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Valorisation of Pulp and Paper Industry Wastes—Incorporation in Bituminous Mixtures for Road Construction

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Abstract: Some wastes from the paper pulp production process are still sent to a controlled waste landfill. These materials can constitute alternative resources for constructing road pavements. The study aimed to characterize and explore the sustainable application of two inorganic wastes resulting from the paper pulp process, the dregs (green liquor wastes) and the grits (slaker wastes), in the production of bituminous mixtures by the analysis of samples prepared with 5 and 10% of dregs and 5 and 10% of grits on the baseline reference bituminous mixture AC 14 surf 35/50. Some relevant mechanical properties of the blends were assessed based on Marshall compression, sensitivity to water and wheel-tracking tests. Additionally, water poured on the loose asphalt and compacted slabs' surface was analysed to determine the portion of harmful chemical compounds leached from the asphalt material. The results show that using dregs presented some technical limitations related to mechanical performance and that the incorporation of grits has an acceptable mechanical behaviour. Moreover, the study shows that the measured leachate resulting from water flow in a reference asphalt mixture and the blends with grits are insignificant. It can be concluded that using grits in asphalt mixtures is a promising technique regarding mechanical behaviour and environmental impacts that need further studies.

Keywords: wastes valorisation; pulp and paper plant; dregs; grits; bituminous mixtures; leachates

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1. Introduction

In 2015, the General Assembly of the United Nations adopted the '2030 Agenda', whose full designation is "Transforming our world: the 2030 Agenda for Sustainable Development" and proposed 17 sustainable development goals (SDG) [1], among which is goal 11—'Sustainable cities and communities'. This goal presents ten targets [2] and intends to make cities and human settlements inclusive, safe, resilient, and sustainable. The focus on cities results from being responsible for 80% of energy consumption and 75% of carbon dioxide emissions [3]. In addition, it is known that, by 2050, it is expected that the population living in urban areas will represent 70% of the world's people [4].

Nowadays, in Europe, cities already consume 50% of the raw materials extracted from nature and that need will be even more significant [5] in the future. It is urgent to develop strategies that make cities sustainable while continuing to offer high standards of quality of life and promote the use of local resources or locally produced by-products, such as waste, to reduce these natural resources. Indeed, according to target 11.6 of SDG 11, which aims to reduce the adverse per capita environmental impact of cities, municipal and other waste management, as well as air quality, should be prioritized [6]. Industries also seek to reduce the amount of waste produced to contribute positively to cities' sustainability. This contribution can occur at several levels. One solution is the recovery of industrial wastes through their incorporation as by-products in other activities instead of sending them to landfills, as is the case of the pulp and paper industry wastes.

1.1. Pulp and Paper Industry at a Glance

The potential environmental impacts of the pulp and paper industry have been considered significant, including global warming, ecotoxicity, human toxicity, acidification and waste production [7]. Among other emissions, wastes should be highlighted, including biomass, sludges, ashes, slags, dust and other non-processed waste, plastic, glass, and food waste, among others [8].

The main pulping process in the pulp and paper industry is the Kraft process [9], with 130 million tons produced yearly worldwide [10]. The process consists of briefly cooking wood shavings with a white liquor (water, sodium hydroxide and sodium sulphide) for hours from 145 °C to 170 °C. The chemicals dissolve the lignin and organic compounds, which are washed, leaving only the fibres. The dissolved wood and chemicals from the weak black liquor are sent to the recovery system. In addition to black liquor, other effluents from pulp washing and beaching are also sent to the chemical recovery system [11]. The chemical recovery process takes place in parallel with the pulp production. Here, the inorganic pulping chemicals are prepared for reuse, while the organic compounds are used for energy recovery [9]. The inorganic chemicals are dissolved in water, forming a substance rich in sodium carbonate and sodium sulphite, the green liquor. Then, quicklime is added to the green liquor during the causticizing process, resulting in the white liquor comprising sodium hydroxide, sodium sulphide and calcium carbonate [11]. The wastes resulting from this process are inorganic, consisting mainly of sodium, sulphur and calcium compounds and are designated as dregs (or green liquor wastes), grits (or slacker wastes) and lime wastes [12].

The importance of managing dregs and grits arises because they still do not have a well-established recovery solution, being deposited in landfills [11]. Given the future limitations imposed by the European Directive 2018/850 of 30.05 [13], it is important to reintroduce these materials in society.

1.2. Recovery of Pulp and Paper Industry Wastes for More Sustainable Cities

Dregs and grits have a high calcium carbonate content, which can be seen as an advantage. Indeed, the added value of this chemical compound is being demonstrated in several industrial sectors. The recovery and/or reutilization of dregs and grits can be applied in the footwear industry [14], in barriers for landfills [15] or for groundwater protection [16]. Grits and dregs have performed well as soil alkalizing agents and nutrient providers [17–20].

Several applications are being tested in the construction sector, which is responsible for 50% of the natural resources extracted in Europe [5]. A better performance was achieved by incorporating 10% grits or dregs in the production of mortars for wall cladding [21]. The ceramic industry is another sector where grits, which do not contain organic compounds, may lead to interesting results [22–24]. Road infrastructure is another area where the utilization of by-products may bring environmental and economic advantages [25]. Among industrial wastes, several studies point out the use of grits and/or dregs to increase the cementation of lime-soil mixtures [26] and as substitutes for aggregates or fillers in bituminous mixtures [25,27,28]. Considering the quantity of natural resources needed to build road infrastructure and the large quantity of grits and dregs disposed of in landfills, incorporating these wastes in transport infrastructure appears as a recovery opportunity to build pavement layers, particularly in asphalt concrete.

1.3. Incorporation of Dregs and Grits in Bituminous Mixtures

A limited number of studies ([25,28]) have evaluated the feasibility of replacing part of the aggregate in asphalt concrete. Modolo et al. [25] assessed the use of grits, dregs, and dregs without lime sludge formed by fine particles. Because dregs have around 50% water content, they required spending energy to dry the materials. The authors tested replacing 5 and 10% of the aggregates' total mass. That study evaluated volumetric properties, Marshall stability and flow, and water damage resistance measured on cylindrical specimens compacted in the laboratory. Although the blends with grits compared with the properties of a reference asphalt concrete without waste, the water damage resistance, assessed by controlling Marshall stability after conditioning in water for 72 h, was slightly lower but acceptable regarding the usual requirements for road construction. On the contrary, blends with 1% to 4% of dregs as collected had inferior performance concerning water damage. This phenomenon occurred because dregs have soluble salts that prevent direct application as a constituent of asphalt concrete. After washing the dregs through a procedure involving watering, heating, stirring and filtration, a considerable improvement occurred in resistance to water damage, comparable to the reference asphalt concrete. Nevertheless, the washing procedure made the dregs' particles finer, recommending using the resulting material as filler for asphalt concrete. According to Modolo et al. [25], the washing procedure conducted in the laboratory can easily be implemented in the pulp and paper industry because the water can be re-processed and, therefore, allows the use of dregs in asphalt concrete.

Passandín et al. [28] used filler from dregs to replace conventional limestone filler in asphalt concrete production. Although filler is just a tiny part of the aggregate blend (around 3% to 5%), it is a critical constituent regarding the adhesion of mastic (bitumen + filler) to the other aggregate particles in moist conditions. The study concluded that dregs as filler is inappropriate because it makes bituminous mixtures prone to water damage. Nevertheless, the results obtained for stiffness and resistance to permanent deformation at 30 °C of bituminous mixtures with dregs as a filler were considered adequate compared to those observed for a reference asphalt concrete with limestone filler. Pasandín et al. [28] identified multiple characteristics of dregs to explain the poor performance against water damage: the high natural water content of dregs (4.1%); elevated fineness that may disturb the bitumen-aggregate adhesion; the existence of cube-shaped crystals and agglomerations; the presence of thenardite, which is water soluble, and cesanite, which is marginally soluble in water; the more significant increase in mastic's viscosity with dregs makes it difficult to cover the aggregates due to inadequate workability.

Considering the state of knowledge on the use of dregs and grits in bituminous mixtures, more studies are needed to assess further the possibility of incorporating dregs and grits to replace part of the aggregate's mass. Apart from the volumetric and Marshall properties of the bituminous mixtures, this study evaluates the water sensitivity, the resistance to rutting at high temperatures and the leaching of loose asphalt concrete or when compacted in a pavement layer. The potential of valuing dregs or grits in bituminous mixtures for transport infrastructures strongly depends on the guarantee of limited harmful compounds leaching into the soil and water.

2. Materials and Methods

2.1. Materials

2.1.1. Natural Aggregates and Bitumen

Coarse crushed gneiss with a maximum particle size of 14 mm, along with limestone sand and filler, formed the aggregates blend of the reference mixture and the predominant part of the blends with grits or dregs. The physical properties of the natural aggregates and the Portuguese requirements based on European standards are summarized in Table 1.

The binder used was standard 35/50 paving-grade bitumen, with a penetration of 45 × 0.1 mm at 25 °C (EN 1426 [38]) and a softening point of 52 °C (EN 1427 [39]).

Table 1. Physical properties of aggregates and specifications requirements.

Properties	Standard	Units	Fraction 8/20	Fraction 4/12	Fraction 0/4	Filler	Req. (*)
Flakiness index (FI)	EN 933-3 [29]	%	FI_{15}	FI_{15}	---	---	FI_{20}
Resistance to fragmentation (LA)	EN 1097-2 [30]	%	LA_{20}	LA_{20}	---	---	LA_{30}
Resistance to wear: micro-Deval (M_{DE})	EN 1097-1 [31]	%	$M_{DE}10$	$M_{DE}10$	---	---	$M_{DE}15$
Polished Stone Value (PSV)	EN 1097-8 [32]	%	PSV_{50}	PSV_{50}	---	---	PSV_{50}
Water absorption (WA)	EN 1097-6 [33]	%	0.5	0.6	0.6	---	$WA_{24}1$
Assessment of fines—methylene blue (MB_F)	EN 933-9 [34]	g/kg	---	---	MB_F10	MB_F10	MB_F10
Voids of dry compacted filler (ν)	EN 1097-4 [35]	%	---	---	---	32	$\nu_{28/38}$
Delta ring and ball (°C)	EN 13179-1 [36]	°C	---	---	---	14	$\Delta_{R\&B}$

(*) In compliance with European standards (EN), the requirements for each parameter are expressed using abbreviations and numerical values, each corresponding to one of the categories delineated in EN 13043 [37] for aggregates.

2.1.2. Grits and Dregs

Dregs and grits are wastes from the cellulose industry derived from the causticization of green liquor and slaker wastes, respectively. The European Waste List amended by Decision 2014/955/EU of 18 December 2014 classifies these wastes (Figure 1) as non-hazardous waste, with European Waste Code (EWC) 030302.

(**a**) (**b**)

Figure 1. Samples of dregs (**a**) and grits (**b**).

Dregs are inorganic and non-hazardous industrial waste produced in the clarification of green liquor and are removed from the process because they have non-procedural elements in their constitution, such as aluminium (Al), barium (Ba), chromium (Cr), copper (Cu), iron (Fe), potassium (K), nickel (Ni) and zinc (Zn) that harm steps such as cooking, bleaching and chemical recovery. Dregs are mainly made up of sodium and calcium carbonates (Na_2CO_3 and $CaCO_3$), hydroxides, and sulphides (Na_2S), presenting a dryness between 40 and 55% and a specific weight between 1100 and 1300 kg/m^3.

The reaction in the eraser creates grits, an inert and non-hazardous material, which must be removed so that the white liquor remains as clarified as possible. In this way, the grits have a significant calcium component, namely calcite ($CaCO_3$), portlandite ($Ca(OH)_2$), pyrsonite ($CaNa_2(CO_3)_2 \cdot H_2O$), brucite ($Mg(OH)_2$) and larnite ($Ca_2SiO_4$) [40]. The main elements in its composition, in addition to calcium (Ca), are sodium (Na) and sulphur (S), also containing phosphorus (P), chloride (Cl^-), magnesium (Mg), potassium (K), aluminium (Al), iron (Fe) and silicon (Si). With a dryness between 85 and 95%, they have a specific weight between 1300 and 1500 kg/m^3.

Dregs and grits have a granular form. Figure 2 shows the particle size distribution of those materials applied in the study.

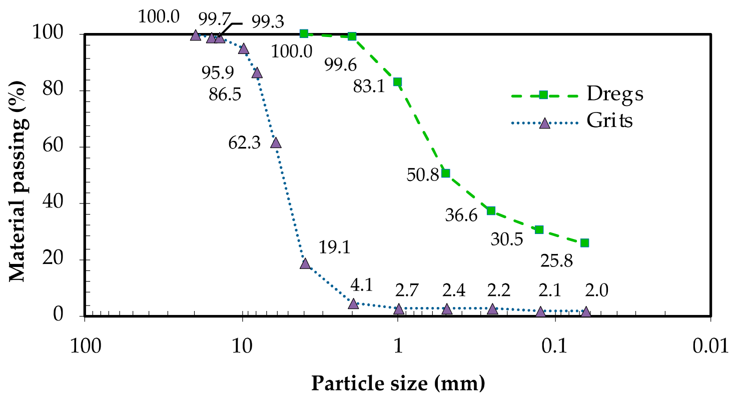


Figure 2. Gradation of dregs and grits.

Table 2 summarises the characterisation of the leachates produced from the dregs and grits valorised in this study, comparing them with the limit values imposed by the Portuguese legislation for their disposal in landfills for non-hazardous waste, revealing no concerns about the use of those wastes. The leachate results were provided by the paper pulp factory.

Table 2. Characteristics of dregs and grits and landfill legal limit values for non-hazardous waste.

<table>
<tr><th>Parameter</th><th>Dregs</th><th>Grits</th><th>Limits for Landfilling of Non-Hazardous Waste by Portuguese Legal Framework</th></tr>
<tr><td>pH</td><td>11.2</td><td>12.3</td><td>-</td></tr>
<tr><td>Chloride, mg/kg</td><td>250</td><td>156</td><td>50,000</td></tr>
<tr><td>Sulphate, mg/kg</td><td>3300</td><td>460</td><td>20,000</td></tr>
<tr><td>Fluoride, mg/kg</td><td rowspan="5"><LOQ</td><td><LOQ</td><td>250</td></tr>
<tr><td>Arsenic, mg/kg</td><td>0.031</td><td>5</td></tr>
<tr><td>Lead, mg/kg</td><td><LOQ</td><td>10</td></tr>
<tr><td>Cadmium, mg/kg</td><td></td><td>2</td></tr>
<tr><td>Barium, mg/kg</td><td></td><td>100</td></tr>
<tr><td>Chromium, mg/kg</td><td>0.08</td><td>0.06</td><td>20</td></tr>
<tr><td>Copper, mg/kg</td><td rowspan="5"><LOQ</td><td rowspan="7"><LOQ</td><td>50</td></tr>
<tr><td>Mercury, mg/kg</td><td>0.5</td></tr>
<tr><td>Molybdenum, mg/kg</td><td>10</td></tr>
<tr><td>Nickel, mg/kg</td><td>10</td></tr>
<tr><td>Antimony, mg/kg</td><td>0.7</td></tr>
<tr><td>Selenium, mg/kg</td><td>0.028</td><td>0.5</td></tr>
<tr><td>Zinc, mg/kg</td><td><LOQ</td><td>50</td></tr>
<tr><td>DOC, mg/kg</td><td>2520</td><td>430</td><td>800</td></tr>
</table>

Table 2. *Cont.*

Parameter	Dregs	Grits	Limits for Landfilling of Non-Hazardous Waste by Portuguese Legal Framework
TOC, mg/kg	36,000	<LOQ	50,000
Mineral oil (C10–C40), mg/kg	<LOQ		999
Benzene, mg/kg			
Toluene, mg/kg			
Ethylbenzene, mg/kg			
m-/p-Xylene, mg/kg			
o-Xylene mg/kg			
(HAP) Naphthalene, mg/kg			100
(HAP) Acenaphthylene, mg/kg			
(HAP) Acenaphthene, mg/kg			
(HAP) Fluorene, mg/kg			
(HAP) Phenanthrene, mg/kg			
(HAP) Anthracene, mg/kg			
(HAP) Fluoranthene, mg/kg			
(HAP) Pyrene, mg/kg			
(HAP) Benzo-(a)-anthracene, mg/kg			
(HAP) Chrysene, mg/kg			
(HAP) Benzo(b)fluoranthene, mg/kg			
(HAP) Benzo(k)fluoranthene, mg/kg			
(HAP) Benzo(a)pyrene, mg/kg			
(HAP) Indene(1,2,3-cd)pyrene, mg/kg			
HAP) Dibenzo-(a,h)-anthracene, mg/kg			
(HAP) Benzo(g,h,i)perylene, mg/kg			
PCB 28, mg/kg			50
PCB 52, mg/kg			
PCB 101, mg/kg			
PCB 138, mg/kg			
PCB 153, mg/kg			
PCB 180, mg/kg			
PCB 118, mg/kg			

LOQ: limit of quantification; TOC: total organic carbon; DOC: dissolved organic carbon; HAP: hazardous air pollutants; PCB: polychlorinated biphenyls congeners.

2.1.3. Bituminous Mixtures' Compositions

Different bituminous mixtures with 5% bitumen content by mass of the total mix were produced with 5% and 10% grits or dregs by mass of the entire aggregate blend, replacing part of the natural aggregate. These percentages have been chosen based on previous studies [25]. Five different mixtures were prepared and compared for each test included in this part of the study: a reference with natural aggregates, two with grits and two with dregs. Table 3 summarizes the blends' compositions.

Table 3. Bituminous mixtures compositions.

Component	Mixtures				
	AC 14 Surf 35/50	AC 14 5% Dregs	AC 14 10% Dregs	AC 14 5% Grits	AC 14 10% Grits
	%	%	%	%	%
Percentage by total mass of the aggregates					
Gneiss 8/20	15.0	17.0	17.0	17.0	17.0
Gneiss 4/12	36.4	40.0	40.0	35.0	30.0
Limestone sand 0/4	45.6	35.0	30.0	40.0	40.0
Limestone filler	3.0	3.0	3.0	3.0	3.0
Dregs	0.0	5.0	10.0	0.0	0.0
Grits	0.0	0.0	0.0	5.0	10.0
Percentage by total mass of the mixture					
Bitumen 35/50	5.0	5.0	5.0	5.0	5.0

The aggregate blend's gradation shown in Figure 3 for the reference mixture fulfils the requirements for the grading envelope usually considered in Portugal for a typical asphalt concrete AC 14 surf 35/50 applicable in surface pavement layers.

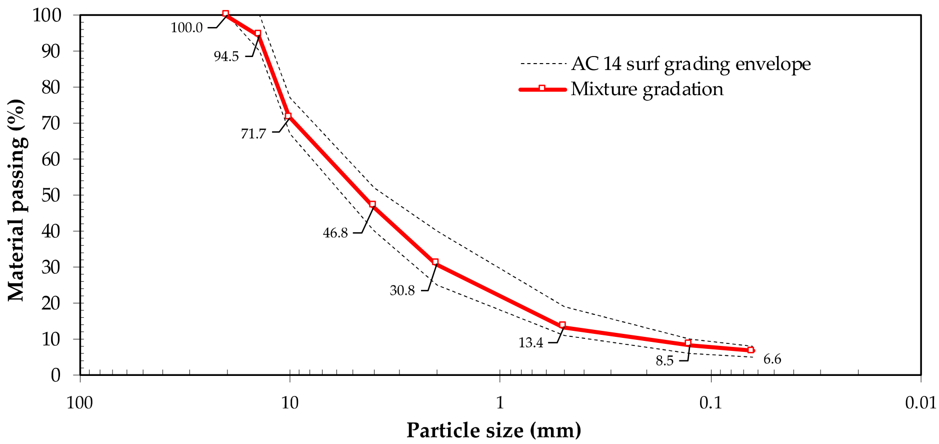


Figure 3. Gradation of the aggregate's blend and grading envelope requirements.

The incorporation of grits or dregs slightly changed the gradation of the asphalt mixtures because the gradation of those materials used to replace part of the aggregate was not very similar to the natural aggregate they substituted (Figure 4).

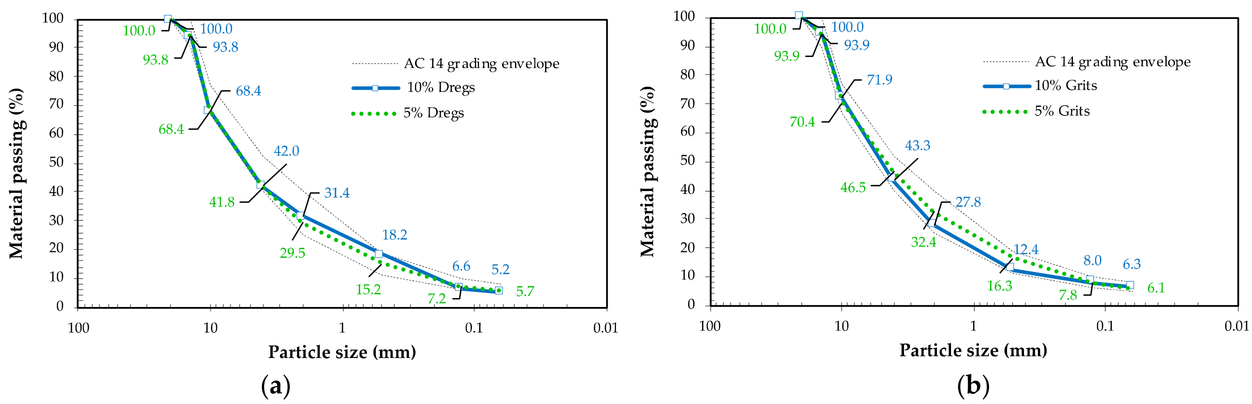


Figure 4. Gradation of the aggregate's blend: (**a**) with dregs; (**b**) with grits.

2.2. Methods

2.2.1. Experimental Plan

The laboratory work comprises two parts. Firstly, an analysis of volumetric properties, Marshall stability and flow, water sensitivity and rutting resistance; secondly, an environmental verification of harmful compounds in leachates was carried out. The results obtained in performed tests serve as a basis for comparison of the influence of adding pulp and paper industry wastes in bituminous mixtures.

Table 4 summarizes the laboratory plan undertaken corresponding to the first part of the study.

Table 4. Experimental plan.

Properties	Parameters	Standard	Test Conditions
Volumetric parameters	Void content (%) VMA: Voids in mineral aggregates (%)	EN 12697-8 [41]	60 °C
Marshall	Stability (kN) Flow (mm)	EN 12697-34 [42]	60 °C
Water sensitivity	ITS: Indirect tensile strength (kPa) ITSR: Indirect tensile strength ratio (%)	EN 12697-12 [43] EN 12697-23 [44]	20 ± 5 °C
Rutting resistance	PRD_{air}: Proportional rut depth (%) WTS_{air}: Mean wheel tracking slope (mm/10,000 cycles)	EN 12697-22 [45]	700 kPa | 50 °C

The second part of the laboratory work is intended to assess the environmental impact resulting from the use of dregs and grits in bituminous mixtures. This assessment aims to study the leachate resulting from the contact of these mixtures with water, and it is based on chemical analysis of the compounds present in collected water and their comparison with regulated limit values.

2.2.2. Production of Bituminous Mixtures and Compaction of Specimens

The bituminous mixtures have been prepared in a heated planetary mixer according to the European Standards EN 12697-35 [46]. After being dried and weighed, the aggregates and the bitumen have been heated between 150 and 170 °C. The mixture was poured into cylindrical moulds and compacted by applying 75 blows per face to obtain samples with 101 mm diameter and 63 mm height, according to the recommendations of EN 12697-30 [47]. For wheel-tracking and leaching tests, the specimens were 305 mm square slabs 40 mm thick compacted with a roller compactor (EN 12697-33 [48]). After heating and drying, the dregs and grits were weighed and added to the blend directly in the mixing bowl. A series of a minimum of three cylindrical samples and two slabs have been prepared for each mixture. Figure 5 shows the manufacturing of mixtures and specimens compaction procedures.

(**a**) (**b**) (**c**) (**d**) (**e**)

Figure 5. Manufacturing procedure and compaction of specimens: (**a**) mixing; (**b**) compaction of slabs with the roller compactor; (**c**) compaction of cylindrical specimens by impact; (**d**) cylindrical specimens; (**e**) slabs.

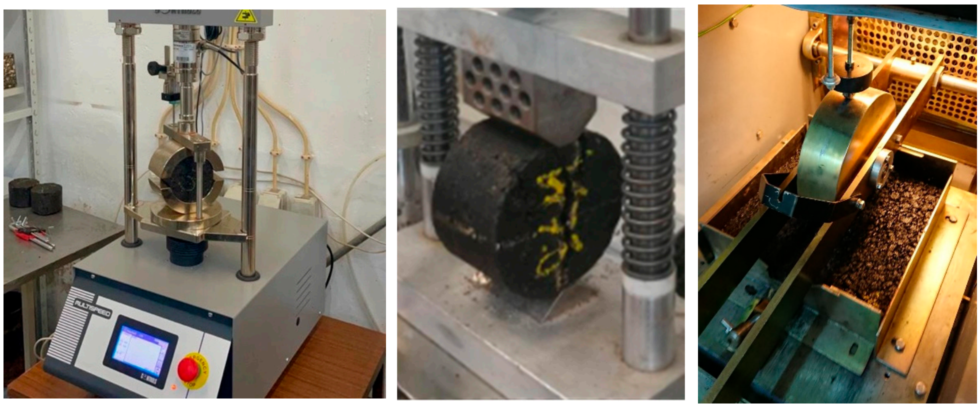
2.2.3. Procedures Applied to Assess the Blends' Properties

The maximum density (EN 12697-5 [49]) and the bulk density (EN 12697-6 [50]) were measured experimentally to assess the considered volumetric properties: the air void content and the voids in the mineral aggregate (VMA). The Marshall compression test delivered the stability, flow and Marshall quotient.

Indirect tensile strength (ITS) tests evaluated the water sensitivity of the bituminous mixtures at 20 °C. Apart from assessing the tensile strength, this test also allows us to evaluate the bituminous mixtures' water sensitivity based on the indirect tensile strength ratio (ITSR), which is the ratio between ITS for wet and dry specimens.

The wheel-tracking test assessed the bituminous mixtures' resistance to rutting after 10,000 passes of a loaded wheel at 60 °C. The output of this test is the variation of rut depth with the number of cycles, which allows evaluating the wheel-tracking slope (WTS_{air}) of the quasi-linear rut depth variation, and the proportional rut depth (PRD_{air}) after 10,000 loading cycles.

Figure 6 illustrates aspects of the mechanical performance tests conducted throughout the study.



(a) (b) (c)

Figure 6. Laboratory tests to evaluate mechanical properties: (**a**) Marshall test; (**b**) indirect tensile strength; (**c**) wheel-tracking test.

2.2.4. Procedures Applied to Assess the Mixtures' Environmental Compliance

The environmental compliance of the bituminous mixtures was evaluated by analysing the contaminants in leachates resulting from the contact of water with the various mixtures. Then, the contaminant concentration was compared with the limit-values established in Portuguese regulations, namely, the Decree-Law n.° 102-D/2020 of 10 December, which regulates the disposal of wastes in landfills, and the Decree-Law n.° 236/98 of 1 August, which establishes the conditions to protect the aquatic environment and to improve water quality according to its use. Two set of tests have been carried out. In the first set, it was intended to evaluate the possible contamination from the bituminous mixtures, as a building material (loose mixtures). In the second set, the objective was to assess the possible contamination from the bituminous mixtures as a structural element (compacted material), in its service conditions. This distinction is fundamental, because, although their compositions are identical, a bituminous mixture or a road pavement have a different initial state and structure. For all the tests carried out, the analysis of the eluate was always performed by an external and accredited laboratory.

The possible contamination resulting from the contact of the bituminous mixtures, as a building material, and water, has been assessed by performing leaching tests. For these tests, the mixtures have been prepared according to EN 12697-35 [46] with loose mixtures. The mixtures, in their disaggregate form with a total of 3 kg for each mixture, were sent to an external laboratory, and the eluate was produced following the procedures of the EN 12457-4 [51].

Two different tests were carried out: a water load test and a surface runoff test, to evaluate the possible contamination resulting from the contact of bituminous mixtures, as a compacted element, and water. These tests aim to study two possible processes of groundwater and soil contamination resulting from the introduction of dregs and grit wastes in the bituminous mixtures. Although road pavements are, by definition and unless designed differently, impervious, one may consider that, due to the existence of microcracks and adverse drainage conditions, rainwater may accumulate on the surface of the pavement and, consequently, percolate through it, reaching the lower layers of the pavement and, namely, the foundation soil of the road structure. If this situation occurs, the percolated water can drag possible pollutants from the surface and the interior of the road pavement, i.e., from the construction material, and contaminate groundwaters and soils. In addition to depending on building material and possible chemical pollutants deposited on the road surface, this situation also hinges on the pollutants' concentration, the adsorption capacity of soil particles, the groundwater level and the degradation level of the pavement [52].

There is no standard for carrying out the water load test and surface runoff test. In fact, these tests were developed to simulate field tests such as lysimeter experiments in a laboratory to assess contamination transport by percolation and surface runoff [53,54]. It should be noted that, based on the findings of the mechanical tests, these experiments have only been carried out on bituminous mixtures with grits (5% and 10% of the total mass of the aggregates). For each percentage, two slabs were prepared, to which a reference AC 14 surf slab was added. The slabs were trimmed to fit the supporting systems previously prepared to perform the tests. The final dimensions of each slab were 23 cm × 30.5 cm × 4 cm (width × length × thickness). For the water load test, five boxes were drilled to accommodate welded iron mesh, capable of supporting the weight of the slab, preventing its deformations and allow water collection (Figure 7a). Afterwards, the contours of each slab have been waterproofed with paraffin, and a water retaining barrier was mounted around the slabs, as illustrated in Figure 7b. A quantity of 500 mL of distilled water was poured over each slab and was allowed to percolate through the slab. This water was collected from the boxes and sent to an external accredited laboratory to assess the existence of pollutants in it and their concentrations.

(**a**) (**b**)

Figure 7. Water load test: (**a**) detail of the supporting box and its slab; (**b**) testing procedure.

The surface runoff tests were carried out on the same slabs, after removing the waterproofing materials. The slabs were tested sequentially, by installing them on the raining system illustrated in Figure 8a. According to the Portuguese road design rulebooks, the minimum transverse slope of a road is 2.5% [55]. This condition was respected by elevating 7.6 mm one side of the slab. The water was falling on the elevated side of the slab and collected in a box bellow the side of the slab with lower elevation. The water volume was defined based on the average annual precipitation in the region of Coimbra/Bencanta. According to the data of the Portuguese Institute for Sea and Atmosphere, between 1981 and 2010 the average annual precipitation was 880.9 mm, with rainfall exceeding:

(i) 1 mm, 94.2 days a year; (ii) 10 mm, 30.9 days a year; (iii) 20 mm, 11.1 days a year and (iv) 30 mm, 3.9 days a year [56]. Considering that significant surface water flow only occurs when the daily precipitation exceeded 10 mm, only these days were considered to simulate water runoff. Considering the surface area of the slab, the rain flow rate of 1.34 L/day was applied. For the experiments, the flow rate was controlled using perforated reservoir system (carboy and perforated lids). Given the reduced daily flow rate, the process was accelerated, draining all the water in twenty minutes. The collected water was then sent for analysis to an external accredited laboratory to verify the existence or not of pollutants in the rained water and their concentrations (Figure 8b). According to Silveira et al. [57], the pH range for rainwater in Coimbra varies between 6.6 and 7, the same range indicated by the water supply company. Therefore, the water pH values were not adjusted for the tests.

(**a**) (**b**)

Figure 8. Surface runoff tests: (**a**) water raining system; (**b**) surface runoff detail.

3. Results and Discussion

3.1. Volumetric Parameters

The results for the air voids and VMA of the studied mixtures are shown in Figure 9.

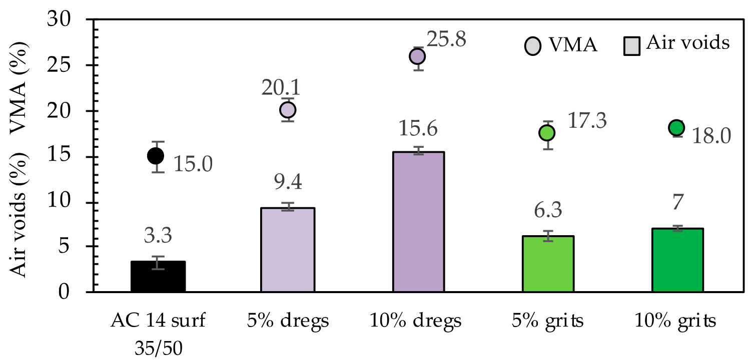


Figure 9. Air voids and VMA.

Portuguese requirements for pavement surface layer regarding dense graded asphalt mixtures, such as AC 14 surf 35/50, are air void content between 3% and 5% and VMA higher than 14%. These requests may be unfulfilled if the blend's composition is based on mechanical parameters, which depend on the in-service exigency regarding strength and durability. Although VMA was higher than the requirements, the combinations with dregs revealed air void content much higher than the requirement limit. This increased porosity will likely reduce strength and increase water sensitivity, as confirmed by the mechanical properties presented later in this document. Regarding the incorporation of grits, despite the air void content being above the usual requirements, it may be acceptable if the mechanical parameters achieve suitable levels.

The aggregate gradation and the mastic formed by the fine aggregate particles and the bitumen are determinants of the high air void content. The differences between the blend's gradations shown in Figure 4 may explain some air void results but do not explain the significant increase in air void content for the mixes with dregs. The typical low sand equivalent of approximately 40% (EN 933-8 [58]), the high plastic index of 13% (ASTM D4318 [59]) and the high methylene blue adsorption of 2.2 g/kg (EN 933-9 [34]) for the fine particles reported by Modolo et al. [25] for the dregs are likely to contribute to a weak affinity between these particles and the binder. It must be emphasized that grits exhibited much higher sand equivalent (81%), and the fine particles were declared non-plastic. Therefore, the mastic did not increase the voids at the same level.

3.2. Marshall Properties

The resistance to external loads of any construction material is a crucial aspect when developing non-traditional sustainable materials. The Marshall compression test is a widespread empirical test that evaluates the stability (strength) of the mixture and the corresponding flow. Moreover, the Marshall quotient (stability/flow ratio) indicates the mixture's ability to resist traffic loads without excessive deformation. Table 5 summarizes the requirements in Portugal for dense-graded mixtures used in pavement surface layers [33]. Figure 10 illustrates the observed stability, flow and Marshall quotient results.

Table 5. Design requirements for a bituminous mixture AC14 surf 35/50 according to Portuguese requirements.

	Requirements
Marshall test	$7.5 \leq$ stability ≤ 15 kN $2 \leq$ flow ≤ 4 mm Marshall quotient ≥ 3 kN/mm

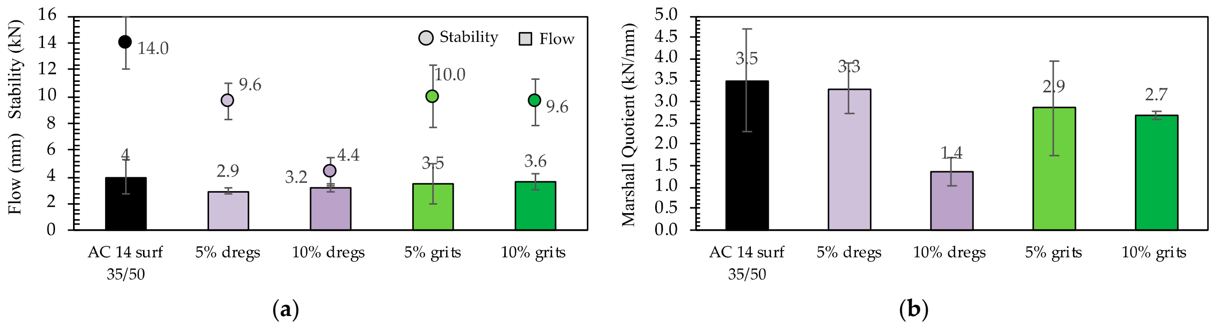


Figure 10. Marshall properties: (**a**) stability and flow; (**b**) Marshall quotient.

Except for the mixture with 10% dregs, which provided a 4.4 kN stability, all the remaining compositions comply with the requirements. As it reached the highest air void content of 15.6%, as shown before, this result was predictable. Despite providing air void content also higher than the maximum recommended value of 5%, the other blends with dregs or grits revealed stability results in the required range. However, it should be noted that the stability values are lower than the reference mixtures, whose result is 14 kN.

Flow results are not significantly affected by adding dregs and grits, continuing to meet specifications. In turn, the Marshall quotient is below the requirements for all the mixes with dregs or grits. These preliminary tests indicate that the incorporation of 10% of dregs is not viable as it violates practically all requirements. The remaining blends showed a reasonable strength to be confirmed in subsequent mechanical assessments regarding water sensitivity and rutting resistance.

3.3. Water Sensitivity

If the water is in contact with the asphalt mixture, there is the risk of decreasing the capacity of bitumen to bond with aggregates, leading to the so-called moisture-induced damage [60]. In the present study, the water sensitivity test delivered the result for ITS and ITSR (ITS_{wet}/ITS_{dry}), summarised in Table 6. As expected, the mixtures with dregs and grits provided lower ITS and ITSR for having higher air void content than the reference mix. Of the three tested mixtures with wastes, only the AC 14 surf 10% grits provided an ITSR close to the usual requirements of 80% [55]. Nevertheless, 75% can be accepted for low-demanding pavements not belonging to the main road national network.

Table 6. Water sensitivity tests results.

Sample	ITS_{dry} (kPa)	ITS_{wet} (kPa)	ITSR (%)
AC 14 surf 35/50	1374.0	1502.0	109.3
AC 14 surf 5% dregs	1310.8	342.8	26.2
AC 14 surf 5% grits	2045.8	1223.4	60.3
AC 14 surf 10% grits	1674.8	1259.4	75.8

Considering that a bituminous mixture for a surface layer pavement is mainly subjected to water damage when in service, the results for water sensitivity allow us to conclude that using dregs as a substitute for aggregates is inappropriate. Based on the results, the mixtures with dregs were not submitted to the wheel-tracking tests for further evaluation. This study confirms the conclusions of Modolo et al. [25] that a direct application in asphalt mixes of dregs as received from pulp and paper production is not possible. Although the results for mixtures with grits concerning water sensitivity are not exceptional, the authors decided to proceed with those blends for the next level of assessment in wheel-tracking tests. The use of an adhesion promotor should be investigated in the future to slightly improve ITSR.

3.4. Rutting Resistance

As in many places, the Portuguese climatic conditions expose the pavement surface layers to high temperatures during a significant part of the year. Therefore, assessing the rutting resistance of the asphalt mixtures is of primary importance. Figure 11 shows the obtained results, and Figure 12 displays the parameters derived from the curves plotted in Figure 11.

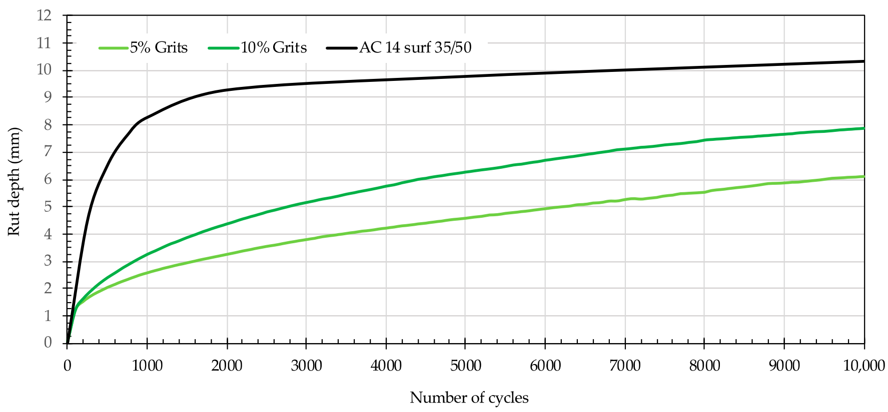


Figure 11. Variation of rut depth in wheel-tracking test results.

The incorporation of grits influences the response of the bituminous mixture under the repeated load of a wheel at 60 °C. Although the cumulative mixtures' deformation (Figure 11) was considerably lower for the mixes with grits, this happened because the reference mix suffered about 90% of its deformation over the initial test phase up to the 2000th cycle. Therefore, the PRD_{air} (ratio between rut depth and slab thickness) was considerably higher for the reference mix than those with grits. Nevertheless, the curves in Figure 11 display that WTS_{air} (curve slope) was considerably higher for the mixes with grits for the range of cycles 5000–10,000; approximately three times more. Higher values of WTS_{air} mean that the deformation rate after the initial slab's densification generally represents asphalt mixtures more prone to suffer rut depth. Usually, the initial rut depth is due to a change in the aggregate skeleton because the mixture's cohesion is not strong enough to avoid some rotation of the coarse aggregate particles. However, this effect may be reduced if the mastic (a blend of fine particles and bitumen) between the coarser particles is stiffer than usual. Despite that this phenomenon was not assessed in this study, the grits are likely to stiffen the mastic and, thus, contribute to a lower rut depth in the first part of the wheel-tracking test, even though the blends with grits had higher air void content.

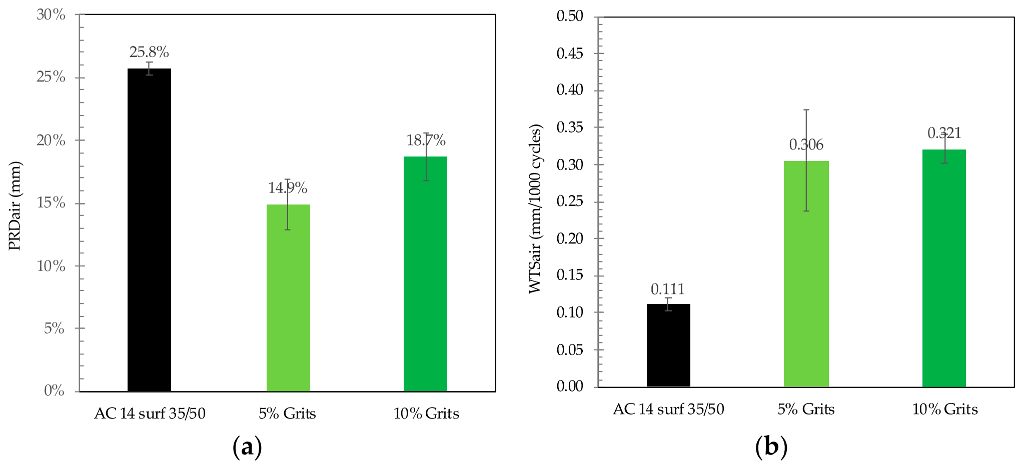


Figure 12. Results derived from wheel-tracking curves: (**a**) PRD_{air}; (**b**) WTS_{air}.

Although the rutting resistance of the mixes with grits is suitable, the results also show that increasing the percentage of grits results in higher deformation of the asphalt mixtures in wheel-tracking tests. This finding requires further investigation, particularly by testing a more comprehensive range of grits content with different gradations and bitumen content.

3.5. Environmental Compliance

Complementarily to the assessment of mechanical properties, the use of wastes in road pavements applications require the verification of environmental compliance to ensure that no harmful compounds are in contact with soils and groundwater. According to previous studies [19,61,62], using grits in soils does not negatively affect the presence of heavy metals, and when the concentrations are traceable, they present values below the regulatory limit values. The high-level pH (~12) confers an alkalinizing behaviour to grits in soils [19] and, in addition, the use of calcium carbonate from grits can be an advantage in acid soils, creating metallics compounds and being less acidic [63].

In the present study, these wastes are not in direct contact with soils since the grits were incorporated in a bituminous mixture used in surface layers in road pavements. However, during the wet seasons, there is the possibility of rainwater after being in contact with grits, transporting potential contaminants, and polluting soils and groundwater. As previously stated, considering the potential presence of harmful compounds in leachate, these were evaluated by carrying out two distinct approaches: an examination of loose mixtures and compacted material as applied to pavements.

Table 7 presents the results of the leaching analysis of the loose mixtures for one sample of each blend. The determination of the parameters chloride, sulphate, fluoride, arsenic, lead, cadmium, barium, chromium, copper, mercury, molybdenum, nickel, antimony, selenium, zinc, and COD was carried out from the eluate, with the remaining parameters being determined using the solid residue as-is.

Table 7. Results of mixtures' organic parameters, eluate analysis from loose mixtures, and landfill legal limits for inert and non-hazardous waste.

Parameter	Limits in Portuguese Legislation		AC 14 Surf 35/50	AC 14 5% Dregs	AC 14 10% Dregs	AC 14 5% Grits	AC 14 10% Grits
	Landfill for Inert Waste	Landfill for Non-Hazardous Waste					
pH	-		9.7	10.3	10.4	10.3	10.5
Water soluble extract, % (m/m)		-		0.26	0.73		
Phenolic index, mg/kg	1			<LOQ	<LOQ	<LOQ	<LOQ
Chloride, mg/kg	800	50,000		15	36		
Sulphate, mg/kg	1000	20,000		720	2000	23	74
Fluoride, mg/kg	10	250					
Arsenic, mg/kg	0.5	5					
Lead, mg/kg	0.5	10		<LOQ	<LOQ		<LOQ
Cadmium, mg/kg	0.04	2					
Barium, mg/kg	20	100	<LOQ	0.01			0.01
Chromium, mg/kg	0.5	20			0.01		0.02
Copper, mg/kg	2	50			<LOQ	< LOQ	
Mercury, mg/kg	0.01	0.5					
Molybdenum, mg/kg	0.5	10			0.02		
Nickel, mg/kg	0,4	10		<LOQ			<LOQ
Antimony, mg/kg	0.06	0.7					
Selenium, mg/kg	0.1	0.5			<LOQ		
Zinc, mg/kg	4	50					
Acid Neutralization Capacity (pH 4.0), mmol/kg	-	-	199	728	585	215	585
DOC, mg/kg	500	800	<LOQ	23	64	<LOQ	10
TOC, mg/kg	30,000	50,000	160,000	140,000	7300	160,000	150,000
Mineral oil (C10–C40), mg/kg	500		1800	480	3300	3400	1700
Benzene, mg/kg							
Toluene, mg/kg							
Ethylbenzene, mg/kg	6	999					
m-/p-Xylene, mg/kg							
o-Xylene, mg/kg			<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
(HAP) Naphthalene, mg/kg							
(HAP) Acenaphthylene, mg/kg							
(HAP) Acenaphthene, mg/kg							
(HAP) Fluorene, mg/kg							
(HAP) Phenanthrene, mg/kg			0.14	0.18	0.18	0.16	0.16
(HAP) Anthracene, mg/kg				<LOQ	<LOQ	<LOQ	<LOQ
(HAP) Fluoranthene, mg/kg						0.06	
(HAP) Pyrene, mg/kg			<LOQ	0.09	0.1	0.06	0.06
(HAP) Benzo-(a)-anthracene, mg/kg				0.06	0.06	0.06	<LOQ
(HAP) Chrysene, mg/kg	100	100	0.12	0.2	0.16	0.11	0.12
(HAP) Benzo(b)fluoranthene, mg/kg				0.08	0.07	0.09	0.09
(HAP) Benzo(k)fluoranthene, mg/kg				<LOQ	0.07	0.06	<LOQ
(HAP) Benzo(a)pyrene, mg/kg				0.08	0.06	0.08	0.05
(HAP) Indene(1,2,3-cd)pyrene, mg/kg				<LOQ			
HAP) Dibenzo-(a,h)-anthracene, mg/kg				0.07	<LOQ	<LOQ	
(HAP) Benzo(g,h,i)perylene, mg/kg			<LOQ	0.37	0.27	0.12	
PCB 28, mg/kg						0.02	<LOQ
PCB 52, mg/kg							
PCB 101, mg/kg							
PCB 138, mg/kg	1	50		<LOQ	<LOQ	<LOQ	
PCB 153, mg/kg							
PCB 180, mg/kg							
PCB 118, mg/kg							

LOQ: limit of quantification; TOC: total organic carbon; DOC: dissolved organic carbon; HAP: hazardous air pollutants; PCB: polychlorinated biphenyls congeners.

The results show that all asphalt mixtures comply with most limits stipulated by legislation, including for landfilling for inert waste. The exception is the blend with 10% dregs, whose sulphate concentration exceeds the landfill limit for inert materials and is only accepted in non-hazardous waste landfills. The concentration of total organic carbon (TOC) is above the values referred to in legislation, for both types of landfills. With the increase in the percentage of incorporation of both wastes, a decrease in the TOC value can be observed, with this decrease being more pronounced with the increase in the incorporation of dregs. Nevertheless, none of the TOC values of these asphalt mixtures exceed the value of the reference surf sample AC 14. Furthermore, Portuguese legislation allows the admission of waste that exceeds the stipulated value if its dissolved organic carbon concentration (DOC) does not exceed 800 mg/kg, which happens in the case of the asphalt mixtures studied.

The evaluation of the polluting potential as a compacted material derives from analysing the collected leachates of the water load and surface runoff tests, whose results are summarized in Tables 8 and 9. Each table shows the average concentration of the compound, the standard deviation for each compound (SD) and the Portuguese regulatory limit values. It should be noted that more harmful compounds have been analysed, namely antimony, arsenic, lead, cadmium, chromium, mercury, selenium, and chlorine. However, in Tables 8 and 9, since bituminous mixtures are commonly used worldwide for road pavements, only the compounds whose concentrations differ from the reference mixture are shown. In addition, most of these compounds present concentrations below the quantification limits; therefore, they do not present any danger to the environment.

Table 8. Results of leachates analysis of the water load tests.

Compound	AC 14 Surf 35/50	AC 14 Surf 5% Grits		AC 14 Surf 10% Grits		DL 236/98	DL 102-D/2020
	(mg/L)	(mg/L)	SD (mg/L)	(mg/L)	SD (mg/L)	(mg/L)	(mg/L)
Barium	0.0016	0.0070	0.0001	0.0016	0.0010	-	100
Copper	0.0010	0.0020	0.0014	0.0975	0.1336	1.0	50
Molybdenum	0.0010	0.0010	-	0.0015	0.0007	-	10
Nickel	0.0020	0.0050	0.0057	0.0010	-	2.0	10
Zinc	0.0280	0.0115	0.0064	0.0420	0.0382	-	50
DOC	7.0000	6.1500	1.2021	13.8500	8.6974	-	800
Fluorine	1.1000	1.0000	-	2.0000	0.8485	-	250
Sulphates	3.5000	7.9500	4.3134	32.5000	12.0208	2000	20,000

Table 9. Results of leachates analysis of the surface runoff tests.

Compound	AC 14 Surf 35/50	AC 14 Surf 5% Grits		AC 14 Surf 10% Grits		DL 236/98	DL 102-D/2020
	(mg/L)	(mg/L)	SD (mg/L)	(mg/L)	SD (mg/L)	(mg/L)	(mg/L)
Cu	0.0050	0.0035	0.0007	0.0065	0.0064	1.0	50
Ni	0.0010	0.0015	0.0007	0.0010	-	2.0	10
Zn	0.0190	0.0100	0.0014	0.0075	0.0021	-	50
DOC	1.3000	1.200	0.1414	1.1000	0.1414	-	800
SO_4	1.0000	1.8500	0.9192	2.4000	0.9899	2000	20,000

The analysis of the leachates resulting from the water load tests (Table 8) shows that none of the compounds reached concentrations close to the limit values. The highest concentrations are obtained for the dissolved organic carbon (DOC) and sulphates for the mixture with 10% grits. The average value for DOC is 13.85 mg/L, with a standard deviation of 8.70 mg/L. However, the limit value established in the Portuguese regulation for waste management is 800 mg/L. Concerning the sulphates, the highest average concentration is

32.50 mg/L for a standard deviation of 12.02 mg/L. Again, the Portuguese regulation for waste management (DL 102-D/2020 of 1.12) and for protection and improvement of the quality of water body (DL 236/98 of 1.08) propose higher limit values, 20,000 mg/L and 2000 mg/L, respectively. These results are in line with the fundamental characterization of grits. Indeed, according to the characterization summarized in Table 2, grits have high levels of dissolved organic carbon (430 mg/kg dry weight) and sulphates (460 mg/kg dry weight).

Another observation can be obtained when comparing the concentration of these two compounds within the three mixtures. Considering the average values and the respective standard deviation, a pattern of increasing concentration with an increase in the percentage of grits incorporation can be identified. Analysing the obtained concentration in the other compounds, the leachates from the water load test in the mixture AC 14 surf 10% grits tend to provide higher concentration, except for nickel, for which the mixture with 5% grits provided higher concentrations for this compound. This result, as well as the observed fluctuation between the two different percentages and the two slabs for each percentage, may derive from two factors. The first is related to heterogeneity resulting from the preparation of the specimens, which can be reduced by improving the mixture technic. The second factor may arise from the water load test itself. No water flowed through the sample cross-section despite the higher air void content. The leachates collected after the water load test flowed from the top of the slab to the collecting vessel through the borders of the samples, which, notwithstanding the waterproofing care, were more permeable than the slabs. By not crossing the slab, some heterogeneity of contact between water and grits in all samples may occur.

The analysis of the leachates collected after the surface runoff tests provided different results. Although the compounds that present higher concentrations are also the DOC and sulphates, the differences between the reference mixture and the mixtures with grits are not considerable. Regardless of the percentage of grits, the DOC concentration is roughly the same. Indeed, considering the average and the standard deviation, the reached concentrations are identical to the ones evaluated for the reference mixture. Concerning the sulphates, the leachates of the mixtures with grits tend to present higher concentrations than the reference mixture, but the differences do not reach the discrepancies observed in the water load test. Also, for this compound, a pattern of increasing concentration with the increasing percentage of grits is visible. Regarding the other compounds, the reference mixture and the mixtures with grits produce leachates with approximately the same concentrations.

The surface runoff test results do not show a significant fluctuation between the two different percentages and the two slabs for each percentage prepared. This observation indicates that, with the absence of surface deterioration on the pavements, the leachate generated is not particularly influenced by the composition of the mixture. This conclusion corroborates the outcomes of previous studies [15,25,63] and demonstrates that, from an environmental point of view, the incorporation of grits in bituminous mixtures does not represent an additional menace in the short-term. Further studies should be engaged to verify the effect of long-term ageing with the Tecnico Accelerated Ageing equipment (TEAGE) [64] in the leachate concentration. This accelerated ageing procedure uses ultraviolet radiation and wet/dry cycles to simulate damaging weather conditions in the long term.

4. Conclusions

Since the water resistance performance of bituminous mixtures incorporating dregs as substitutes for part of natural aggregate is weak, this study confirms that using dregs from the pulp and paper industry is inappropriate for that goal. Nevertheless, grits, another waste from the same industry, have the potential to be valorised in bituminous mixtures for transport infrastructures' pavement. Additionally, the findings showcase no concerns regarding the possible leaches of harmful compounds into the soil and the groundwater if grits are incorporated as a constituent of asphalt concrete.

The specific conclusions drawn from the laboratory results presented in this paper are summarised as follows:

(i) The use of grits increased void content in asphalt concrete (6.3% and 7%, instead of 3% of the reference), and Marshall stability ($S \geq 7.5$ kN) and flow ($f \leq 4$ mm) met requirements.
(ii) Water sensitivity increased with grit incorporation ($ITSR \leq 80\%$), suggesting the need for further studies, possibly with adhesion promoters.
(iii) The resistance against rutting in grit mixes is appropriate, but the deformation regarding WTS_{air} increased as the percentage of grits increased, requiring further investigation.
(iv) TOC values released from loose asphalt mixtures with grits exceeded legislation recommendations but remained below values for conventional reference asphalt concrete; because the DOC values did not exceed 800 mg/kg, asphalt mixtures with grits meet requirements for acceptance in non-hazardous materials landfills.
(v) Leachate measurements from runoff on compacted asphalt concrete with grits indicate no additional threats.

Further studies must be conducted to analyse different ranges of grits content and the effect of ageing on the mechanical behaviour and leachate release.

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