Effects of Using Mine Tailings from La Unión (Spain) in Hot Bituminous Mixes Design

Antonio José Tenza-Abril 1,*, José Miguel Saval 1, Victoria Eugenia García-Vera 2,*, Afonso Miguel Solak 1, Teresa Real Herráiz 1 and José Marcos Ortega 1

1 Department of Civil Engineering, University of Alicante, 03690 Alicante, Spain; jm.sav@ua.es (J.M.S.); afonsosolak@gmail.com (A.M.S.); teresa.real@ua.es (T.R.H.); jm.ortega@ua.es (J.M.O.)
2 Departamento de Arquitectura y Tecnología de la Edificación, Universidad Politécnica de Cartagena, 30203 Murcia, Spain; victoria.eugenia@upct.es
* Correspondence: ajt.abril@ua.es; Tel.: +34-96-5903-400 (ext. 2729)

Received: 18 December 2018; Accepted: 10 January 2019; Published: 14 January 2019

Featured Application: The results of the study show that wastes from the La Union mining district in Spain have adequate properties to serve as coarse aggregates for use in the fabrication of AC16S wearing courses and may be considered as an alternate source given the scarcity of high-quality aggregates in this region in Spain.

Abstract: Currently, political policies aimed at curbing the abuse of natural resources have given rise to a conscientiousness leading to the reevaluation of wastes. Wastes generated from previous mining operations greatly impact the environment, often leaving a legacy of elevated concentrations of heavy metals in the surrounding soil and water. In this study, two types of waste from the mining district of La Union (Spain) were used to study their use as a component of road wearing courses. The physical and mechanical characteristics were determined to identify the optimal content of bitumen, as well as the fatigue resistance using the four-point beam fatigue test, in all the mixtures manufactured. The mine tailings exhibited adequate physical and mechanical properties to be utilized as a coarse aggregate for a wearing course. The results indicate that one of the studied mine tailing forms could be used as a wearing course component, since it has properties similar to a control mix that is typically used in wearing course construction.

Keywords: mine tailings; waste; Marshall Stability and flow tests; hot mix asphalt; fatigue resistance; permanent deformation; moisture sensitivity; environment

1. Introduction

Currently, political policies aimed at curbing the abuse of natural resources, along with problems associated with increasing quantities of waste and their disposal, have given rise to a conscientiousness leading to the reevaluation of these wastes.

Wastes generated from abandoned mines greatly impact the environment [1]. One of the most important effects of mining is the vast quantities of waste that is generated during the process of extracting ore from the minerals [2]. These residues often have a significant environmental impact because of the elevated concentrations of heavy metals that they contain [1–3].

In the case of the mining district of La Union, situated in the region of Murcia (Spain), the mining developments are about 3000 years old, making this region one of the oldest mining regions in Spain. The exploited minerals were principally sulfurous ores rich in silver and lead. Mining activities in this area ended at the end of the 20th century due to social and environmental pressure [4]. Mining operations in this area have exacted a toll on the landscape, causing the collapse of mine workings...
through subsidence and these effects persist in the area. Herrera et al. [5] used the SAR interferometry technique for monitoring subsidence of the mining galleries and mapping ground movements in open pit mining in La Unión [6]. Additionally, high concentrations of Pb, Zn, Cu, and As [7,8] have contaminated the soil and the aquifers [9,10]. Currently, there is interest in developing the site into a tourist attraction, but this activity is on hold until the environmental damage due to mining activities is ameliorated.

Increasing demand and cost, as well as the lack of good-quality aggregates for use on wearing courses, are factors to take into account in promoting the re-use of wastes. As a consequence of the success of some studies in incorporating waste products in construction materials in order to reduce the demand on natural resources [11], many studies have aimed at the incorporation of wastes in bituminous mixes [12]. Some successful examples of using wastes in the manufacture of bituminous mixes are the use of bituminous slurry surfacing with crumb rubber for reducing the noise of the wearing course [13]; using waste materials for low temperature bituminous mixes production [14–16]; and using alternative fillers to improve the mechanical properties [17], such as sewage sludge ash [18].

There are a large number of existing studies that have examined the total or partial substitution of natural aggregates with waste products [19]. The use of slag [20–22], municipal solid waste ash left after incineration [23], left-over waste from marble production [24,25], plastics [26,27], glass [28], and demolition rubble [29,30] are some examples of wastes used in the fabrication of bituminous mixes.

Taking into account the trends in the industrial sector and the fact that the mining district in La Unión has a large volume of waste material for use, in this study, we investigate the use of mine tailings as an aggregate for making hot bituminous AC16S-type mixes for use in wearing courses.

Since the mine tailings have a suitable Polished Stone Value (PSV) for using as a coarse aggregate in wearing courses, the aim of the present work was to investigate the feasibility to design AC16S-type mixes with two different wastes from La Unión mine district (Spain)—using Spanish guidelines. In particular, the fatigue resistance measured using the four point beam fatigue test on prism-shaped specimens is examined in all the mixtures manufactured. The use of these wastes could minimize the extraction of raw materials and they could serve as an alternative for the large volume of mine tailings accumulated. This opens up a possible means of environmental restoration in the La Unión mining district.

2. Materials and Methods

2.1. Materials

Mine tailings (MT) and well cuttings (WC) from the mining district of La Unión (Spain) were used in this study (Figure 1) as a coarse aggregate. A porphyry aggregate (PA) was used as a benchmark for coarse aggregates of up to a 4 mm size.

WC are produced during mine access shaft excavations with a generated volume in the order of 0.51 mm³. As may be seen in Figure 1, individual fragments are flaky and show a homogeneous distribution of aggregate of between 50 and 150 mm.

MT of the Cabezo Rajao mine, made up of waste rock left after mineral extraction, is currently about 3.01 mm³ [10] in volume. These tailings are of heterogeneous morphology (Figure 1), ranging from sand grains to 300 mm blocks. The image of Figure 1, taken with a scanning electron microscope, shows an elevated porosity that may be of importance in the fabrication of bituminous mixes. The samples were taken at various points and altitudes in the waste dump. In order to reutilize these tailings, it was necessary to grind them with a laboratory crusher to reduce their size.
Figure 1. Wellbore cuttings (WC) in the upper photos and mine tailings (MT) in the lower ones. Included are scanning electron microscope images. (a) WC deposits in the mine district of La Unión; (b) scanning electron microscopy (SEM) micrograph of WC sample; (c) MT disposal; (d) SEM micrograph of MT sample.

Table 1 shows the oxides that are encountered in quantities of larger than 0.02%, according to chemical analysis.

Table 1. Chemical composition of well cuttings (WC) and mine tailings (MT).

| Component | WC  | MT    |
|-----------|-----|-------|
| Na₂O      | 0.89| -     |
| MgO       | 1.18| 1.18  |
| Al₂O₃     | 18.67| 1.71 |
| SiO₂      | 66.45| 9.72 |
| P₂O₅      | 0.16| 0.44  |
| SO₃       | 0.16| 23.51 |
| K₂O       | 2.44| 0.04  |
| CaO       | 0.04| 1.36  |
| TiO₂      | 0.62| 0.11  |
| MnO       | 0.09| 3.73  |
| Fe₂O₃     | 9.14| 36.02 |
| CuO       | -   | 0.05  |
| ZnO       | 0.03| 15.22 |
| Nb₂O₅     | -   | 0.36  |
| PbO       | 0.05| 1.12  |

Coarse and fine aggregates were classified as materials retained on and passing through the 4 mm sieve, respectively. The coarse porphyry aggregate (PA) was used in fractions of 6/12 mm and 12/18 mm. The aggregate is typically used in this region in the fabrication of wearing courses.

In all the mixtures studied, a fine aggregate limestone sand was used in a 0/4 mm fraction, along with a limestone mineral filler, produced by grinding the natural aggregate. Bitumen of 35/50-penetration grade was used for the mixtures, which is typically used in the region. Its properties are given in Table 2.
Table 2. Properties of the 35/50 bitumen.

| Characteristics            | Units | 35/50 |
|----------------------------|-------|-------|
| Penetration (25 °C)        | mm/10 | 40.0  |
| Softening point            | °C    | 53.8  |
| Penetration index          | -     | -0.80 |
| Specific weight            | kg/m³ | 1030  |

High-quality aggregates are required to make the wearing course. The level of quality is measured through parameters such as the Los Angeles abrasion loss (%), the flakiness index (%), and the polished stone value. Table 3 lists the principle physical and mechanical properties of the aggregates and the values of the limits established by the Spanish norm, PG-3 [31], for each of the aggregates used to make wearing courses.

Table 3. Test results for the aggregate types used in the mixes.

| Aggregate Properties                  | Standard Test Method | Limit | Coarse Aggregate | Fine Aggregate | Filler |
|---------------------------------------|----------------------|-------|------------------|----------------|--------|
| Apparent particle density (kg/m³)     | UNE EN 1097-6        | -     | 2937             | 2750           | 2837   | 2719   | -      |
| Dry particle density (kg/m³)          | UNE EN 1097-6        | -     | 2869             | 2641           | 2617   | 2641   | -      |
| Saturated surface dry density (kg/m³) | UNE EN 1097-6        | -     | 2892             | 2681           | 2695   | 2669   | -      |
| Water absorption after 24 h (%)       | UNE EN 1097-6        | -     | 0.8              | 1.5            | 2.96   | 1.1    | -      |
| Flakiness index (%)                   | UNE EN 933-3         | ≤20–30| 13.5             | 28.5           | 15.5   | -      | -      |
| Los Angeles Abrasion loss (%)         | UNE EN 1097-2        | ≤20–25| 10               | 19             | 21     | -      | -      |
| Polished Stone value                  | UNE EN 1097-8        | ≥56–44| 54               | 67.3           | 81.5   | -      | -      |
| Bulk density (kg/m³)                  | UNE EN 1097-3        | 500–800|                |                |        | 620    |        |

The flakiness index for WC limits its utilization to low-intensity road applications and weight categories of T32 or less according to Spanish norms (Traffic category T32 refers to the following interval of Annual Average Daily Heavy Traffic: 50 ≤ AADTH < 99). MT has a mean Los Angeles abrasion loss coefficient that is greater than that of WC and PA, making its use limited to the T3 traffic level (50 ≤ AADTH < 200). Both mining wastes (WC and MT) exhibit an accelerated polishing value that is adequate for wearing course use, being much higher than that of PA.

As may be observed in Table 3, the properties of the MT and WC mine wastes comply with the limits required for aggregates in PG-3, the Spanish norm. There is no limitation on the density of the aggregates utilized in hot bituminous mixes. MT and WC aggregates had lower densities and higher absorption rates when compared with PA. These factors have a significant influence on the demand for bitumen in the fabrication of bituminous mixes. The flakiness index of MT and WC wastes is higher than the reference aggregate (PA). This could be due to the rock crushing method, since jaw crushers, used to reduce the size of mining wastes WC and MT, tend to make longer particles than other types of crushers [32,33].

2.2. Mix Design

In order to perform the study, AC 156 Surf 35/50 S (AC16S) bituminous mixes were fabricated according to Spanish norms. Table 4 shows the aggregate gradation of the mixes fabricated with the control aggregate (AC-PA), with well cuttings (AC-WC), and with mine tailings (AC-MT), along with the aggregate grading curve established for bituminous mixes according to Spanish specifications.

Cylindrical samples, plates, and slabs with different bitumen contents were prepared for this study. The bitumen content for the AC-PA and AC-WC was set at 3% in the samples with the lowest content and was incremented by 0.5% to a maximum of 5.5% in the samples with the highest bitumen content. The bitumen content for AC-MT samples ranged from 3.5% to 6% in 0.5% increments, except for the samples used for Marshall tests, which ranged from 3% to 6.5%.
Table 4. Aggregate grading curve and limit values for AC16S mixes.

| Sieve Size (mm) | Limit Values (%) | AC-PA | AC-WC | AC-MT |
|-----------------|------------------|-------|-------|-------|
| 22              | 100              | 100   | 100   | 100   |
| 16              | 100–90           | 97.3  | 97.5  | 95    |
| 8               | 75–60            | 63.3  | 61.5  | 71    |
| 4               | 50–35            | 45.3  | 44.5  | 46    |
| 2               | 38–24            | 36.5  | 36.3  | 37.4  |
| 0.5             | 21–11            | 16.5  | 16.3  | 16.4  |
| 0.250           | 15–7             | 10.3  | 10.1  | 9.9   |
| 0.063           | 7–3              | 6.0   | 6.0   | 5.7   |

2.3. Experimental Methods

2.3.1. Marshall Tests

For these tests, three samples for each bitumen concentration were prepared. The mixes were compacted using an automatic Marshall compactor applying 75 blows per side, according to the UNE EN 12697-30 norm. The apparent density (UNE EN 12697-6), the percentage of air voids in the mix, and the percentage of voids in the mineral aggregate (UNE EN 12697-8) were computed. After the test, the stability and Marshall flow were determined according to the UNE EN 12697-34 norm. The Marshall quotient, which is the ratio of stability to flow, was also obtained because it may be used to give an indication of mixture stiffness.

2.3.2. Water Sensitivity

The experimental procedure was conducted according to the UNE EN 12607-12 standard. This test is performed for determining the effect of the water in the bituminous mixes since water causes a loss of adhesion between the bitumen and the surface of the aggregate. The test involves manufacturing six cylindrical specimens compacted with an impact compactor by applying 50 blows on each side for each level of bitumen content. The specimens were divided into two different sets—a dry set and a wet set. The dry set was stored at 15°C. The wet set samples were saturated in water and then vacuum sealed for 30 ± 5 min. Then, the wet specimens were immersed in a water bath at 40°C for 72 h. Afterwards, the indirect tensile strength (ITS) of each specimen ($IT_{SW}$ for the wet samples and $IT_{SD}$ for the dry samples) was performed at 15°C. The indirect tensile strength ratio ($ITSR$) was calculated according to Equation (1). The minimum $ITSR$ value recommended by Spanish technical specifications is 85%.

$$ITSR = 100 \frac{IT_{SW}}{IT_{SD}}$$  (1)

2.3.3. Permanent Deformation

The permanent deformation was performed by applying a cyclic load through a wheel loaded on a rectangular specimen (300 × 400 × 60 mm), according to the UNE EN 12697-22 standard. The parameter obtained was the slope of the rutting curve ($WTS_{air}$ in mm/10^3 cycles) produced after 5000 and 10,000 cycles ($d_{5000}$ and $d_{10000}$ respectively) and determined according to Equation (2).

$$WTS_{air} = \frac{d_{10,000} - d_{5000}}{5}$$  (2)

PG-3 recommends $WTS_{air}$ values lower than 0.07 mm or 0.1 mm each 10^3 cycles for heavy and light traffic, respectively.
2.3.4. Fatigue Resistance

Fatigue resistance of AC 16 S mixes was measured using the four point beam fatigue test on prism-shaped specimens in accordance with annex D of the UNE EN 12697-24 norm. The tests were carried out in a climate-controlled room at a constant 20 °C temperature. The specimens were subjected to periodic loads, as required by the four-point beam fatigue test, with free rotation and horizontal translation at all load and reaction points. The load frequency used in testing was 30 Hz, with a deformation amplitude of 150 µm/m. The criterion of failure by fatigue was defined as the number of cycles (Nf) necessary for the complex modulus to be reduced by 50%.

3. Results and Discussion

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results and their interpretation as well as the experimental conclusions that can be drawn.

3.1. Marshall Parameters

Figures 2 and 3 give the results of apparent density, air voids (Vh), and voids in the mineral aggregate (VMA) obtained according to the norms noted in Section 2.3.1, which in turn may be used to determine the optimal percentage of the bituminous binder. The figures give the mean values of each parameter corresponding to each studied percentage of bitumen, along with error bars that represent the standard deviation. Additionally, the equation of the best second-order polynomial fit and the associated value of R² have also been included.

Figure 2. Apparent density as a function of bitumen content for the AC-PA, AC-WC, and AC-MT mixes. The error bars represent ±1 standard deviation. The best second-order polynomial fit and the square of the multiple correlation coefficient, R², are also shown.

In accordance with the results and in order to comply with the PG-3 Spanish norm for bituminous AC16S mixes made for wearing courses, the air void content in the mix, (Vh), should be between 4–6% and the voids in the mineral aggregate, (VMA), should be greater than 15%. Furthermore, Table 5 includes the percentage of binder necessary to obtain the 4% and the 6% Vh obtained through the polynomial fit and the percentage of bitumen to obtain the minimum VMA, attained by setting the derivative of the VMA polynomial to zero to find the appropriate local minimum for each aggregate.
As may be observed in Figure 2, the apparent density of the AC-WC and AC-MT mixes is less than that of the control AC-PA aggregate. This is principally due to the lower density of the mine wastes, as indicated by Table 3.

Figure 3 gives the mean Vh and VMA as a function of bitumen content for each of the aggregate mixes. As may be observed (Figure 3a), the data and fitting polynomials for Vh decrease with increasing bitumen in the mix. This tendency is consistent with the idea that increasing the amount of bitumen in the mix allows a greater filling of the pore volume. The AC-PA and AC-WC aggregates show similar behavior; that is, the same quantity of bitumen gave similar values to the air voids, Vh. However, the AC-MT mixes needed a greater amount of bitumen to obtain the same air void content. This is due to the higher absorption of the MT aggregate that produces a drop in the effective bitumen volume, so that a greater quantity of bitumen was necessary to cover the aggregate and to reduce the air void content to the necessary value, as shown in Table 3. The percentage of bitumen necessary for the AC-PA and AC-WC to comply with Spanish technical specifications was similar in these two mixes, as shown in Table 5 and in Figure 3.

Figure 3b also shows the mean values of the VMA quantity as a function of bitumen content for each aggregate mix. The best second-order polynomial fit in this case has a convex form and the recommended bitumen dosage corresponds to the descending part of the curve, as the mix is more compactable in that region. If a bitumen dose is chosen that corresponds to the rising part of the curve, the bitumen displaces the aggregates, which could result in plastic flow within the mix. In Figure 3, it is apparent that all of the mixes have a VMA value larger than 15% over the entire range of bitumen contents studied. The AC-PA mix achieves a minimum VMA with a low bitumen content.

Table 5. Percentage of bitumen necessary to obtain 4–6% air void content in AC-PA, AC-WC, and AC-MT mixes. Included are the percentages of bitumen binder corresponding to the minimum percentage of void content in mineral aggregate (VMA), and the minimum VMA is given in parenthesis.

| AC 16 Surf 35/50 S | Percentage of Bitumen Necessary |
|--------------------|---------------------------------|
|                    | AC-PA  | AC-WC  | AC-MT  |
| 4% Vh              | 4.54   | 4.72   | 5.89   |
| 6% Vh              | 3.68   | 4.11   | 5.11   |
| Minimum VMA        | 3.91 (15.05%) | 5.02 (15.00%) | 5.53 (17.58%) |

Figure 3. (a) Air void content (Vh) and (b) voids in the mineral aggregate (VMA) of the AC-PA, AC-WC, and AC-MT mixes. The error bars represent ±1 standard deviation. Included are the equations of the best fit second-order polynomials and their R² value.
contents studied. The AC-PA mix achieves a minimum VMA with a low bitumen content (Table 5), which indicates that it may suffer from plastic deformation at bitumen dosages larger than 3.91%. In any case, the AC-WC and AC-MT mixes achieve a minimum VMA at a larger bitumen dose.

Figure 4 gives the values for the Marshall Stability and the Marshall flow as a function of bitumen content for each of the studied mixes. Once again, the data represents the mean bitumen content and standard deviation computed from measurements made on three specimens. Additionally, the graph shows the best fit second-order polynomial along with its $R^2$ value that verifies a good fit. As Figure 4 shows, the AC-PA mix shows a drop in stability with increasing bitumen content. However, the AC-WC and AC-MT mixes show an increase in stability with increasing bitumen content up to a point where both reach a maximum value of about 4.7%, after which both slowly decrease for a higher bitumen content. The results show that the mixes made with mine wastes are less sensitive to binder content.

As may be seen in Figure 4, the deformations that were produced in the AC-WC and AC-MT mixes were less than that of the control mix (AC-PA). The AC-MT mixes showed the least deformation, probably because the effective bitumen content of these mixes was less than those of the other analyzed mixes.

Figure 5 shows the Marshall quotient and its best second-order polynomial fit as a function of bitumen content for the studied mixes. The AC-PA mix had a higher Marshall quotient with a low bitumen content than the AC-WC and AC-MT mixes, indicating that these mixes are more rigid and more resistant than the mixes made with mine wastes.
3.2. Water Sensitivity

Figure 6 shows the mean measured dry ($\text{ITS}_d$) and wet ($\text{ITS}_w$) Indirect Tensile strength, as well as the Indirect Tensile Strength Ratio ($\text{ITSR}$, on the right axis) for the specimens as a function of bitumen content for each of the studied mixes. The error bars represent $\pm 1$ standard deviation in each of the measurements. The dotted line on the graph gives the minimum value of $\text{ITSR}$, which corresponds to the Spanish norm [31].

As may be seen from Figure 6, the wet tested specimens experienced a loss of indirect tensile strength when compared to their dry counterparts, due to a loss in adhesion and cohesion in the mastic bitumen. The AC-WC mixes had higher indirect tensile strength than the other mixes.
The \( \text{ITSR} \) value of all of the mixes increased with increasing bitumen content, principally due to the fact that the thickness of the mastic layer is greater in mixes with a higher bitumen content [37]. As may be observed in the figure, the values of \( \text{ITSR} \) for the AC-PA control mixes exhibited \( \text{ITSR} \) values in excess of 85% in specimens with a bitumen content higher than 3.5%. The AC-WC mixes exhibit maximal \( \text{ITSR} \) values in specimens with a bitumen content higher than 4.5%. The AC-MT mixes did not comply with the minimum 85% requirement for any of the bitumen contents studied, which is an indication of low adhesivity between the binder and the aggregate. The low \( \text{ITSR} \) of the AC-MT mixes is also due to that fact that a significant part of the bitumen is absorbed by the aggregate, which lowers the effective bitumen in the mix, and consequently, the thickness of the binder film that covers the aggregate, which, in turn, promotes the disassociation of the aggregate under exposure to water.

### 3.3. Permanent Deformation

In Figure 7, the mean Wheel tracking slopes (\( WTS_{\text{air}} \)) as a function of bitumen content for the various mixes are shown. The data was obtained from the tests described in Section 2.3.3. The horizontal lines in the graph represent the maximum permitted value (according to Spanish norms) of the \( WTS_{\text{air}} \) parameter for both high-volume and low-volume heavy vehicle traffic.

![Figure 7](image_url)

**Figure 7.** Wheel tracking slope of the AC-PA, AC-WC, and AC-MT mixes. The horizontal lines represent the Spanish norms for high and low volumes of heavy vehicle traffic.

As may be observed, the AC-PA mixes, made with the control aggregate, exhibited a low Wheel tracking slope for bitumen contents of less than 4.5%, in compliance with the norms; however, with bitumen content increasing to 5–5.5%, the Wheel tracking slope increased significantly. This likely occurs because, for a bitumen content greater than 4%, the mix is in the ascending part of the VMA curve, which corresponds to a region associated with excessive flow and deformation, since the bitumen occupies spaces where the mineral framework separates.

The AC-WC and AC-MT mixes were in compliance with Spanish norms (less than 0.07–0.1 mm/\( 10^3 \) load cycles) at all levels of bitumen content studied. This indicates good resistance to permanent deformation. These results coincide with the Marshall deformation results given in Figure 4, in which the mixes with mine wastes exhibited less deformation than the control mix.

### 3.4. Optimum Bitumen Content

As established by the PG-3 norm, the AC16S mixes, used in wearing courses, should have a minimum bitumen content of 4.5%. This value may be adjusted if the aggregate density is a value other than 2650 kg/m\(^3\), according to Equation (3).
\[ \alpha = \frac{2650}{\rho_d} \]  

where \( \alpha \) is the correction factor, and \( \rho_d \) is the density of the particle aggregate in kg/m\(^3\).

Table 6 gives the minimum bitumen content and range required for aggregate density compliance with Spanish norms for each studied AC16S mix according to the PG-3 norm [31]. As shown in the Table 6, the AC-WC mix performs similarly to the control AC-PA mix. Technically speaking, the AC-MT mixes were not viable because they were not in compliance with the ITS\(R\) required, having insufficient water resistance.

Table 6. Particle density of the aggregates and correction coefficient for obtaining the minimum binder content. The percentage of bitumen required for Spanish norm compliance for air void content, retained strength index, and the Wheel tracking slope for each mix are shown, as well as the bitumen content interval where the mix is in compliance.

| Mixture Properties | AC-PA | AC-WC | AC-MT |
|--------------------|-------|-------|-------|
| \( \rho_d \) (kg/m\(^3\)) | 2897  | 2745  | 2774  |
| Correction factor \( \alpha \) (%) | 0.915 | 0.965 | 0.955 |
| Minimum bitumen content (%) | 4.12  | 4.34  | 4.30  |
| \( V_h \) (4–6%) | 4.54–3.68% | 4.72–4.11% | 5.89–5.11% |
| ITS\(R\) (\( \geq \)85\%)) | \( \geq \)3.5\% | \( \geq \)4.5\% | No |
| WTS\(_{air}\) (\( \leq \)0.07 mm) | \( \leq \)4.5\% | \( \leq \)5.5\% | \( \leq \)6\% |
| Optimum bitumen content (%) | 4.12–4.5\% | 4.5–4.94\% | No |

3.5. Fatigue Resistance

Gardete et al. [38] indicated that traditional design methods, such as the Marshall method, can provide mixtures with an acceptable performance. However, the lack of flexibility in the design values can lead to ill-adapted mixtures. Taking into account in-service conditions (as fatigue performance) leads to an improvement of the overall performance of the pavement. Traffic loads are cyclical and the repeated passage of these loads induces a fatigue process [39]. Fatigue is of importance for concrete structures subjected to repetitive loading, such as bridges [40] or railway slab tracks under traffic loads [41]. However, there is still a lack of common criteria about the necessary number of tests or sample size. For high-strength concrete, the studies are still limited [42,43]. However, in bituminous mixes, there are several standardized methods for determining the fatigue characteristics of asphalt concrete mixtures—uniaxial tension/compression; 2, 3, and 4 point bending; and indirect-tension tests [44].

In this research, the fatigue resistance was obtained through a four point besting test carried out on strain control and with a repetitive sinusoidal loading configuration, as can be seen in Figure 8a. Figure 8b illustrates an example of the fatigue results on AC-PA, AC-WC, and AC-MT samples. Since the load and displacement were continuously measured during the test, parameters like dynamic modulus, phase angle, and dissipated energy could easily be calculated and plotted, as can be seen in the example of Figure 8b. Shown are the dynamic modulus, phase angle, and dissipated energy as a function of number of test cycles for typical tests. It is apparent that the dynamic modulus decreases with the number of cycles. The phase angle increases with the number of cycles, demonstrating the degradation of the mix, as well as its loss of rigidity. Over the length of the test, which simulates the useful life of the road service, the energy dissipated per cycle is reduced as the sample suffers from fatigue effects.
Table 7 summarizes the mean fatigue testing results for the dynamic modulus; phase angle; and the initial, final, and accumulated dissipated energies of each of the mixes as a function of bitumen content. Additionally, the number of cycles necessary for a 50% reduction in the initial value of the dynamic modulus is presented [45]. As may be observed from the results at a low bitumen content, the phase angles are low, indicating the fragility of these mixes. At a low bitumen content, the mineral skeleton of the mix is unable to support deflections greater than 150 μm/m, which causes failure at a lower number of cycles. However, with an increase in the amount of bitumen content, the mix becomes more flexible, increasing the viscous component, as may be seen in the increasing values of the phase angle. This improvement increases the number of cycles necessary to induce fatigue in the mix.

In the AC-WC mix, the mix with a 3% bitumen content broke during the pre-testing phase. With a higher bitumen content, the dynamic modulus was approximately constant, with values similar to those of the AC-PA mix. The AC-MT mix had slightly lower dynamic modulus values than the control. The AC-WC and AC-MT mixes took a greater number cycles to fatigue, around 20–25% higher, with a bitumen content greater than 5% and 5.5%, respectively.

Figure 8. (a) Four-point bending beam fatigue testing equipment used for testing the samples. (b) Some examples of the typical test results for fatigue testing of the studied mixes.
Table 7. Results for the Fatigue resistance test. Included are the value of the dynamic modulus; the phase angle; and the initial, final, and accumulated dissipated energies of each of the mixes as a function of bitumen content. Also included is the number of cycles necessary for a 50% reduction of the original value of the dynamic modulus.

| Mix   | Bitumen Content (%) | Dynamic Modulus (Mpa) | Phase Angle (degrees) | Initial Dissipated Energy (kJ/m³) | Final Dissipated Energy (kJ/m³) | Cumulative Dissipated Energy (mJ/m³) | Number of Cycle for Failure |
|-------|---------------------|-----------------------|-----------------------|-----------------------------------|---------------------------------|---------------------------------------|-----------------------------|
| AC-PA |                     |                       |                       |                                   |                                 |                                       |                              |
| 3.0   | 8716                | 19.29                 | 0.122                 | 0.117                             | 0.741                           |                                       | 5218                         |
| 3.5   | 18,144              | 16.41                 | 0.04                  | 0.22                              | 0.313                           |                                       | 2171                         |
| 4.0   | 12,981              | 19.81                 | 0.3005                | 0.2325                            | 55.552                          |                                       | 205,311                      |
| 4.5   | 11,812              | 19.05                 | 0.238                 | 0.174                             | 94.067                          |                                       | 622,503                      |
| 5.0   | 11,724              | 22.46                 | 0.2985                | 0.192                             | 167.831                         |                                       | 690,228                      |
| 5.5   | 11,860              | 24.62                 | 0.315                 | 0.212                             | 193.143                         |                                       | 745,548                      |
| AC-WC |                     |                       |                       |                                   |                                 |                                       |                              |
| 3.0   | 12,138              | 17.42                 | 0.229                 | 0.1695                            | 2.46                            |                                       | 12,517                       |
| 3.5   | 13,263              | 17.61                 | 0.2675                | 0.1715                            | 7.3965                          |                                       | 35,367                       |
| 4.0   | 11,058              | 19.16                 | 0.2575                | 0.18                              | 109.025                         |                                       | 492,152                      |
| 4.5   | 12,759              | 19.04                 | 0.218                 | 0.1605                            | 172.113                         |                                       | 906,580                      |
| 5.0   | 11,323              | 19.42                 | 0.24                  | 0.183                             | 186.352                         |                                       | 889,465                      |
| 5.5   | 9685                | 18.19                 | 0.225                 | 0.1555                            | 171.435                         |                                       | 900,233                      |
| 6.0   | 9593                | 20.06                 | 0.2335                | 0.153                             | 149.8205                        |                                       | 801,971                      |

4. Conclusions

In this study, the properties of well cuttings and mine tailings were compared with a porphyry aggregate, typically used in constructing wearing courses. Standard tests were conducted to determine the usefulness of these mine waste products in the fabrication of road surfaces. We next fabricated AC 16 Surf 35/50 S bituminous mixes with the mine wastes and the control aggregate and carried out a number of standard tests on samples of these mixes. The principle conclusions were:

(a) Both of the studied wastes have physical and mechanical properties that permit their utilization in the fabrication of wearing courses.

(b) The behavior of the AC-WC mix is similar to that of the control. The test results for this aggregate were slightly better than those of the porphyry control mix at similar bitumen contents in terms of compliance with the Spanish PG-3 norms.

(c) The AC-MT mix required an elevated level of bitumen binder to comply with the requirement for the void percentage in the mix and, furthermore, exhibited poor resistance to water damage. It was out of compliance with the minimum requirements for wearing courses.

(d) The AC-WC and AC-MT mixes were more resistant to fatigue than the AC-PA control mix for bitumen contents of 5–5.5%, respectively.

The results of the study show that, of the two wastes studied, wellbore cuttings from the La Union mining district in Spain have adequate properties to serve as coarse aggregates for use in the fabrication of AC16S wearing courses and may be considered as an alternate source given the scarcity of high-quality aggregates in this region in Spain. Additionally, the use of these aggregates would contribute to the environmental restoration of this area.
Author Contributions: Some of the results included in this paper were obtained in the PhD thesis carried out by A.J.T.-A. at the University of Alicante (Spain), under the supervision of J.M.S. A.J.T.-A. wrote the paper. A.J.T.-A., V.E.G.-V., A.M.S., T.R.H., and J.M.O. performed the experiments. J.M.S. supervised the research work and revised the paper. All authors contributed to conceiving and designing the experiments, and to analyzing and discussing the results.

Funding: This work was financed by the University of Alicante through Projects VIGROB-256 and GRE10-28 and by the Valencian Community through project GV/2012/113.

Acknowledgments: We would like to thank José Manuel Berenguer Prieto of the Los Serranos Company for allowing the use of their laboratory to carry out the dynamic tests.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ashley, P.M.; Lottermoser, B.G.; Collins, A.J.; Grant, C.D. Environmental geochemistry of the derelict Webbs Consols mine, New South Wales, Australia. *Environ. Geol.* 2004. [CrossRef]

2. Lee, C.H.; Lee, H.K.; Lee, J.C. Hydrogeochemistry of mine, surface and groundwaters from the Sanggok mine creek in the upper Chungju Lake, Republic of Korea. *Environ. Geol.* 2001. [CrossRef]

3. Margui, E.; Salvadé, V.; Queralt, I.; Hidalgo, M. Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes. *Anal. Chim. Acta* 2004, 524, 151–159. [CrossRef]

4. Robles Arenas, V.M. Caracterización hidrogeológica de la Sierra de Cartagena-La Unión (SE de la Península Ibérica). Impacto de la minería abandonada sobre el medio hidrico. *TDX* 2007. [CrossRef]

5. Herrera, G.; Tomás, R.; Vicente, F.; Lopez-Sanchez, J.M.; Mallorqui, J.J.; Mulas, J. Mapping ground movements in open pit mining areas using differential SAR interferometry. *Int. J. Rock Mech. Min. Sci.* 2010. [CrossRef]

6. Herrera, G.; Tomás, R.; Lopez-Sanchez, J.M.; Delgado, J.; Mallorqui, J.J.; Duque, S.; Mulas, J. Advanced DInSAR analysis on mining areas: La Union case study (Murcia, SE Spain). *Eng. Geol.* 2007. [CrossRef]

7. Conesa, H.M.; Robinson, B.H.; Schulin, R.; Nowack, B. Metal extractability in acidic and neutral mine tailings from the Cartagena-La Unión Mining District (SE Spain). *Appl. Geochem.* 2008. [CrossRef]

8. Gonzalez-Fernandez, O.; Queralt, I.; Carvalho, M.L.; Garcia, G. Elemental analysis of mining wastes by energy dispersive X-ray fluorescence (EDXRF). *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 2007. [CrossRef]

9. Robles-Arenas, V.M.; Rodriguez, R.; García, C.; Manteca, J.I.; Candela, L. Sulphide-mining impacts in the physical environment: Sierra de Cartagena-La Unión (SE Spain) case study. *Environ. Geol.* 2006. [CrossRef]

10. García-García, C. Impacto y Riesgo Ambiental de los Residuos Minero-Metalúrgicos de la Sierra de Cartagena-La Unión (Murcia-España). Ph.D. Thesis, Universidad Politécnica de Cartagena, Cartagena, Spain, 2004.

11. Ma, F.; Sha, A.; Lin, R.; Huang, Y.; Wang, C. Greenhouse gas emissions from asphalt pavement construction: A case study in China. *Int. J. Environ. Res. Public Health* 2016, 13, 351. [CrossRef]

12. Alvarez, D.A.; Aenlle, A.A.; Tenza-Abril, A.J. Laboratory evaluation of hot asphalt concrete properties with Cuban recycled concrete aggregates. *Sustainability* 2018, 10, 2590. [CrossRef]

13. Bueno, M.; Luong, J.; Terán, F.; Viñuela, U.; Vázquez, V.; Paje, S. Noise Reduction Properties of an Experimental Bituminous Slurry with Crumb Rubber Incorporated by the Dry Process. *Coatings* 2014, 4, 602–613. [CrossRef]

14. Woszuk, A.; Franus, W. A Review of the Application of Zeolite Materials in Warm Mix Asphalt Technologies. *Appl. Sci.* 2017, 7, 293. [CrossRef]

15. Xiao, F.; Li, R.; Zhang, H.; Amirkhanian, S. Low Temperature Performance Characteristics of Reclaimed Asphalt Pavement (RAP) Mortars with Virgin and Aged Soft Binders. *Appl. Sci.* 2017, 7, 304. [CrossRef]

16. Moon, K.H.; Falchetto, A.C.; Wang, D.; Riccardi, C.; Wistuba, M.P. Mechanical performance of asphalt mortar containing hydrated lime and EAFSS at low and high temperatures. *Materials* 2017, 10, 743. [CrossRef] [PubMed]

17. Sangiorgi, C.; Tataranni, P.; Mazzotta, F.; Simone, A.; Vignali, V.; Lantieri, C. Alternative Fillers for the Production of Bituminous Mixtures: A Screening Investigation on Waste Powders. *Coatings* 2017, 7, 76. [CrossRef]
18. Jose Tenza-Abril, A.; Miguel Saval, J.; Cuenca, A. Using Sewage-Sludge Ash as Filler in Bituminous Mixes. J. Mater. Civ. Eng. Mater. Civ. Eng. 2015. [CrossRef]

19. Kowalski, K.; Król, J.; Bankowski, W.; Radziszewski, P.; Sarnowski, M. Thermal and Fatigue Evaluation of Asphalt Mixtures Containing RAP Treated with a Bio-Agent. Appl. Sci. 2017, 7, 216. [CrossRef]

20. Ahmedzade, P.; Sengoz, B. Evaluation of steel slag coarse aggregate in hot mix asphalt concrete. J. Hazard. Mater. 2009. [CrossRef]

21. Pasetto, M.; Baldo, N. Mix design and performance analysis of asphalt concretes with electric arc furnace slag. Constr. Build. Mater. 2011. [CrossRef]

22. Pasetto, M.; Baldo, N. Performance comparative analysis of stone mastic asphalts with electric arc furnace steel slag: A laboratory evaluation. Mater. Struct. Constr. 2012. [CrossRef]

23. Amin, M.N.; Khan, M.I.; Saleem, M.U. Performance evaluation of asphalt modified with municipal wastewaters for sustainable pavement construction. Sustainability 2016, 8, 949. [CrossRef]

24. Rubio, M.C.; Moreno, F.; Belmonte, A.; Menéndez, A. Reuse of waste material from decorative quartz solid surfacing in the manufacture of hot bituminous mixes. Constr. Build. Mater. 2010. [CrossRef]

25. Rubio-Gámez, M.C.; Menedez, A.; Moreno-Navarro, F.; Belmonte, A.; Ramírez, A. Mechanical properties of hot bituminous mixtures manufactured with recycled aggregate of Silestone(R) waste. Mater. Constr. 2011, 61, 49–60. [CrossRef]

26. Baghaee Moghaddam, T.; Karim, M.R.; Syammaun, T. Dynamic properties of stone mastic asphalt mixtures containing waste plastic bottles. Constr. Build. Mater. 2012. [CrossRef]

27. Costa, L.; Peralta, J.; Oliveira, J.; Silva, H. A New Life for Cross-Linked Plastic Waste as Aggregates and Binder Modifier for Asphalt Mixtures. Appl. Sci. 2017, 7, 603. [CrossRef]

28. Arabani, M. Effect of glass cullet on the improvement of the dynamic behaviour of asphalt concrete. Constr. Build. Mater. 2011. [CrossRef]

29. Paranavithana, S.; Mohajerani, A. Effects of recycled concrete aggregates on properties of asphalt concrete. Resour. Conserv. Recycl. 2006. [CrossRef]

30. Pérez, I.; Toledano, M.; Gallego, J.; Taibo, J. Mechanical properties of hot mix asphalt made with recycled aggregates from reclaimed construction and demolition debris. Mater. Constr. 2007, 57, 17–29. [CrossRef]

31. Ministerio de Fomento. Pliego de Prescripciones Técnicas Generales para Obras de Carreteras y Puentes (PG-3); Dirección General de Carreteras, Ministerio de Fomento, Ed.; Ministerio de Fomento: Madrid, Spain, 2015.

32. Bengtsson, M.; Evertsson, C.M. Measuring characteristics of aggregate material from vertical shaft impact crushers. Miner. Eng. 2006. [CrossRef]

33. Bouquet, M.N.; Descantes, Y.; Barcelo, L.; de Larrard, F.; Clavaud, B. Experimental study of crushed aggregate shape. Constr. Build. Mater. 2007. [CrossRef]

34. Hinislioglu, S.; Agar, E. Use of waste high density polyethylene as bitumen modifier in asphalt concrete mix. Mater. Lett. 2004. [CrossRef]

35. Sengul, C.E.; Aksoy, A.; Iskender, E.; Ozen, H. Hydrated lime treatment of asphalt concrete to increase permanent deformation resistance. Constr. Build. Mater. 2012. [CrossRef]

36. Zoorob, S.E.; Suparma, L.B. Laboratory design and investigation of the properties of continuously graded Asphaltic concrete containing recycled plastics aggregate replacement (Plastiphalt). Cem. Concr. Compos. 2000. [CrossRef]

37. Sengoz, B.; Agar, E. Effect of asphalt film thickness on the moisture sensitivity characteristics of hot-mix asphalt. Build. Environ. 2007. [CrossRef]

38. Gardete, D.; Picado-Santos, L.; Capitão, S. Improving bituminous mixture performance by optimizing the design compaction energy—A cost effective approach for better pavements. Constr. Build. Mater. 2018. [CrossRef]

39. Moreno-Navarro, F.; Rubio-Gámez, M.C. A review of fatigue damage in bituminous mixtures: Understanding the phenomenon from a new perspective. Constr. Build. Mater. 2016, 113, 927–938. [CrossRef]

40. Lantsoght, E.O.L.; Van Der Veen, C.; De Boer, A. Proposal for the fatigue strength of concrete under cycles of compression. Constr. Build. Mater. 2016. [CrossRef]

41. Ortega, J.J.; Ruiz, G.; Yu, R.C.; Afanador-Garcia, N.; Tarifa, M.; Poveda, E.; Zhang, X.; Evangelista, F. Number of tests and corresponding error in concrete fatigue. Int. J. Fatigue 2018. [CrossRef]

42. Weinberg, K.; Khosravani, M.R. On the tensile resistance of UHPC at impact. Eur. Phys. J. Spec. Top. 2018. [CrossRef]
43. Khosravani, M.R.; Silani, M.; Weinberg, K. Fracture studies of Ultra-High Performance Concrete using dynamic Brazilian tests. *Theor. Appl. Fract. Mech.* 2018. [CrossRef]

44. Di Benedetto, H.; de La Roche, C.; Baaj, H.; Pronk, A.; Lundström, R. Fatigue of bituminous mixtures. *Mater. Struct.* 2004. [CrossRef]

45. Kakade, V.B.; Reddy, M.A.; Reddy, K.S. Rutting performance of hydrated lime modified bituminous mixes. *Constr. Build. Mater.* 2018. [CrossRef]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).