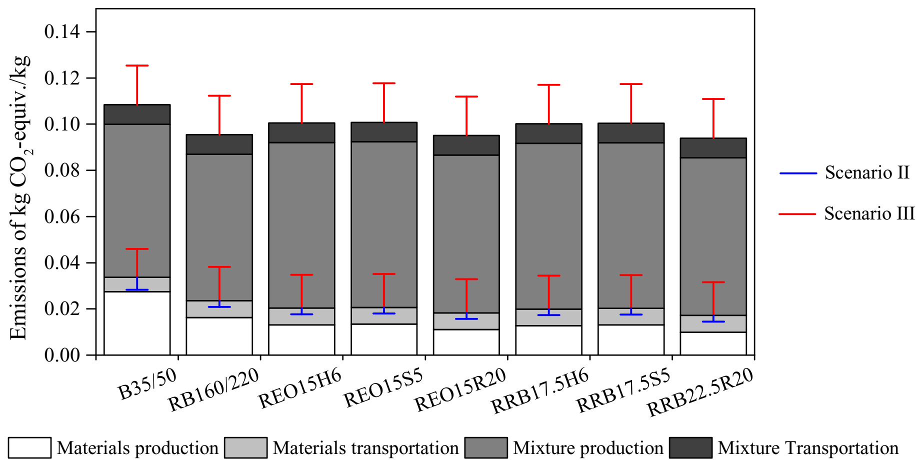

Fig. 3. CO_2-equivalent emissions of the different SMA recycled asphalt mixtures and the different scenarios.

kg for the RB15R20 modified binder and 0.107 kg CO_2-equiv./kg for the EO7.5R20 modified binder) lower than those of the mixture produced with conventional B35/50 bitumen (0.108 kg CO_2-equiv./kg). The higher amount of crumb rubber (20%), whose CO_2-equivalent emissions value is much lower than that of the conventional bitumen emissions value, makes the emissions of CR modified mixtures to reach similar or lower CO_2 emission values, when compared to the control mixture with the B35/50 bitumen (even with the increase of mixing temperature).

It is also possible to observe that the mixtures with HDPE exhibit CO_2-equivalent values (0.110 and 0.109 kg CO_2-equiv./kg) higher than those of the control mixture with B35/50 bitumen, but lower than those estimated for the SBS mixtures (0.111 kg CO_2-equiv./kg). This behavior could be due to two main factors. The first one is related to the higher amount of polymer used (even if it is only 1%, it decreases the emissions associated with conventional bitumen production) and the second concerns to the fact that the HDPE CO_2 emission values are lower than those of the virgin SBS. The mixtures with recycled engine oil bottoms (RB) decreased 2.5%–7.5% the CO_2 emissions in comparison to those with bitumen modified with waste engine oil (EO).

Although the emissions from mixtures production have a significant impact on the final emissions (higher emission level), they were similar in all asphalt mixtures with modified bitumen. The emissions resulting from the mixture transportation were also equivalent for all studied solutions. Therefore, the highest variation is related to materials production emissions, where the presence of waste materials decreases the CO_2-equivalent emissions.

When comparing scenario II (asphalt plant facility in the quarry) to the base scenario (I), it is possible to observe that the emissions related to materials transportation are almost non-existent, which could be due to the fact of aggregates correspond to 94.2% of SMA mixtures weight. Moreover, in scenario III, where the distances increase for the triple, the emissions increase on average 0.029 kg CO_2-equiv./kg, maintaining the final emissions tendencies.

In the case of recycled asphalt mixtures, as can be observed in Fig. 3, when compared with the control asphalt mixture with B35/50 bitumen (without RAP material), the former present lower CO_2-equivalent emissions, even though there is a need to increase the temperature during stage III (mixtures production). The lower emission values in the first stage (materials production) are related to the aggregates substitution by 50% RAP, a waste material with much lower CO_2 emission values (almost 50%).

Once more, it was observed that the recycled SMA mixtures with CR and with conventional B160/220 bitumen exhibit the lowest emissions (0.094 and 0.095 kg CO_2-equiv./kg, respectively), followed by those with EO and HDPE or SBS (0.101 kg CO_2-equiv./kg) and those with RB and HDPE or SBS (0.100 kg CO_2-equiv.kg). In this type of mixtures, the recycled engine oil bottoms (RB) influence is not so noticeable, because only a part of final binder results from the addition of bitumen modified with waste materials (the other part is already in the RAP material).

When analyzing the different scenarios, it is possible to observe that the asphalt plant located in the quarry site does not reduce so drastically the materials transportation emissions, when compared to the mixtures without RAP material. Even though the amount of RAP material is lower than the total amount of virgin aggregates necessary to produce SMA mixtures (without RAP), it still has to be transported to the asphalt plant, resulting in a lower emission reduction. In scenario III, due to the increase of the distances for both the materials and the construction site, the emissions increased an average of 0.031 kg CO_2-equiv./kg.

In conclusion, the recycled SMA mixtures show the lowest CO_2-equivalent emissions due to the use of RAP material that partially replaces the virgin aggregates and reduces the amount of new bitumen needed. In the case of SMA mixtures without RAP material and with bitumens modified with waste materials, their emissions are lower than those of the mixture produced with a commercial modified binder, even though they are higher than the control mixture with B35/50. Consequently, the use of waste materials (waste engine oil, recycled engine oil bottoms, and polymers) in bitumen modification and RAP material contributes to a reduction in CO_2-equivalent emissions.

5. Conclusions

The scope of this work was to analyze the water contamination effect and carbon dioxide emissions SMA mixtures with high rates of waste materials. Thus, a chemical analysis was carried out to assess the presence of heavy metals in the eluates that were in contact with the mixtures. Furthermore, CO_2 emissions resulting from mixtures production were also estimated. The developed SMA mixtures, produced with different waste materials (i.e., waste engine oil, recycled engine oil bottoms, waste polyethylene, crumb rubber, and RAP material), were also compared with control mixtures with commercial binders. The most relevant conclusions of this work are those presented below:

- All the SMA mixtures evaluated fulfill the maximum limits specified for the presence of heavy metals (regardless of the quantities of waste materials used), which guarantee the safety of their use to the environment and human health;

- Moreover, the use of these SMA mixtures produced with high rates of waste materials would decrease the volume of natural resources consumed and, at the same time, the landfill volume needed for the waste materials evaluated in this study;
- Regarding CO_2 emissions, the recycled SMA mixtures present lower emission values due to the use of RAP material and the decrease the use of new aggregates and bitumen. On the other hand, the SMA mixtures produced with bitumens modified with waste materials (but without RAP) show lower emission values than the control SMA mixture produced with the commercial modified bitumen, meaning that the addition of waste materials contributes to the reduction of CO_2 emissions;
- All SMA mixtures produced with CR have reduced CO_2 emissions due to the low amount of CO_2-equivalent per mass unit of crumb rubber and the high amount of CR used (20%);
- The reduction of the distance between the quarry and the asphalt plant has more impact on the emissions resulting from the transportation of the SMA mixtures without RAP material than of the recycled SMA mixtures (the first one is close to zero). However, it does not compromise the final variation of CO_2 emissions (the recycled mixtures still show lower emission values). The increase of the distances for the triple, which corresponds to scenario III, rises the emissions by around 0.03 kg CO_2-equiv./kg for all SMA mixtures;
- Thus, the SMA mixtures with high rates of waste materials present several advantages, since they decrease the use of natural resources and landfill volumes, present reduced CO_2 emissions and do not present ecotoxic leachates. Therefore, these SMA mixtures are clean solutions with prospective use in the paving industry from a circular economy point of view.

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