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Development of Cold In-Place Recycling with Bitumen Emulsion and Biomass Bottom Ash

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Abstract: Power generation from biomass is one of the most promising energy sources available today. However, this industry has a series of wastes derived from its activity, mainly biomass fly ash and biomass bottom ash. Biomass bottom ash is a waste that has no current use and, in most cases, is deposited in landfills. In turn, road construction is one of the activities that produces the most pollution, as it requires huge amounts of raw materials. Therefore, this research proposes the use of biomass bottom ashes, in an unaltered form, for the formation of cold in-place recycling with bitumen emulsion. This type of mixture, which is highly sustainable owing to the use of a high percentage of waste, was made with reclaimed asphalt pavement, biomass bottom ash, water, and bitumen emulsion. To this end, the grading curve of the materials was analyzed, different bituminous mixtures were made with varying percentages of emulsion and water, and the mechanical properties of the mixtures were analyzed. At the same time, the same type of mix was made with reclaimed asphalt pavement and commercial limestone aggregate, in order to compare the results. The tests showed a better mechanical behavior of the bituminous mixes made with biomass bottom ash, maintaining physical properties similar to those of conventional mixes. In short, it was confirmed that the production of this type of mix with biomass bottom ash was feasible, creating sustainable materials that reuse currently unused waste and avoid landfill disposal.

Keywords: biomass bottom ash; energy production; waste-to-energy; reclaimed asphalt pavement; cold in-place recycling with bitumen emulsion; filler; circular economy; sustainable construction

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1. Introduction

The development of the population's well-being has led to a significant consumption of natural resources and a high environmental impact [1]. However, this development has provided substantial benefits to society, and new ways of meeting people's needs and minimising environmental impact must be sought [2].

All sectors have a significant environmental impact. In particular, the construction sector is one of the sectors with the greatest environmental impact [3]. This is because of the huge quantities of raw materials it consumes, poorly optimised production processes, and high greenhouse gas emissions [4]. Road construction in particular requires high quality materials for large and long infrastructures. Nevertheless, roads are essential communication links for the population, as they are the basis for the economic development of a nation and prevent the isolation of the population. For this reason, it is necessary to develop new materials for road construction, more specifically for bituminous mixes, which are the costliest as well as an environmentally and economically important element [5].

In line with the above, various research projects have been carried out in which more optimised processes are used for the formation of bituminous mixtures or industrial by-products are incorporated as substitutes for conventional raw materials [6]. The use of industrial waste for the manufacture of bituminous mixtures has several advantages: on the one hand, it avoids the extraction of new raw materials; on the other hand, it reduces greenhouse gas emissions and environmental impact by reducing the percentage of raw materials; and in turn, it avoids the landfilling of industrial waste by giving it a new life.

Therefore, there are several investigations where waste has been used in bituminous mixtures. Some of the wastes used were electric arc furnace slag [7–9], ladle furnace slag [10,11], fly ash [12], crap tyres [13], recycled glass [14], recycled concrete aggregate [15], and so on. In most cases, acceptable properties of the asphalt mixes formed were achieved, thanks to the exhaustive study of the wastes and their physical, chemical, and mechanical characterisation.

In line with the above, the production of electrical and thermal energy using biomass currently accounts for 14% of the total energy supply [16], as in recent years, there has been an increase in the number of processes implemented using biomass [17]. Moreover, its importance in the global energy supply is expected to increase steadily in the coming years and it is considered to be one of the most promising renewable energy sources [18,19]. However, this type of energy also has disadvantages that need to be overcome in order to achieve a more sustainable development. One of the main disadvantages is the production of waste. The waste produced is mainly of two types, biomass fly ash and biomass bottom ash [20]. Fly ash is produced in the filtrate of gases produced in the combustion of biomass. Consequently, these ashes have a high proportion of oxides, which is why they have been used in different research for various purposes. For example, biomass fly ash has been used as a partial substitute for cement [21], as an additive to concrete [22], for the development of geopolymers [23], and even for nanotechnology [24]. On the other hand, biomass bottom ash is the residue obtained directly from the grate of the biomass combustion furnace. Unlike fly ash, biomass bottom ash has had little use in new materials. In most cases, it is landfilled or dumped on poor quality roads. It should be noted that both fly ash and biomass bottom ash have different chemical, physical, and mechanical characteristics depending on the biomass used [25,26]. Therefore, the study for the use of these ashes must be individual for each type of biomass, analysing the main critical points that will determine the viability of their use for a specific material. The main critical points are particle size, density, the existence of heavy metals, the existence of contaminating elements, the percentage of organic matter, and the determination of the presence of expansive chemical compounds.

Based on the above, and taking as fundamental premises the reduction of raw material extraction in road construction and the use of biomass bottom ash [27], in this research, bituminous mixes are developed with biomass bottom ash from the combustion of almond shells and alpeorujo. The bituminous mixture developed is a cold in-place recycling with bitumen emulsion [28]. This type of mix has significant environmental advantages over other types of mixes: on the one hand, it uses the existing milled and aged road surface as aggregate; on the other hand, the mix is formed at ambient temperature thanks to the use of bituminous emulsion; moreover, all operations (pavement milling, conformation of the bituminous mix, spreading, and compaction) are carried out directly on the infrastructure in a short time; consequently, there is no transport of the reclaimed asphalt pavement to the mixing plant and, therefore, no greenhouse gas emissions; finally, the high safety of this technique for workers and the low influence on traffic should be emphasised.

Biomass bottom ash in this type of mixture, a cold in-place recycling with bitumen emulsion, has two main functions: to correct the granulometry of the milled pavement by providing the fine fraction of the aggregate, as usually, the milled pavement has a low proportion of fine aggregate and filler; on the other hand, to provide cementitious properties to the mixture of water and bituminous emulsion, developing better mechanical characteristics. These cementitious properties of biomass bottom ash derive directly from its chemical composition and have been corroborated by different authors [29,30].

Therefore, for the development of this research, the biomass bottom ash and the reclaimed asphalt pavement (RAP) were physically and chemically characterised. Subsequently, different bituminous mixtures were formed with recycled pavement and biomass bottom ash, and varying percentages of precoating water and bituminous emulsion. The specimens were tested to determine their physical properties, as well as their simple compressive strength. In addition, the results were compared with those obtained with the same type of mixture made with limestone aggregate, which is usual in this type of technique. The results showed an increase in the strength of the mixes made with biomass bottom ash compared with the mixes made with limestone aggregate, while maintaining similar physical properties that are acceptable by the standards. In short, it was found that the addition of biomass bottom ash to the recycled pavement for the formation of a cold in-place recycling with bitumen emulsion produces a quality bituminous mixture, with properties acceptable by the regulations and with a high percentage of residues. In other words, a sustainable material for road construction is obtained.

2. Materials and Methods

This section describes the materials used in this research, as well as the tests carried out to evaluate the bituminous mixtures made with reclaimed asphalt pavement (RAP) and biomass bottom ash (BBA).

2.1. Materials

The materials used in this research correspond mainly to industrial wastes or by-products. In turn, commercial materials such as limestone aggregate were used to evaluate the quality of the incorporation of the waste. In this way, the advantages that can be achieved in the bituminous mixtures conformed with the use of BBA can be verified.

The materials used, waste or commercial materials, were used in an unaltered form. That is, the products were taken directly from the producing industry to evaluate their physical and chemical characteristics without any type of treatment.

It should be noted that all the materials were dried at a temperature of 105 ± 2 °C for 24 h to eliminate humidity. This simple process to be carried out at industrial level was executed at laboratory level with the sole purpose of reducing the variables that could influence the test results. However, the existence of humidity in the materials would not be detrimental to the final product; it would simply have to be taken into account in order to carry out a correct dosing of the materials.

In turn, the BBA used, which is the main by-product of this research, was analyzed over time. The chemical and physical analyses carried out in different production batches reflected the unalterability of the mentioned properties, so that the characteristics were maintained in different production batches. This fact is essential, as it is essential for the use of a residue that its properties be unalterable. Otherwise, a product of higher or lower quality would be created depending on the production batch, as is the case, for example, with sewage sludge.

The following sections describe the materials used, describing their origin and general characteristics.

2.1.1. Biomass Bottom Ash (BBA)

BBA, as previously mentioned, corresponds to the residue of the energy generation industry from the combustion of almond shells and alpeorujo. These BBAs are produced in industries in the region of Andalucía, Spain. In these industries, the combustion of different types of biomass is produced, mainly related to the agricultural sector. In this particular case, the biomass used derives from the combustion of almond shells and alpeorujo.

The sample was taken directly from the producing industry without alteration, i.e., the sample contained all the particle sizes produced in the industry. This sample was dried according to the procedure described above and used for the different tests detailed in the methodology. The preparation of BBA for the different tests is detailed in the methodology.

2.1.2. Reclaimed Asphalt Pavement (RAP)

The reclaimed pavement belongs to the road that joins the towns of Linares and Bailen, in Spanish territory. This pavement showed clear signs of ageing, as there were cracks in irregular patterns on the surface. This type of defect represents the loss of the volatile and elastic part of the bitumen owing to the passage of time and, consequently, the loss of resistance to repeated tensile loads.

This pavement was milled with machinery similar to the one that would be used in the execution of the cold in-place recycling with bitumen emulsion in order to perform the laboratory tests as reliably as possible. The sample of the milled pavement was taken to the laboratory to carry out the subsequent tests detailed in the methodology.

2.1.3. Bitumen Emulsion

The bitumen emulsion used in this research is a cationic slow breaking emulsion, named after the European standard C60B5 REC. This type of slow breaking emulsion is very appropriate for RAP, as its longer breaking time makes it possible to coating the smallest aggregates. It should be noted that, depending on the aggregate size, the emulsion used will be different, i.e., bituminous mixtures with a higher proportion of coarse aggregate will use faster breaking bituminous emulsions than bituminous mixtures with a high proportion of fine aggregate. At the same time, it is necessary to mention that a bituminous emulsion is a suspension of bitumen in water. The emulsion of these two immiscible materials is achieved through a suitable manufacturing process and the use of emulsifiers. Depending on the nature of the emulsifier, the emulsion will have greater or lesser compatibility with the aggregate. Therefore, the emulsion in contact with the aggregate must break, i.e., produce the separation of bitumen and water. The bitumen remains adhered to the aggregate and the water evaporates by natural processes. Therefore, the additional and main advantage of this technique is that it can be performed at ambient temperature without the need for high temperature conformation. In this particular case, a slow cationic emulsion compatible with the RAP was used, as well as with the BBA used.

For further details, Table 1 shows the technical characteristics of the bitumen emulsion used.

Table 1. Technical details of the bitumen emulsion C60B5 REC.

Characteristics	**Unit**	**Standard**	**Min.**	**Max.**
Original Emulsion				
Particle polarity	-	UNE EN 1430	Positive	
Breaking value	g	UNE EN 13075-1	170	
Binder content (per water content)	%	UNE EN 12846-1	58	62
Efflux time (2 mm, 40 °C)	s	UNE EN 12846	15	70
Residue on sieving (0.5 mm)	%	UNE EN 1429	-	0.10
Setting tendency (7 days storage)	%	UNE EN 12847	-	10
Water effect of binder adhesion	%	UNE EN 13614	90	-
Binder after Distillation (UNE EN 1431)				
Penetration (25 °C; 100 g; 5 s)	0.1 mm	UNE EN 1426	-	270
Softening point	°C	UNE EN 1427	35	-
Evaporation Residue (UNE EN 13074-1)				
Penetration (25 °C; 100 g; 5 s)	0.1 mm	UNE EN 1426	-	330
Softening point	°C	UNE EN 1427	35	-
Stabilizing Residue (UNE EN 13074-2)				
Penetration (25 °C; 100 g; 5 s)	0.1 mm	UNE EN 1426	-	270
Softening point	°C	UNE EN 1427	35	-

2.1.4. Limestone Aggregate

Limestone aggregate is a material usually used in cold in-place recycling with bitumen emulsion for the correction of the grading curve. This aggregate belongs to the area of Andalucía, Spain, as do the other materials.

Limestone aggregate is derived from calcareous rocks. Calcareous is a sedimentary rock composed mainly of calcium carbonate ($CaCO_3$), generally calcite, although it frequently presents traces of magnesite ($MgCO_3$) and other carbonates.

The limestone aggregate has an adequate adhesiveness with bitumen emulsion, as well as with bitumen. The particle density of the limestone aggregate used was 2.62 Tn/m^3, with a bulk density in kerosene of 0.70 Tn/m^3. The plasticity index was very low, reflecting a value of less than 5. The resistance of the limestone aggregate is lower than that of a siliceous aggregate. However, it is adequate for the type of bituminous mixture developed in this research.

2.2. Methodology

The methodology detailed in this research shows the tests carried out to evaluate the suitability of the use of BBA as filler material for reclaimed asphalt pavements and the cold in-place recycling with bitumen emulsion conformation.

The methodology followed is objective and sequential, being collected in the Circular Order 8/2001 [31]. This Spanish, European standard describes the procedure to be followed for the formulation of cold in-place recycling with bitumen emulsion. It should be noted that, although this regulation has been repealed, it was used in this research because it has been used in hundreds of successful cases in Spain. In addition, it allows the physical and mechanical properties to be adequately characterised, the optimum combination of materials to be determined with a high degree of accuracy, and the differences between mixtures made with biomass bottom ash and those made with limestone aggregate to be correctly evaluated.

First, BBA and RAP were chemically and physically characterized. Then, an optimum combination of RAP and BBA was defined according to the grading envelope established by the aforementioned regulations. It should be remembered that BBAs have two different functions in the bituminous mix: on the one hand, they correct the RAP particle size to provide fine aggregate, and on the other hand, they provide the cementitious characteristics of the BBA to increase mechanical strength.

Subsequently, the compatibility of the aggregates with the bitumen emulsion used was evaluated and the maximum density of the mixture was obtained. This higher density will correspond to a higher mechanical strength. At the same time, different bituminous mixtures were conformed with different percentages of emulsion and precoating water, evaluating which were the optimum percentages that develop the highest mechanical resistance of the bituminous mixture. These results were compared with those obtained with bituminous mixtures made with RAP and limestone aggregate.

In the following sections, each of the phases developed in this research is described in detail for further clarification and to be able to reproduce the results objectively.

2.2.1. Characterization of Initial Materials

First, the materials used in this research must be characterized chemically and physically. These materials or by-products are BBA and RAP.

The first of the chemical tests performed on BBA was elemental analysis. This test quantifies the percentage of carbon, hydrogen, nitrogen, and sulfur present in the sample. For this purpose, the BBA sample was calcined at a temperature of 950 degrees, analyzing the gases produced in this combustion.

Subsequently, and because of the fact that BBA is a mainly inorganic material, the X-ray fluorescence test was performed. This test allows the quantification of the chemical elements with the highest atomic weight in the sample.

However, it should be noted that the chemical elements have greater or lesser activity, even contaminating power, depending on the chemical compound in which they are combined. Therefore, it is essential to determine the chemical compounds present in BBA. For this purpose, the X-ray diffraction test was performed.

Finally, the BBA leachate test was carried out according to the UNE-EN 12457-3 standard. The leachate obtained from this test was analyzed to determine that the concentrations of potentially contaminating elements were lower than the limits set by the standard [32]. This ensures that the use of BBA in bituminous mixtures for roads will not produce subsequent negative effects on the environment.

Once the chemical composition of BBAs was analyzed, their physical properties were determined. The first of the tests performed was the particle density test, UNE-EN 1097-7. This test is essential to assess whether volumetric corrections are necessary, owing to a density different from that of a conventional aggregate. In turn, the bulk density test in kerosene, UNE-EN 1097-3, evaluates the specific surface of the material, as well as whether or not the material is powdery. A powdery material will present problems in the proportioning of the material in the factory and will absorb excessive percentages of binder, because the bulk density must be within the established limits. The plasticity index determines the existence of a clayey particle. These particles can damage the final material due to expansivity problems, so it is desirable that the plasticity index be as low as possible.

It should be remembered that BBAs have two different functions in the bituminous mix under study. One of them is the correction of the granulometric curve of the milled pavement. Therefore, it is essential to determine the particle size curve of BBA, UNE-EN 933-1. In this way, the percentage of combination of BBA with RAP can be calculated to obtain a grading curve formed with both materials that is within the grading envelope defined by the aforementioned standard.

RAP was also evaluated through different chemical, physical, and mechanical tests. First, the grading curve of the milled pavement was analyzed according to the UNE-EN 933-1 standard. Subsequently, the binder was separated from the coarse aggregates, fine aggregates, and filler, according to standard UNE-EN 12697-1. Once the different materials making up the RAP were separated, the bitumen was analyzed. This binder was evaluated by means of penetration tests, standard UNE-EN 1426, and the softening point test, standard UNE-EN 1427. On the other hand, the coarse aggregate, fine aggregate, and filler of the aged bituminous mix were evaluated through different physical and mechanical tests. The test of determination of resistance to fragmentation, standard UNE-EN 1097-2, was carried out on the coarse aggregate of RAP in order to evaluate its resistance. The determination of the percentage of crushed and broken surfaces in coarse aggregate particles, according to UNE-EN 933-5, and the flakiness index, according to UNE-EN 933-3, were also determined. The RAP fine aggregate was characterized with the sand equivalent test, UNE-EN 933-8 standard, and the plasticity index, UNE-EN ISO 17892-12, to determine the presence of colloidal or clayey particles that could damage the new asphalt mixture.

With the tests carried out, the feasibility of using RAP for the conformation of new bituminous mixtures was assessed, as well as the usefulness of BBA as an additive.

2.2.2. Bituminous Mixtures' Manufacturing and Testing

Once the initial materials were analyzed, different bituminous mixtures were formed. First, and according to the grading curves of BBA and RAP, the optimum combination of both materials was obtained. This optimum combination should produce a grading curve within the grading envelope defined by the standards detailed above for this type of bituminous mix.

With this optimum combination of materials, the modified Proctor test was carried out, according to the UNE 103501 standard. The modified Proctor test provides, for a given material, the humidity necessary to obtain the maximum compaction density. This humidity is called optimum humidity and coincides with the theoretical fluid content (TFC) for this research. The theoretical fluid content would be the percentage of fluids to be added to the combination of RAP and BBA, these fluids being the precoating water plus the bitumen emulsion.

However, the theoretical fluid content must be corrected for the properties of the emulsion; this new percentage is called the optimum fluid content (OFC). The optimum fluid content is determined by means of the coating test, NLT-389/00 standard. This test is performed with a fixed percentage of emulsion, 3% on aggregate, and variable percentages of precoating water, from CTF to CTF–2%. The optimum percentage of fluids is determined according to the achieved coating, with the optimum percentage of fluids being the one subsequently used in the different families of bituminous mixtures formed.

Spanish regulations establish that, for this type of bituminous mixture, the percentage of emulsion over aggregate must be between 2.5% and 4% over aggregate. Therefore, different families of bituminous mixtures were made with RAP and BBA with emulsion percentages between 2.5% and 4%, with increments of 0.25% and with varying percentages of precoating water. The precoating water was equal to the difference between the optimum fluid content and the emulsion percentage.

The families of bituminous mixtures were made according to NLT-161/98. For this purpose, RAP was mixed with BBA in the determined proportion, subsequently adding the corresponding percentages of water and emulsion for each group of test samples. The resulting mixture was poured into a standard mold to apply the compaction load. This load consisted of an initial pressure of 1 MPa and then the application of a load of 21 MPa in a time of 2 to 3 min. Finally, the test specimens were stripped and subjected to the curing process at a temperature of 50 ± 2 °C for at least 3 days and up to constant mass. This process is carried out to eliminate water from the emulsion and to obtain the final properties of the mixture.

Subsequently, the physical properties of the bituminous mixtures made from the different families were determined. These properties are the maximum density according to standard UNE-EN 12697-5, the bulk density according to standard UNE-EN 12697-6, and the voids index according to standard UNE-EN 12697-8. The test samples from each family or group of samples were then separated into two groups to study the effect of water on the bituminous mix. This test is called the immersion-compression test, according to standard NLT-162/00. One of the subgroups of test samples from each family is immersed in water at a temperature of 49 ± 2 °C for 4 days. The other subgroup of specimens is subjected to ambient conditions (20 ± 2 °C). Finally, the test samples of the two subgroups of samples, for each family, are subjected to the simple compressive strength test according to the NLT-161/98 standard, determining the influence of water on the strength of the bituminous mixture.

It should be noted that, in order to determine the quality of the incorporation of BBA for the formation of recycled pavements in situ with bitumen emulsion, families of bituminous mixtures were also made with RAP and limestone aggregate, in the same proportion of combination with RAP as BBA and with the same procedure described above. These test samples were also physically and mechanically evaluated through the tests mentioned above.

2.2.3. Determination of the Optimum Combination of Materials

The results obtained from the different families of bituminous mixtures manufactured, with varying percentages of emulsion and precoating water, were analyzed to determine which percentage of emulsion and water produced the highest mechanical strength and, in turn, obtained acceptable physical properties according to the aforementioned standards. For this purpose, the values of resistance to simple compression without immersion were graphically represented. In this way, it was easy to evaluate graphically which was the optimum emulsion percentage, as long as this percentage obtained an adequate simple compressive strength with immersion and acceptable physical properties. This process carried out for bituminous mixes incorporating BBA was also performed for bituminous mixes made with limestone aggregate.

Once the theoretical percentage of bitumen emulsion was determined, test samples were again formed according to the described procedure and the physical and mechanical tests mentioned above were performed again. In this way, the properties of the bituminous mix were corroborated with the percentage of emulsion obtained graphically.

Finally, the results of the tests performed on the bituminous mixes with BBA and limestone aggregate were compared, showing objectively the advantages of incorporating BBA.

3. Results

This section shows the results of the tests mentioned in the methodology and their discussion.

3.1. Characterization of Initial Materials

As detailed in the methodology, BBAs were first characterized chemically and physically. The first of the tests performed was the elemental analysis, showing the results detailed in Table 2.

Table 2. Elemental analysis of biomass bottom ash (BBA).

Sample	Nitrogen, %	Carbon, %	Hydrogen, %	Sulfur, %
BBA	0.400 ± 0.008	4.410 ± 0.090	0.540 ± 0.001	0.000 ± 0.001

The elemental analysis test shows low percentages of sulfur and nitrogen. This is positive, as these chemical elements are potentially contaminating. On the other hand, the reduced percentage of carbon and hydrogen represents the inexistence of organic matter, as well as a reduced percentage of carbonated or hydrated compounds. This is to be expected considering the production process of the residue.

The elemental analysis test showed that the BBA is a mainly inorganic material; therefore, it is essential to perform the X-ray fluorescence test to determine the chemical elements present. The results of this test are shown in Table 3.

Table 3. X-ray fluorescence of BBA.

Compound	wt, %	Est. Error
K_2O	45.2	0.25
CaO	8.98	0.14
SiO_2	8.96	0.14
SO_3	6.43	0.12
Cl	4.72	0.11
MgO	4.04	0.10
P_2O_5	3.56	0.09
Al_2O_3	1.64	0.06
Fe_2O_3	0.864	0.0430
Na_2O	0.623	0.0310
ZnO	0.197	0.0098
TiO_2	0.0728	0.0036
SrO	0.0533	0.0027
MnO	0.0312	0.0020
Rb_2O	0.0237	0.0037
NiO	0.0221	0.0016
CuO	0.0207	0.0021
Cr_2O_3	0.0105	0.0020

As can be seen, the main element in the BBA is potassium, which is to be expected if one takes into account that the ashes come from the combustion of almond shells and alpeorujo. Other chemical elements such as calcium, silicon, magnesium, phosphorus, and aluminum are also present. These chemical elements are common in BBA according to different authors. The non-existence or low proportion of contaminating chemical elements such as heavy metals is noteworthy. However, to corroborate that there will be no contamination by these chemical elements, a leachate test was subsequently carried out.

Chemical elements have greater or lesser activity depending on the chemical compound in which they are found. Therefore, for the determination of these chemical compounds, the X-ray diffraction test was performed, showing the results shown in Figure 1.

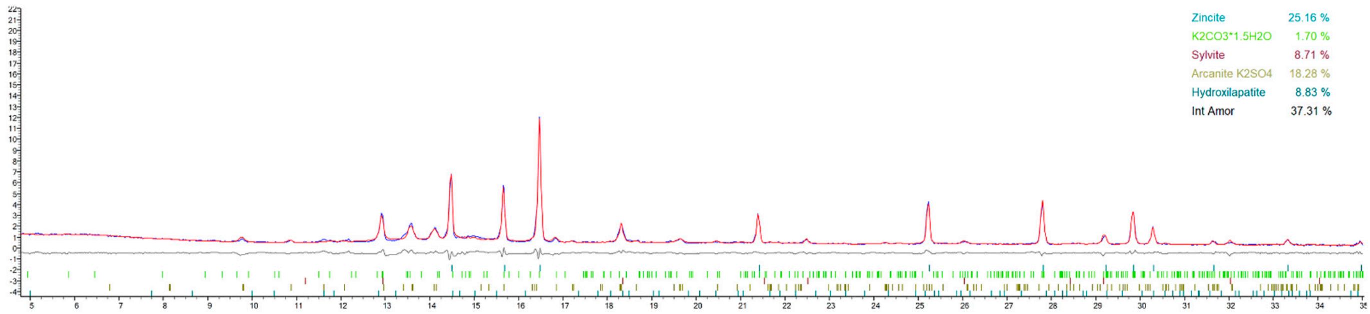

Figure 1. Results of X-ray diffraction of biomass bottom ash (BBA).

In the BBA diffractogram, the high content of amorphous or non-diffracting material stands out. The main phases identified are silicates, potassium carbonate, sylvite, and arcancite. The silicates present seem to be responsible for providing the cementitious characteristics of the BBA corroborated by different investigations. In addition, the existence of potassium carbonate ensures the dimensional stability of the BBA, not producing expansivity problems. This fact is due to the fact that expansivity occurs in the carbonation process and not later. The existence of sylvite and arcancite coincides with the results obtained in the X-ray fluorescence test, because previously, a significant percentage of chlorine and sulfur could be observed. However, these chemical compounds are more stable than other sulfur and chlorine compounds, so they should not present problems of contaminant leaching. To corroborate this fact, leachate tests were carried out to determine that the concentrations of these chemical elements in the leachate were lower than the limits established by Spanish-European regulations [32]. The results of the leachate test are shown in Table 4.

Table 4. Concentration of chemical elements in biomass bottom ash leachate compared with regulatory limits.

Element	BBA, mg/kg	Maximum Limits, mg/kg
Ba	0.182 ± 0.005	17
Cd	0.002 ± 0.001	0.009
Cr	0.002 ± 0.001	0.5
Mo	0.001 ± 0.001	0.5
Ni	0.009 ± 0.001	0.4
Pb	0.001 ± 0.001	0.5
Se	0.002 ± 0.001	0.1
V	0.003 ± 0.001	1.3
Zn	0.012 ± 0.001	1.2
As	0.002 ± 0.001	0.5
Cu	0.009 ± 0.001	2
Hg	-	0.01
Sb	0.001 ± 0.001	0.06
Chloride	134 ± 3	800
Sulphates	86 ± 3	377

The leachate test shows that the concentration of the polluting elements set by the regulations is lower than the limits established by these Spanish-European regulations [32]. It should be noted that the chlorine and sulfur elements detected in the X-ray fluorescence and X-ray diffraction tests have produced a reduced leaching. Heavy metals are found in low concentration, mainly because these elements are difficult to find in the biomass used.

Once the chemical characterization of BBA was completed, physical tests were carried out. First, the grading curve of BBA was determined. This grading curve is shown in Figure 2.

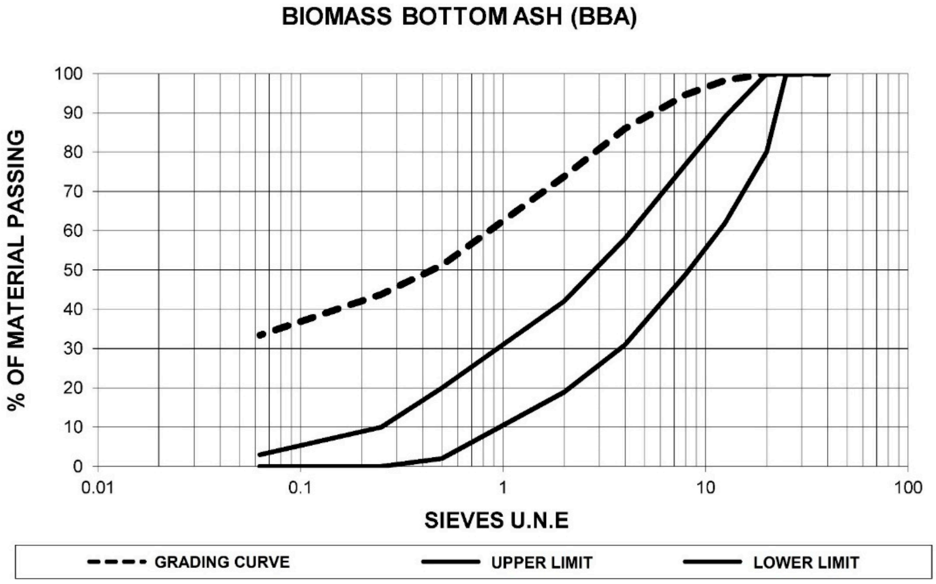

Figure 2. BBA grading curve.

The grading curve of BBA corresponds to a continuous grain size in which there is a high proportion of fine aggregate and filler. Therefore, BBAs are valid for correcting the grading curve of RAP, as the latter lacks the smaller particles.

On the other hand, it is essential to determine the physical properties of BBA. The particle density, bulk density in kerosene, and plasticity index tests are shown in Table 5.

Table 5. Density and plasticity tests for the fine portion of BBA.

Test	Standard	Value/Unit
Particle density	UNE-EN 1097-7	2.54 ± 0.07 t/m^3
Bulk density	UNE-EN 1097-3	0.45 ± 0.01 t/m^3
Plasticity index	UNE-EN ISO 17892-12	No plasticity

The particle density of biomass bottom ash is similar to that of a commercial filler, 2.65 t/m^3. Therefore, it is not necessary to correct the volumetric dosage of ash as a filler, and its incorporation is similar to that of other conventional materials. In turn, the bulk density in kerosene is slightly lower than that of a commercial filler, even though it is acceptable by the regulations. This lower bulk density reflects a higher specific surface area of BBA, making it possible to absorb a higher percentage of bitumen. This is not a problem, as a higher percentage of bitumen provides the bituminous mix with greater resistance to repeated tensile loads and fatigue, as long as there are no problems of bleeding. On the other hand, it is worth noting the null value of the plasticity index. This is to be expected if the chemical composition of BBA and its cementitious properties are taken into account. Consequently, the absence of clayey particles that could cause expansivity problems is assured.

On the other hand, RAP was analyzed to determine the feasibility of its use in cold in-place recycling with bitumen emulsion. The first of the tests carried out was the determination of the grading curve. The grading curve of RAP is shown in Figure 3.

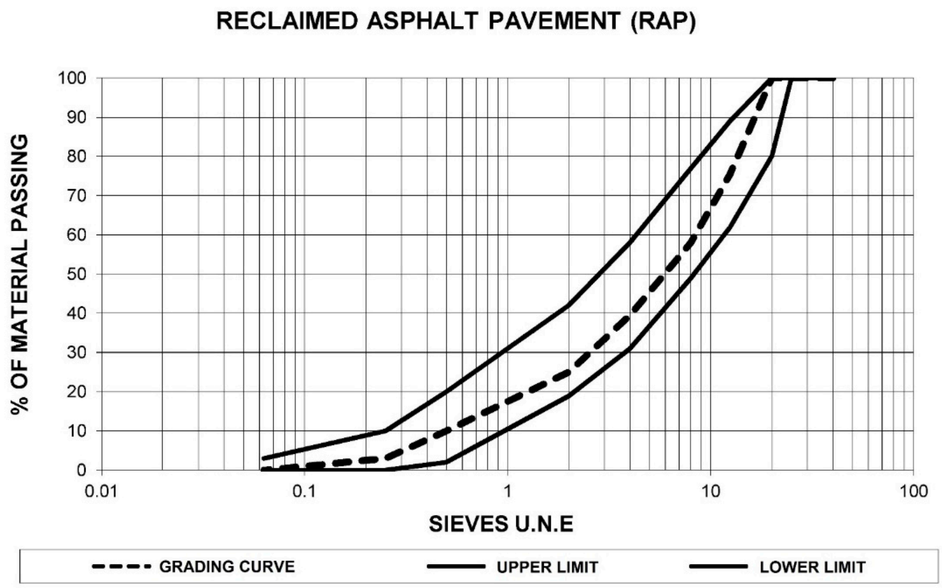

Figure 3. RAP grading curve.

The grading curve of RAP shows a particle size composed essentially of larger particles, i.e., mainly coarse aggregate. This grading curve will be corrected with the addition of BBA to comply with the envelope grading defined by Circular Order 8/2001 [31] and for the development in the bituminous mix of the interesting cementitious characteristics of ashes.

Subsequently, the binder and aggregate were separated according to the aforementioned standard UNE-EN 12697-1. In this way, the characteristics of the bitumen and the aggregate that made up the primitive bituminous mixture existing in the infrastructure could be analyzed.

The binder extracted from the RAP represented a percentage of 4.2% about the aggregate by mass. This bitumen was analyzed through penetration and softening point tests, with the values shown in Table 6.

Table 6. Tests of binder extracted from reclaimed asphalt pavement (RAP).

Test	Standard	Value/Unit
Penetration (25 °C; 100 g; 5 s)	UNE-EN 1426	8 ± 1 (1/10) mm
Softening point	UNE-EN 1427	91 ± 2 °C

The results of the penetration and softening point tests reflect the characteristics of an aged bitumen. The appearance of cracks along the infrastructure corroborates this fact, owing to the loss of the elastic elements of the bitumen because of its continuous exposure to weathering and repeated traffic loads. However, it should be noted that the percentage of bitumen is adequate for the bituminous mix made at the start, not causing plastic deformation problems that could render the RAP unusable for subsequent use in new bituminous mixes. The bitumen analyzed and aged seems to correspond at the beginning to a B40/50 bitumen, usual in the infrastructures developed in the region of Andalusia owing to the high temperatures reached during the summer months.

On the other hand, the coarse aggregate, fine aggregate, and filler were analyzed to determine the feasibility of using RAP. The results of the physical and mechanical tests of RAP are shown in Table 7.

The results of the physical and mechanical tests show that RAP has aggregates of acceptable quality for reuse in cold in-place recycling with bitumen emulsion. The strength of the aggregate used, as well as the shape of the particles, reflects the usefulness of the aggregate initially used for use in bituminous mixtures of medium traffic roads. In turn, it is the reduced value of the sand equivalent test, as well as the plasticity index, showing the quality of the aggregate to avoid subsequent expansivity problems.

Table 7. Tests of the coarse aggregate and fine aggregate of RAP.

Coarse Aggregate		
Test	**Standard**	**Value/Unit**
Determination of percentage of crushed and broken surfaces	UNE-EN 933-5	91 ± 2%
Flakiness index	UNE-EN 933-3	86 ± 2 °C
Los Angeles Test method	UNE-EN 1097-2	20 ± 1%
Fine Aggregate		
Test	**Standard**	**Value/Unit**
Plasticity index	UNE-EN ISO 17892-12	3.4 ± 0.1%
Sand equivalent	UNE-EN 933-8	81 ± 2%

Therefore, and based on the characterization of the chemical and mechanical physical properties of BBA and RAP, it can be stated that both materials are acceptable for use in different bituminous mixtures, specifically and according to this research, in cold in-place recycling with bitumen emulsion.

3.2. Bituminous Mixtures' Manufacturing and Testing

Once the constituent materials of the bituminous mix, RAP and BBA, were characterized, we proceeded to determine the percentage of combination of both materials to obtain, on the one hand, a grading curve within the envelope grading defined by the standards; and on the other hand, to incorporate a sufficient percentage of BBA to improve the mechanical characteristics of the bituminous mix conformed, thanks to the cementitious properties of the BBA corroborated by different authors. Based on the grading curves of the two materials, it was defined that the optimum percentage of combination corresponded to 90% RAP and 10% BBA. The composite grading curve for the combination of both products in the detailed proportion is shown in Figure 4.

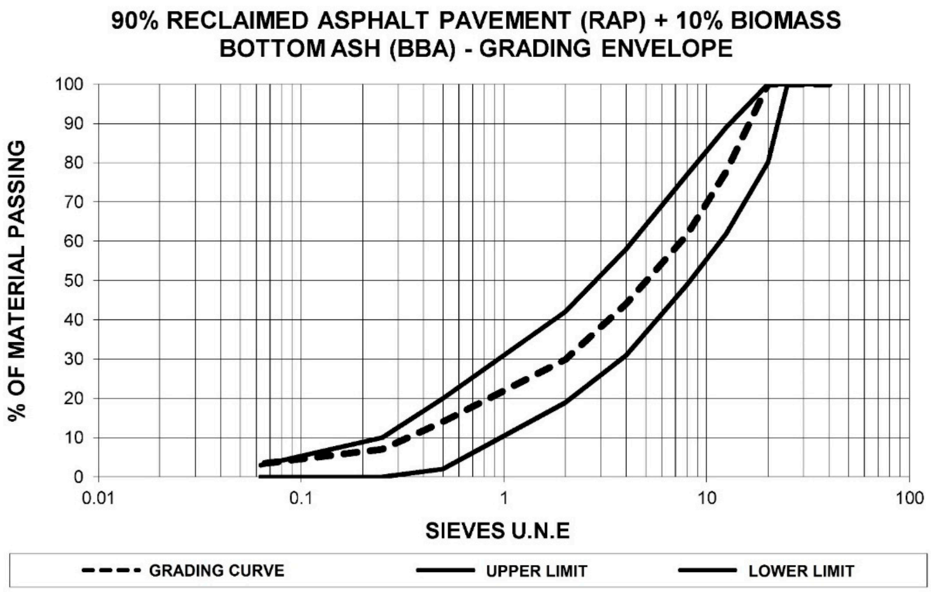

Figure 4. Graph of the grading curve for the combination of 90% RAP and 10% BBA, referenced to the grading envelope of Circular 8/2001 [31].

Once the grading curve composed of the combination of both materials in the detailed proportion was defined, the modified Proctor test was performed. This test, as mentioned above, defines the optimum percentage of water to be added to obtain the maximum density, because, usually, the highest density corresponds to the highest mechanical strength. The optimum humidity percentage that favors the highest density is called theoretical fluid content in this research. The results of the modified Proctor test for the different percentages of water are shown in Figure 5.

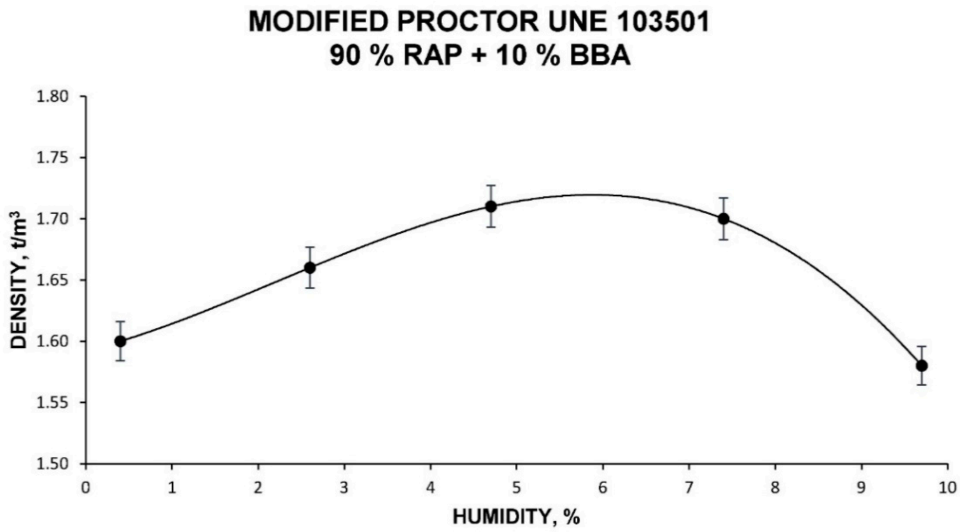

Figure 5. Graph of the modified Proctor compaction test UNE 103501 for the combination of 90% RAP and 10% BBA.

Based on the results of the modified Proctor test, it can be observed that a percentage of 6% humidity provides the highest density, being 1.72 t/m^3. This optimum humidity will be equal to the theoretical fluid content, corresponding to the percentage of emulsion plus the percentage of precoating water.

However, the bitumen emulsion must have adequate compatibility with the aggregate and provide superior resistance; therefore, to determine the optimum fluid content, the coating test is carried out. This test is performed with the particle size defined above, composed of the combination of RAP and BBA in the percentages detailed, and a fixed percentage of emulsion of 3%. The percentages of precoating water are variable between the theoretical fluid content and two percentage points below. Images of the coating tests are shown in Figure 6.

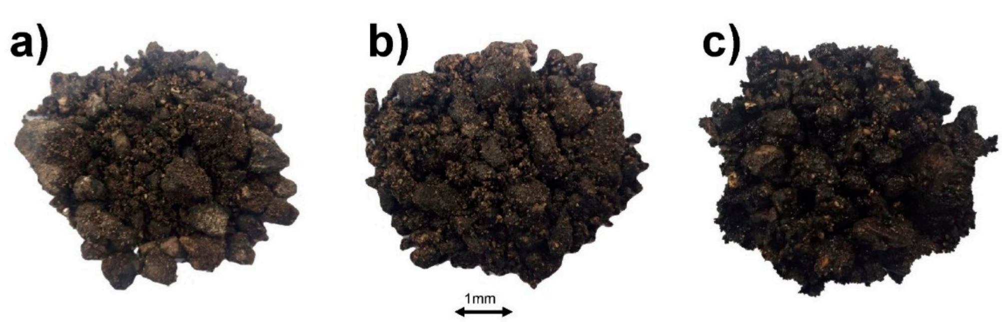

Figure 6. Coating test NLT-196/84 for RAP, BBA, and 3% emulsion with different percentages of precoating water. (**a**) 1% water-to-aggregate. (**b**) 2% water-to-aggregate. (**c**) 3% water-to-aggregate.

Figure 6 clearly shows how the best envelopment of the aggregate, RAP plus BBA, by the bitumen emulsion corresponds to the percentage of 3% emulsion over aggregate and 3% precoating water. Therefore, the optimum fluid content will be 6%.

According to the detailed regulations, the optimum fluid content is equal to the percentage of emulsion plus the percentage of water; in turn, the regulations specify that the percentage of emulsion must be between 2.5% and 4%. Therefore, different families of bituminous mixtures were manufactured with emulsion percentages between 2.5% and 4% with emulsion percentage increments of 0.25%. The precoating water for each of the families was equal to the difference between the optimum fluid content and the emulsion percentage. Table 8 shows the different families of mixtures conformed, as well as the percentages of emulsion and water added for their manufacture. It should be noted that these test samples were made with RAP and BBA (RAP + BBA), as well as with RAP and limestone aggregate (RAP + C). In this way, the benefits of the incorporation of BBA could be objectively evaluated in comparison with the commercial materials usually used for cold in-place recycling with bitumen emulsion.

Table 8. Families of test samples conformed with RAP and BBA or limestone aggregate.

	1	**2**	**3**	**4**	**5**	**6**	**7**
% emulsion	2.50	2.75	3.00	3.25	3.50	3.75	4.00
% water	3.50	3.25	3.00	2.75	2.50	2.25	2.00

Once the emulsion and water percentages were defined, as well as the combination of RAP and BBA or limestone aggregate, the different test samples were conformed according to the procedure detailed in the methodology. Once the different families of test samples had been made, the pertinent physical tests were carried out to determine the viability of the bituminous mixtures.

The first of the physical tests performed was the maximum density test. This test is essential to evaluate the physical properties of the bituminous mixtures. The results of this test for the bituminous mixtures with BBA and limestone aggregate are shown in Figure 7.

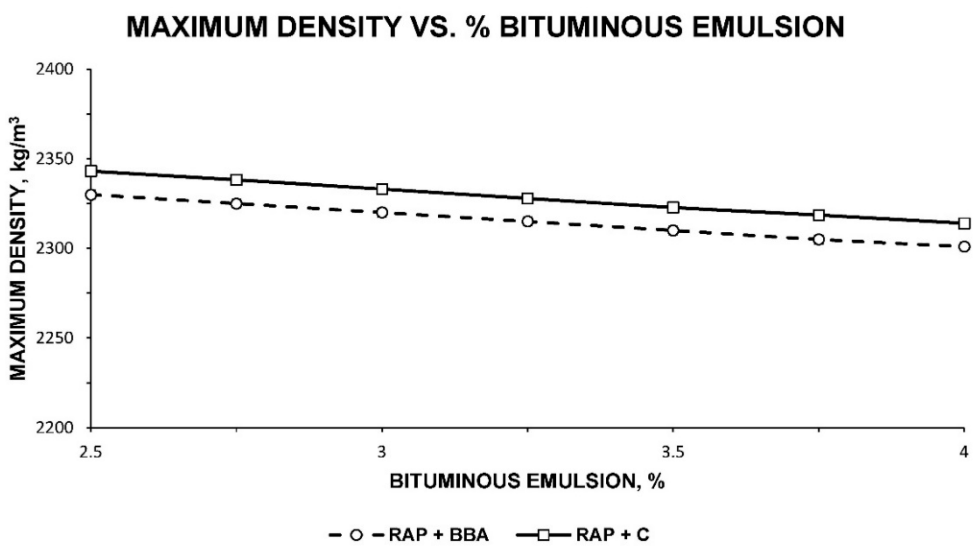

Figure 7. Graph of the results of the maximum density test, standard UNE-EN 12697-5, for bituminous mixes made with RAP and BBA (RAP + BBA), as well as for bituminous mixes with RAP and limestone aggregate (RAP + C).

As can be seen, the maximum density of bituminous mixtures made with limestone aggregate and RAP is higher than the maximum density of bituminous mixtures made with RAP + BBA. This fact is mainly due to the higher density of limestone aggregate with respect to BBA, which is not problematic in principle.

In turn, the bulk density of the bituminous mixtures, i.e., the density taking into account the voids in the mixture, is shown in Figure 8.

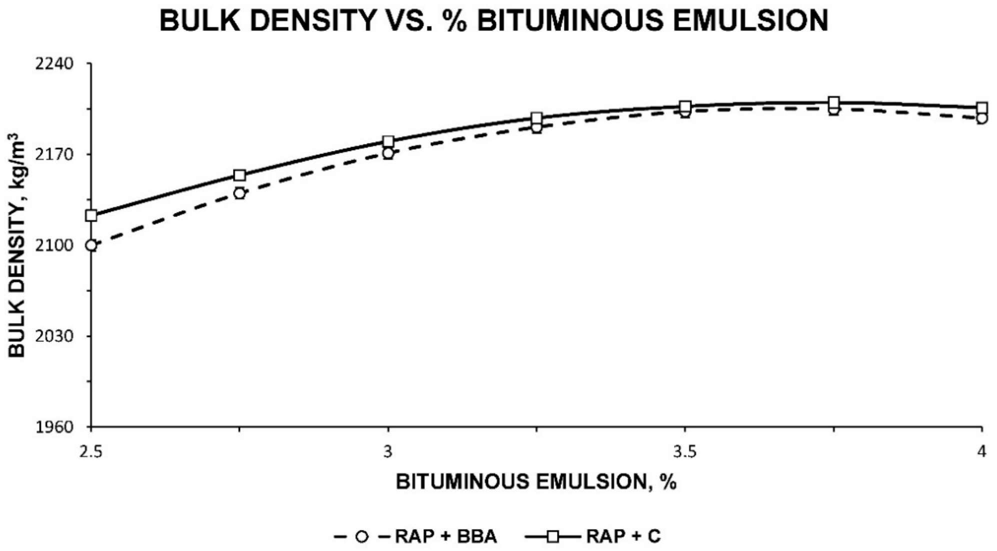

Figure 8. Graph of the results of the bulk density test, standard UNE-EN 12697-6, for bituminous mixtures made with RAP and BBA (RAP + BBA), as well as for bituminous mixtures with RAP and limestone aggregate (RAP + C).

In this case, the densities of the mixtures conformed with BBA and limestone aggregate are practically similar, as a higher percentage of emulsion for both materials leads to greater compaction of the mixture and, consequently, a higher bulk density.

Finally, one of the most interesting parameters in bituminous mixtures was calculated: the void content in the mixture. The results of this test are shown in Figure 9.

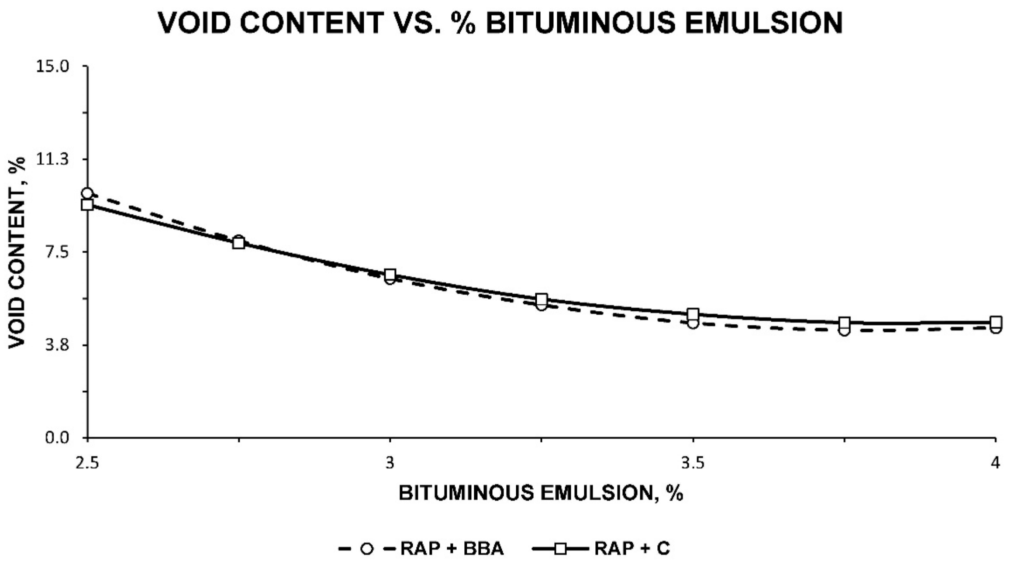

Figure 9. Graph of the results of the void content test, standard UNE-EN 12697-8, for bituminous mixtures made with RAP and BBA (RAP + BBA), as well as for bituminous mixtures with RAP and limestone aggregate (RAP + C).

Graph of the results of the voids content test, standard UNE-EN 12697-8, for bituminous mixtures made with RAP and BBA (RAP + BBA), as well as for bituminous mixtures with RAP and limestone aggregate (RAP + C).

The contents of voids in the mixture of bituminous mixtures made with BBA and limestone aggregate are similar in principle. Therefore, the incorporation of this residue, BBA, does not impair the physical properties of the final bituminous mix and obtains acceptable results similar to those obtained with conventional materials.

Finally, in order to evaluate the mechanical characteristics of the asphalt mixtures, a simple compression test was performed. This test was performed for all groups of samples, evaluating the effect of water on their cohesion. The results of this test are shown in Figure 10 for the bituminous mixtures formed with RAP and BBA or limestone aggregate, with and without water immersion.

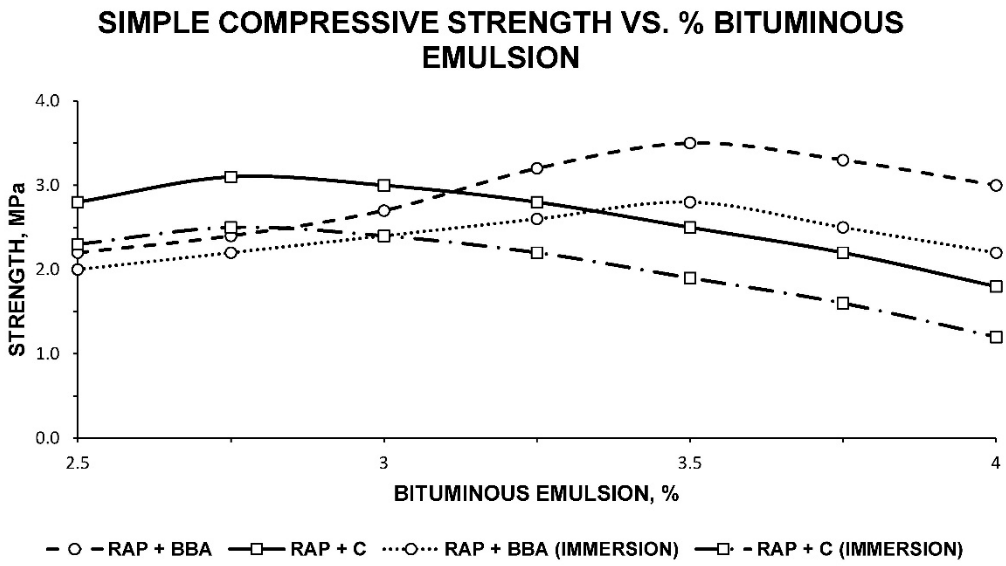

Figure 10. Graph of the results of the simple compressive strength test with and without immersion, standard NLT-162/00, for bituminous mixtures made with RAP and BBA (RAP + BBA), as well as for bituminous mixtures with RAP and limestone aggregate (RAP + C).

The simple compressive strength test with and without immersion of the detailed bituminous mixtures clearly shows a higher bitumen absorption in the bituminous mixtures made with RAP and BBA. This higher percentage of bitumen absorption is due, as detailed above, to the higher specific surface area of the BBA. Therefore, the bituminous mixture made with BBA and RAP is capable of developing a longer working life, as the bitumen is in charge of supporting the repeated traction loads that occur in the infrastructure due to the continuous passage of vehicles. In turn, it is worth noting the higher mechanical strength without immersion and with immersion of bituminous mixes made with BBA compared with bituminous mixes made with limestone aggregate, mainly due to the cementitious properties of the ashes. In short, bituminous mixes made with limestone aggregate have a lower percentage of bitumen absorption, as well as a lower compressive strength with and without immersion.

3.3. Determination of the Optimum Combination of Materials

Once the physical and mechanical properties of the bituminous mixtures made with RAP and BBA or limestone aggregate had been determined, the optimum combination of materials was determined. For this purpose, and based on the simple compression test without immersion, the optimum percentage of emulsion and the percentage of precoating water were obtained graphically, the latter corresponding to the difference between the optimum fluid content and the percentage of emulsion. The bituminous mixture made with RAP and BBA achieved optimum results of resistance to simple compressive strength without immersion with 3.5% emulsion. The bituminous mixture with RAP and limestone aggregate obtained the highest mechanical resistance to simple compressive strength without immersion with 2.75% emulsion. It should be noted that the simple compressive strength test was chosen as the conditioning test for obtaining the optimum combination of materials because cold in-place recycling with bitumen emulsion should above all have a higher strength. However, the physical properties of the bituminous mixtures formed with these optimum emulsion percentages must be acceptable according to the standards, as well as the simple compressive strength after immersion. In order to corroborate the properties of the bituminous mixtures with the optimum combination of materials, test samples of RAP and BBA, as well as RAP and limestone aggregate, were again carried out, giving the values shown in Table 9.

Table 9. Families of test samples formed with RAP and BBA or limestone aggregate.

Optimal Job Mix Formula			
Test	**Standard**	**RAP + BBA**	**RAP + C**
Precoating water, % of aggregate	-	2.5	3.25
Emulsion, % of aggregate	-	3.5	2.75
Maximum density, t/m^3	UNE-EN 12697-5	2.31 ± 0.06	2.34 ± 0.05
Bulk density, t/m^3	UNE-EN 12697-6	2.20 ± 0.06	2.15 ± 0.05
Void content, %	UNE-EN 12697-8	4.60 ± 0.14	7.90 ± 0.18
Dry compressive strength, MPa	NLT-162/00	3.52 ± 0.08	3.12 ± 0.07
Immersion compressive strength, MPa	NLT-162/00	3.01 ± 0.07	2.61 ± 0.07
Preserved resistance index, %	NLT-162/00	86 ± 2	84 ± 2

The aforementioned regulation establishes that the simple compressive strength without immersion must be greater than 3 MPa and the simple compressive strength with immersion greater than 2.5 MPa, maintaining a retained strength greater than 75%. These values are limiting for medium and high traffic roads. Therefore, both bituminous mixtures made with BBA and limestone aggregate obtain acceptable results.

In turn, it can be stated that the incorporation of BBA for the manufacture of cold in-place recycling with bitumen emulsion results, on the one hand, in a higher mechanical resistance to simple compressive strength and after immersion, even with a higher percentage of residual bitumen; in addition, a higher bitumen absorption that will condition a longer working life of the bituminous mix; and, finally, physical properties similar to those obtained with the use of commercial materials. The higher mechanical strength of BBA mixes seems to corroborate previous research defining BBA as a material with cementitious properties, thanks to its chemical composition.

4. Conclusions

The tests carried out in the methodology allow us to obtain a series of partial conclusions that are detailed below and allow us to corroborate the final conclusion of this research. These partial conclusions are as follows:

- BBAs are mainly inorganic materials. The main chemical elements that compose it are potassium, calcium, silicon, magnesium, and phosphorus, with chlorine and sulfur also present.
- The main chemical compounds of BBA are silicates, potassium carbonate, sylvite, and arcancite. These compounds are mainly responsible for the cementitious characteristics corroborated by different researchers.
- The leachates from BBA show concentrations of potentially contaminating elements below the limits set by Spanish-European regulations. Therefore, its use as a filler in bituminous mixtures is acceptable.
- The density of the BBA particles is similar to that of other commercial materials, presenting an acceptable bulk density in kerosene according to regulations and con-

ditioning a greater specific surface area susceptible to the absorption of a higher percentage of bitumen. It is worth mentioning the null plasticity index of the BBA, avoiding the non-existence of subsequent expansivity problems.

- The bituminous mixtures conformed with RAP and BBA had similar physical properties to the bituminous mixtures made with RAP and limestone aggregate.
- Cold in-place recycling with bitumen emulsion conformed with BBA had higher mechanical strength than the same type of bituminous mix made with limestone aggregate.
- The bituminous mixes evaluated show a higher bitumen absorption with the incorporation of BBA, thus conditioning a longer service life owing to the tensile strength of repeated traffic loads.

Based on the detailed partial conclusions, it can be stated that the use of BBA as a filler material for RAP and the manufacture of cold in-place recycling with bitumen emulsions is acceptable, providing superior mechanical characteristics to those achieved by this same type of mixture made with conventional materials and obtaining similar physical properties. It should be noted that the use of BBA has different advantages, not only at a technical level as demonstrated in this research, but also at an environmental level, as the use of this waste, currently unused, avoids its deposition in landfills, reduces the extraction of new raw materials, and creates sustainable materials framed within the new circular economy.

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