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# Evaluation of Copper Leaching for Subsequent Recovery from the Waste Dumps of the Linares Mining District and Their Use for Construction Materials

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**Abstract:** The development of the population's well-being involves the use of different raw materials. However, metallic elements such as copper are currently scarce due to their intensive use in different sectors. Therefore, new sources of raw materials that provide these elements, are of lower cost, and use waste for their extraction must be sought. For this reason, in this research, different waste dumps of the mining district of Linares (Spain) are studied to evaluate the existence of recoverable copper by hydrometallurgical techniques. The material from the waste dump selected as potentially viable is leached with different sulfuric acid solutions (0.25, 0.5, 1, and 2 mol) and at different times, obtaining copper concentrations usable for subsequent hydrometallurgical processes. In addition, in order to develop an environmental hydrometallurgy, the leach waste is characterized, and bituminous mixtures are made with it. The results of the present investigation showed that it was possible to recover 80% of the copper in the waste dumps of the Linares mining district with 1 and 2 mol solutions of sulfuric acid. At the same time, the waste from the leaching process was found to be suitable for use as an aggregate in bituminous mixtures. Therefore, bituminous mixtures were conformed, and it was obtained that the optimum percentage of bituminous emulsion was 6.95% for the proposed granulometry. This emulsion percentage, which corresponds to a residual bitumen percentage of 4.17%, showed particle loss test results of 14% and 18% after immersion. In addition, the stability test values for the Marshall test with the above-mentioned bitumen emulsion percentage and leaching waste showed a stability of 8.99 KN. This fact demonstrates the quality of the bituminous mixture made with the leaching waste for use in bituminous mixtures. Consequently, it can be affirmed that in the present investigation, a significant percentage of copper has been extracted from the waste dumps of the mining district of Linares (Spain) and that the waste after processing can be used in bituminous mixtures, there being a closed cycle of materials in which no waste is produced.

**Keywords:** hydrometallurgy; metallic elements recovery; mining waste; bituminous mixture; circular economy; sustainability; construction materials

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## 1. Introduction

Mining is an essential activity for maintaining the well-being of the population [1]. It is through this industry that resources essential to daily life are obtained [2]. Consequently, the disappearance of this activity cannot be envisaged. However, mining operations produce a number of environmental impacts that need to be taken into account and reduced as much as possible [3,4]. One of the most important environmental impacts of mining activity is the production of waste [5]. This waste derives mainly from the extraction of the material and the concentration of the elements of interest, whereby there is extracted material that is separated and deposited in landfills. This material, which is currently of no use, has, in some cases, contaminating elements and chemical compounds that can cause a significant impact on the environment if not properly treated [6]. Consequently, it must be studied and evaluated how to make use of these mining wastes and incorporate them into new materials to avoid environmental pollution [7–9].

It should be noted that environmental regulations regarding mining are becoming increasingly restrictive [10]. However, in the past, there were no such environmental regulations, and waste was deposited without precaution. These waste deposit derivatives from former mining operations now cause significant pollution of surface water, groundwater, flora, fauna, landscape, etc. [11,12]. Specifically, in Linares, the area on which this research focuses, several authors have corroborated the contamination produced by mining waste [13]. At the same time, it is important to highlight that the mining waste produced in other times with less efficient equipment still contains important percentages of the main extraction element of the mine since it could not be concentrated by the old techniques. Moreover, because the demand for different minerals has been changing according to the development of the population, these wastes contain in some cases minerals that are economically viable to extract nowadays [14]. This is the case of the Linares lead mines, where the lead sulfides extracted in the past are associated mainly with copper sulfides, as well as other elements that, because they are of no economic interest or because they are difficult to extract using the old techniques, are found in the mining waste [15].

Based on the above, the purpose of this article is to study different waste dumps in the Linares mining district to evaluate the existence of copper, as well as to select the waste dump with the highest copper content for copper extraction by hydrometallurgical methods.

It should be noted that copper is one of the most demanded elements nowadays. This fact is due to its properties, being mainly its excellent electrical conductivity, good thermal conductivity, its malleability, resistance to corrosion, etc. This fact causes copper to be used in several areas such as energy, construction, military, naval, etc. [16]. Therefore, it is an essential element currently that has a high price due to the reduction of its reserves [17].

Worldwide, 80% of copper is extracted by pyrometallurgical techniques and 20% by hydrometallurgical processes [18]. However, the decrease in reserves, the existence of reserves with low percentages of copper, and the existence of this mineral, mainly copper sulfide, associated with other minerals, have made hydrometallurgical techniques economically unviable [19,20]. It is, therefore, necessary to develop economically profitable hydrometallurgical techniques that extract copper from materials with low copper content, such as mining waste [21]. This economic profitability is achieved through the use of robust techniques capable of adapting to variation in the chemical composition of the raw materials, slow recovery, and very low processing cost [22].

The hydrometallurgical techniques suitable for this system are currently carried out with acidic solutions and atmospheric pressure because the cost of this process is very low [23]. However, as mentioned above, the process is much slower and can take up to several months.

It also should be noted that the extraction of copper by hydrometallurgical techniques also produces a residue from the process [24]. This residue, based on a new circular economy, must be used as raw material for new products [25]. In this case, and due to the fact that the construction sector is one of the most demanding of raw materials and, in turn, one of the most polluting [26], the residue from the leaching process of the Linares mine waste dumps was used as aggregate for bituminous mixtures for roads. This waste, mainly granite, was conformed with bitumen emulsion to create a bituminous mix of discontinuous grading capable of withstanding the traffic loads of medium to low traffic roads in the area. The incorporation of leaching residues into bituminous mixtures was chosen as the best option because, as mentioned above, road construction requires huge quantities of raw materials [27]. Furthermore, the selection of this type of mix is due to the fact that it is a sustainable mix, incorporating bitumen emulsion as a binder, [28] and it possesses suitable mechanical and physical properties [29].

In short, this research studies the recovery of copper by hydrometallurgical techniques through the leaching with sulfuric acid solutions of materials from waste dumps, or dumps, from lead mines in the mining district of Linares. For this purpose, several waste dumps from the district were analyzed, the one with the highest percentage of copper was selected, and the waste was subjected to leaching with acidic media, measuring the pH, the electrical conductivity, and the concentration of copper in the recovered leachate continuously during the test time. After the leaching process, the residue was used as an aggregate for bituminous mixtures.

These bituminous mixtures would provide a suitable use of the leach residue and could create new bituminous mixtures for various roads in order to avoid the extraction of new raw materials and to avoid landfilling of the leach residue. Specifically, the conformed bituminous mixture was a discontinuous grading with leach residue and bitumen emulsion. This sustainable bituminous mixture was tested to determine its physical and mechanical properties by means of maximum density, bulk density, void content, simple compressive strength, and Marshall test.

## 2. Materials and Methods

### *2.1. Materials*

The materials used in this research are mainly from the waste dumps of the Linares mining district and commercial products. The commercial materials used in the methodology are distilled water, sulfuric acid, and bitumen emulsion. The first two materials mentioned were used for the first stage of the work, in which the material from the selected dump was leached with different acid solutions at atmospheric pressure and ambient temperature. The bitumen emulsion was used in the second stage of this research to conform bituminous mixtures using the leaching residue. These materials are described in detail in the following sections.

#### 2.1.1. Mining Waste Dumps

The residues assessed come from the waste dumps belonging to the mining district of Linares, Spain. This area was intensively mined mainly for lead. At the same time, and to a much lesser extent, silver was extracted as a secondary element of the argentiferous galena.

The mines in the Linares district were exploited for hundreds of years, until the end of the 20th century, when they ceased to operate. The cessation of their activity was mainly due to the enormous drop in lead prices, as it was no longer such an essential element for society, as well as the lack of research into new lead seams. As a result, there are several abandoned infrastructures and enormous quantities of mining waste derived from the exploitation of these mines all over the Linares area. Therefore, mining waste is currently a major environmental problem in the area.

In this mining waste, as is usual in lead sulfide formations, there are other chemical compounds associated with these mining wastes. Among the main chemical elements in the residues are copper, zinc, and even arsenic. More specifically, residue from waste dumps is rather random in size. Mainly, the particle size is 10 to 15 cm. These waste dump particles are essentially composed of granite, as this is the country rock of the exploited lead seam. This granite is fissured, presenting in its cracks other types of hydrothermal chemical compounds. This fact is easily observed in Figure 1.

Consequently, the milling of the waste rock will occur mainly through these cracks, as they are the weakest points of the joint. Therefore, this milling exposes the hydrothermal chemical compounds present in the cracks for leaching under acidic media, atmospheric pressure, and ambient temperature. Finally, the leaching residue, being granite, will be used as aggregate for bituminous mixes destined for roads.


**Figure 1.** Sample of waste dump showing cracks filled with hydrothermal chemical compounds.

Among all the waste dumps existing in the mining district of Linares, the waste dumps selected for the present study correspond to the mine workings of San Andrés, Arrayanes, and La Cruz.

#### 2.1.2. Sulfuric Acid and Water

The sulfuric acid used in this investigation had a purity of 96% with a molar mass of 98.08 g/mol. This acid was diluted with different concentrations of distilled water with the aim to obtain sulfuric acid solutions of different molarities. In this way, it was possible to check the concentration of copper produced with different acid solutions at atmospheric pressure and at different periods of time. Therefore, the use of distilled water was necessary to obtain the different sulfuric acid solutions.

The distilled water used had a colorless liquid appearance, a density at 20 °C of 0.995 g/cm$^3$, a pH of 7, a conductivity in µS/cm of 2.5, a silica percentage of 0.003 mg/L, and a hardness measured in mg/L $CaCO_3$ of 0.3.

#### 2.1.3. Bitumen Emulsion

In this research, with the aim of carrying out an environmentally sustainable project in which the waste produced was zero and usable materials were obtained for society, the by-products of the leaching of the waste dumps, after the extraction of the interesting metallic elements, were used as raw material for the conformation of bituminous mixtures. It is therefore essential to define the main elements used in the conformation of these bituminous mixtures, namely, the leaching residue (aggregate) and the bitumen emulsion (binder).

The bitumen emulsion is the binder of the bituminous mix of discontinuous grading conformed with the leaching residues. In other words, the emulsion is the element that binds the aggregates (leaching residues) together to withstand the tensile loads of traffic. The advantage of using bitumen emulsions over traditional bitumen lies in the fact that they can be conformed at ambient temperature, as well as extended and compacted. Consequently, the CO2 emissions from the process are much lower, as it is not necessary to heat the entire bituminous mix to a temperature of 180 °C. However, the bitumen emulsion must be compatible with the aggregate used, in this case the leaching residue. Therefore, a cationic emulsion with medium breaking time was selected, more specifically, the bitumen emulsion C60BF3 MBA. The technical data sheet of the bitumen emulsion C60BF3 MBA used is detailed in Table 1.

**Table 1.** Technical details of the bitumen emulsion C60BF3 MBA used.

| Characteristics | Unit | Standard | Min. | Max. |
|---|---|---|---|---|
| **Original Emulsion** | | | | |
| Particle polarity | - | UNE EN 1430 | Positive | - |
| Breaking value (Forshammer filler) | g | UNE EN 13075-1 | 70 | 155 |
| Binder content (per water content) | % | UNE EN 12846-1 | 58 | 62 |
| Oil distillate content | % | UNE EN 1431 | - | 5 |
| Efflux time (2 mm. 40 °C) | s | UNE EN 12846 | 40 | 130 |
| Residue on sieving (0.5 mm) | % | UNE EN 1429 | - | 0.10 |
| Setting tendency (7 days storage) | % | UNE EN 12847 | - | 5 |
| 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 | - | 220 |
| 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 | - | 220 |
| Softening point | °C | UNE EN 1427 | 35 | - |

### 2.2. Methodology

First, the mining district of Linares was studied in order to identify those waste dumps belonging to different mine workings that could present viable percentages of interesting metallic elements such as copper. The selected waste dumps were visited to take samples of representative materials, taking into account the most abundant formations therein and collecting this type of material. Subsequently, the material from the different samples was treated for subsequent analysis with micro-X-ray fluorescence tests, identifying the existence of copper in the dumps. Based on the results obtained, the dump with the highest potential percentage of copper was selected for extraction by hydrometallurgical techniques.

The selected waste dump was analyzed in more detail by taking samples from different points of the waste dump in order to quantify in more detail the chemical elements present, the percentage of copper present, as well as the variability of the results. For this purpose, samples were taken and, subsequently, analyzed chemically. Once the chemical composition of the selected waste dump was evaluated, the material was milled and leached in acidic media. These acidic media consisted of sulfuric acid solutions of different molarities (0.25 mol, 0.50 mol, 1.00 mol, and 2.00 mol), measuring the pH, electrical conductivity, and copper concentration at different times. With these data, it was possible to obtain the appropriate leaching solution and the time required for the recovery of an economic percentage of copper.

The leaching residue was subjected to a leachate test in order to determine its suitability for the conformation of bituminous mixtures. This process was carried out in order to assess that the leachate from the aggregate did not cause significant environmental contamination. Subsequently, the leaching residue was subjected to different physical and mechanical tests to determine its suitability as an aggregate for bituminous mixtures.

Finally, and having determined the suitability of the leaching residue for conformation bituminous mixtures, different discontinuous grading and bitumen emulsion bituminous mixtures were conformed. These bituminous mixtures were conformed with increasing percentages of binder and were subsequently subjected to physical and mechanical tests in order to establish the optimum percentage of bitumen emulsion that developed the best properties.

The following sections describe the tests carried out in greater detail in the different blocks into which this research is divided.

2.2.1. Analysis of the Different Waste Dumps in the Mining District of Linares

The waste dumps selected were those known as San Andrés, Arrayanes, and La Cruz. These waste dumps correspond to the deposition of waste from mining operations over decades, so that at the three study points, they have a volume of thousands of cubic meters. As detailed above, these waste dumps were considered in this investigation due to the existence of abundant bibliographical references that testified the existence of polymetallic sulfides, essentially copper.

The samples were taken at different points of the waste dumps. For this purpose, the UNE-EN 932-1 standard was applied for taking samples in large depositions of material. In this way, it was possible to obtain a final sample of 20 kg as representative as possible of the waste dumps analyzed.

The samples from the three waste dumps were dried at a temperature of 105 ± 2 °C and, subsequently, reduced in size according to UNE-EN 932-2. The subsample obtained was milled to a particle size of less than 100 micrometers for chemical characterization. These samples from each waste dump were analyzed by micro-X-ray fluorescence. The equipment used was the Bruker M4 Tornado energy dispersive micro-X-ray fluorescence spectrometer (M4 Tornado, Bruker, Billerica, MA, USA). The analysis of the samples with the microfluorescence equipment provided a rapid elemental composition of each waste dump, thus, allowing us to select the potentially viable waste dump for further leaching and copper extraction.

2.2.2. Chemical Characterization of the Selected Waste Dump

Once the three samples from the three waste dumps had been analyzed, the waste dump of greatest interest for copper element recovery was selected. The selected waste dump sample was further reduced according to UNE-EN 932-2 to obtain sufficient material with a particle size of less than 100 micrometers for detailed chemical characterization.

The first of the chemical tests carried out was elemental analysis. This test makes it possible to detect and quantify the percentages of carbon, nitrogen, hydrogen, and sulfur present in the sample. For this, the sample is calcined at a temperature of 1000 ± 5 °C, and the gases are analyzed with LECO's commercial TruSpec Micro equipment (TruSpec Micro, LECO, St. Joseph, MI, USA).

In order to provide further information on the sample, the loss-on-ignition test was also performed. This test shows the difference in mass in percentage that exists between the sample before and after calcination at 1000 ± 5 °C. This loss of mass of the sample corresponds mainly to the organic matter in the sample, the loss of volatile elements, or the transformation of hydrated or carbonated chemical compounds.

Finally, and because the nature of the sample is mainly inorganic, the X-ray fluorescence test was performed. This test, performed with the commercial ADVANT'XP+ equipment (ADVANT'XP+, Thermo Fisher, Waltham, MA, USA) was also performed to determine the percentage of copper in the sample. The determination of the percentage of copper is essential to assess the percentage recovery occurring in the leachate, as well as the feasibility of mining.

The chemical characterization of the selected waste dump sample not only allows the accurate determination of the percentage of copper in the sample, but also identifies critical points where special attention should be paid.

2.2.3. Leaching in Acidic Media and Atmospheric Pressure

Once the chemical composition of the selected waste dump sample was analyzed, we proceeded to study the leaching of copper with different sulfuric acid solutions at different leaching times and atmospheric pressure.

First, the sample of the selected waste dump was milled, and different representative sub-samples were obtained according to the UNE-EN 932-2 standard. The grading curve of the crushed waste dump sample was determined using the UNE-EN 933-1 grading curve analysis test. The milling was carried out with a double purpose: on the one hand, to reduce the sample size so that it was easier to handle in the industrial process; on the other hand, and due to the fact that the granite of the waste dump was pre-cracked and in these cracks there were copper hydrothermal chemical compounds, the milling produced the fracture of the rock through these cracks obtaining, consequently, the exposure of the interesting chemical compounds to the acid dissolution.

Once the sample was crushed, the leaching test was carried out in acidic media and with different solutions. The samples selected for leaching had a mass of 300 ± 0.1 g, after drying to remove humidity. The sulfuric acid solutions, 3000 ± 10 mL volume per process, were 0.25 mol, 0.50 mol, 1.00 mol, and 2.00 mol. The use of these low molarity solutions is motivated by different reasons: on the one hand, the use of low molarity solutions of sulfuric acid develops a leaching residue that is easier to treat afterwards; on the other hand, a lower concentration of sulfuric acid makes it possible to increase the working life of the equipment; and finally, higher molarities of sulfuric acid would create a higher percentage of sludge that is difficult to treat. Furthermore, it should be noted that the use of the aforementioned solid/liquid ratio is to avoid the need to carry out subsequent concentration processes at a higher economic cost, as would be the case if higher temperatures than ambient were used.

The leaching process was carried out in equipment specially designed for the research. This equipment consisted mainly of sieves that retained the sample and an upper pulverizer. The sprayer sprayed the sample remaining on the sieves, depositing the fluid by gravity in a leaching tank. The fluid from the leach tank was continuously pumped into the pulverizer for a continuous recirculation process. This process was maintained constant during the 35 days of testing without interruption, controlling the temperature at 25 ± 1 °C. It should be noted that the operation of the equipment is very similar to that of the industrial process, in which large quantities of material are irrigated with acid solutions that are continuously recirculated. The image of the equipment can be seen in Figure 2.

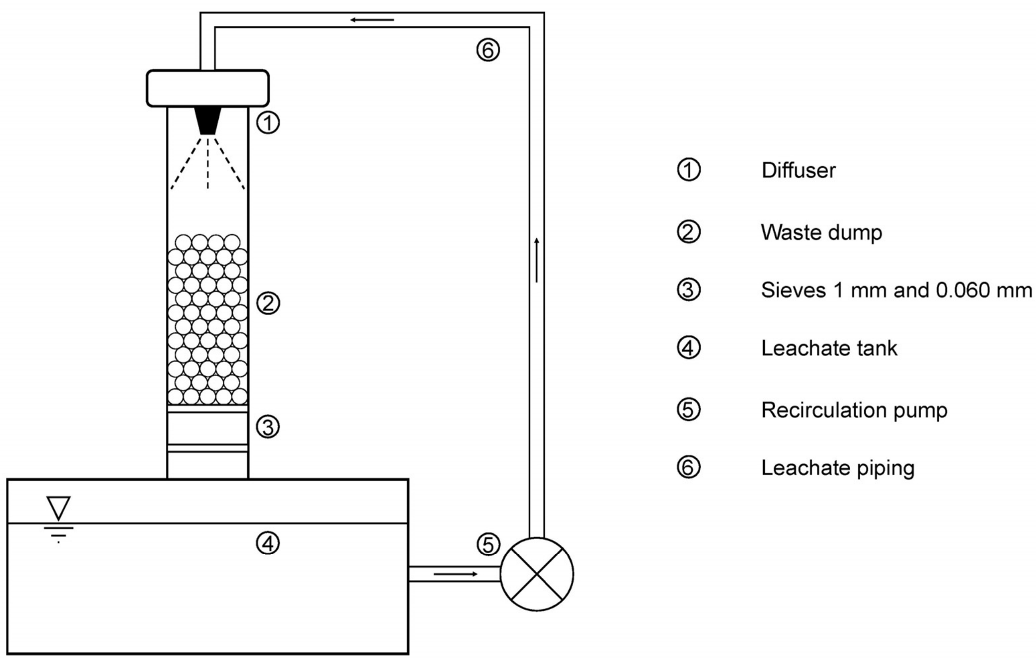


**Figure 2.** Leachate equipment for leaching of mining waste in acidic media, ambient temperature, and atmospheric pressure.

This process was carried out for the four detailed sulfuric acid solutions, measuring the pH and electrical conductivity of the solution every 24 h. In addition, samples were taken every 24 h for subsequent analysis by inductively coupled plasma mass spectrometry (7900, Agilent, Santa Clara, CA, USA). For the chemical analysis with the detailed equipment, standardized standards of the chemical element copper were used, repeating each measurement three times to obtain statistically reliable results. In this way, the percentage of copper leached in the solution used and at different times could be verified, as well as the percentage of recovery that occurred with respect to the total copper in the sample.

With the results of the variation of the pH of the solution, the variation of the electrical conductivity, as well as the concentration of copper in the different solutions for different times, the optimum solution was determined, as well as the time necessary for the leaching of copper at an economically viable recovery percentage.

#### 2.2.4. Characterization of the Leaching Residue

Once the solution that developed a leaching of copper from the waste dump was selected in a viable time, a significant amount of material was leached in order to study the leaching residue produced after the leaching process.

The leaching residue, after the leaching process with the conditions set, was evaluated chemically, physically, and mechanically. This characterization was carried out with the aim of determining the quality of the residue after the copper extraction process for use in bituminous mixtures, thus, developing a sustainable process in which the residues produced are zero and feed different industries of essential raw materials, such as copper and aggregates for bituminous mixtures.

First, and due to the fact that the leaching residues come from leaching processes with sulfuric acid, as well as from materials in which heavy metals are usually found, we proceeded to analyze the leachate from the residue in order to determine that its use did not entail significant environmental problems. This leaching residue test is essential for the use of aggregates in bituminous mixtures for road infrastructures. To this end, the leaching test was carried out in accordance with the UNE-EN 12457-3 standard, detecting the presence of contaminating elements in high proportion, comparing them with the limits set by Spanish regulations, and limiting their use for the proposed purpose.

Once the feasibility of using the leaching residue had been chemically determined, a series of physical and mechanical tests were carried out to evaluate its possible use in bituminous mixtures.

The leaching residue was tested for: particle density according to the UNE-EN 1097-7 standard in order to determine if volumetric corrections were necessary due to a density different from that of a conventional aggregate, 2.65 $t/m^3$; the sand equivalent test according to UNE-EN 933-8 to determine the presence of colloidal particles; the percentage of crushed and broken surfaces test according to UNE-EN 933-5; and the flakiness index test according to UNE-EN 933-3 to determine the shape of the particles and their suitability for use in bituminous mixtures. In order to determine the resistance of the leaching residue, resistance to fragmentation tests were carried out in accordance with the UNE-EN 1097-2 standard to qualify the strength of the material, as well as tests for resistance to freezing and thawing cycles (UNE-EN 1367-1 standard) to evaluate the resistance to thermal fatigue of the aggregate and determination of the polished stone value (UNE-EN 1097-8 standard) to quantify the resistance to the continuous friction of the tire.

These chemical, physical, and mechanical tests allowed an objective assessment of the quality of the leaching residue for use in bituminous mixtures.

#### 2.2.5. Bituminous Mixtures Conforming and Testing

Once the chemical, physical, and mechanical suitability of the leaching residue had been analyzed, the bituminous mix used was formulated and named a discontinuous grading mixture, hereinafter referred to as AF12. This type of bituminous mix was developed with the fundamental aim of obtaining a sustainable, low-cost mix with a high use of waste.

It should be noted that in this work, the best practice guide provided by the Technical Association for Bitumen Emulsions (hereinafter ATEB) will be used for the formulation of bituminous mixes. This guide was written by experts in the field and sets out the necessary steps for assessing the suitability of a mixture of this type.

The grading curve of the leaching residue was that established by the envelope grading curve detailed in the aforementioned standard. This grading curve, shown in Figure 3, was intermediate between the upper and lower limit of the grading envelope in order not to induce more variables.

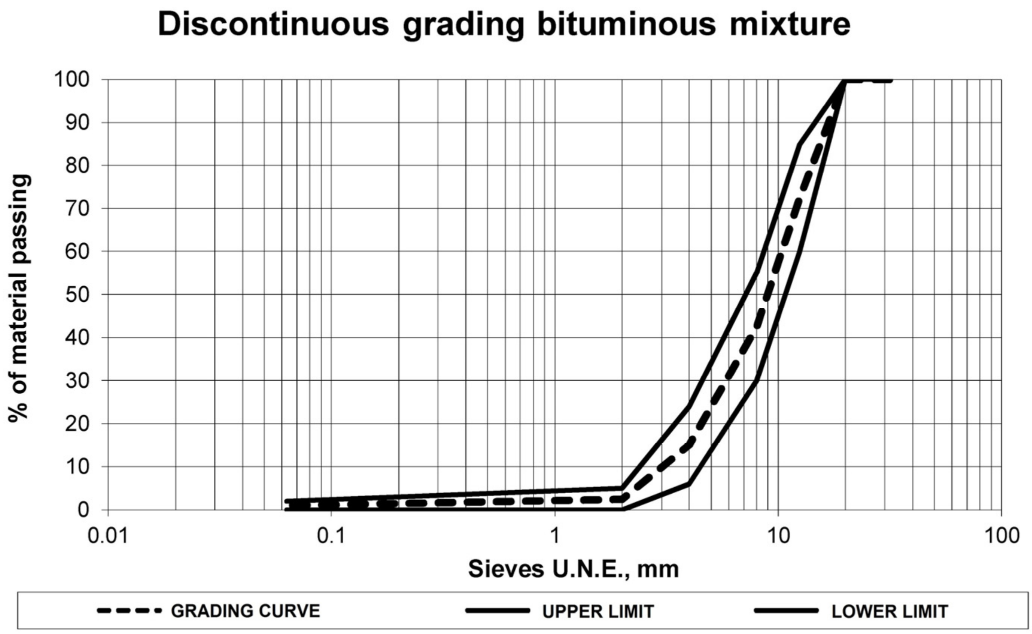


**Figure 3.** Grading curve of the bituminous mixture conformed with leaching residue and bitumen emulsion.

Once the grading curve had been defined, the analysis of the compatibility of the aggregate with the emulsion to be used was carried out. For this purpose, the coating test was carried out in accordance with the NLT-196/84 standard. This test evaluates the quality of the aggregate's coating by the emulsion and, consequently, the quality of the final mix to be developed.

First, the minimum percentage of emulsion, residual bitumen, that the bituminous mix could contain was calculated. To do this, the percentage of emulsion to be added to the bituminous mix was calculated according to the mathematical formula described by ATEB in its good practice guide. It should be noted that the bitumen emulsion is mainly composed of bitumen and water, and that after the mixture is spread, the water evaporates by natural processes. Therefore, the calculation of the percentage of residual bitumen from the percentage of bitumen emulsion is immediate if the technical data sheet of the bitumen emulsion is known. In this case the bitumen emulsion used had a residual bitumen percentage of 60%. The formula provided by ATEB for this type of bituminous mixture is based on the specific surface area of a conventional aggregate and is detailed below.

$$BR = (K/100) \cdot (1.5A + 2.5B + 4C + 6D + 9E + 12F) \quad (1)$$

where:

BR = Proportion of residual bitumen on the dry mass of the aggregates.

K = Coefficient of enrichment, the value of which is 1 in the wearing course and 0.9 in the lower course.

A = Proportion of aggregates retained by the sieve UNE 20 mm.

B = Proportion of aggregates passing through the sieve UNE 20 mm and retained by the sieve UNE 8 mm.

C = Proportion of aggregates passing through the sieve UNE 8 mm and retained by the sieve UNE 4 mm.

D = Proportion of aggregates passing through the sieve UNE 4 mm and retained by the sieve UNE 2 mm.

E = Proportion of aggregates passing through the sieve UNE 2 mm and retained by the sieve UNE 0.063 mm.

F = Proportion of aggregates passing through the sieve UNE 0.063 mm.

Consequently, and according to the grading defined above, the ATEB formula determined a residual bitumen content of the aggregate of 3.5%, corresponding to a percentage of bitumen emulsion of the aggregate of 5.8%. Once the optimum point was calculated empirically using the formula provided by ATEB, different families of test samples were made with increasing percentages of bitumen from 0.25% onwards. As mentioned above, when conforming, it must be taken into account that the water in the emulsion will be evaporated later, so the reference values are the bitumen that will remain in the bituminous mix after evaporation.

The test samples of each family of specimen with increasing percentages of bitumen were conformed and compacted according to UNE-EN 12697-30. Subsequently, all the test samples were subjected to a curing process to eliminate the water from the emulsion. For this purpose, the Marshall type test samples manufactured were leveled with the mold so that they could be placed on sieves with an opening of less than 2 mm. The subsequent curing process consisted of 2 days at a temperature of 75 $\pm$ 2 °C and 5 more days at a temperature of 90 $\pm$ 2 °C (the curing processes are detailed in ATEB). During the curing process, binder drainage must be continuously observed; for this purpose, a filter paper was placed at the bottom of the test samples during the curing process. The test sample family that caused binder drainage was considered as null, and consequently, the percentage of bitumen or emulsion in this family was the maximum permissible. Therefore, the bituminous mixes viable for use were those incorporating a percentage of emulsion from the minimum set by ATEB to the maximum produced by binder drainage.

After curing, the test samples were stripped and subjected to a series of physical tests to determine the general physical properties. The first test samples were tested for maximum density, according to UNE-EN 12697-5; bulk density, according to UNE-EN 12697-6; and void characteristics in the mix, according to UNE-EN 12697-8.

Subsequently, and in order to determine the resistance of the bituminous mixtures to fracture and aggregate pull-out, the particle loss test was carried out in accordance with the UNE-EN 12697-17 standard for all families of mixtures. In turn, in order to evaluate the influence of water on the bituminous mix and, consequently, to determine the compatibility between the aggregate and the emulsion, the same type of test was carried out with immersion in water at 45 $\pm$ 1 °C for 24 h, in accordance with standard NLT-362/92.

In this way, the quality of the mastic conformed with the filler and bitumen in the emulsion could be determined. However, due to the incorporation of high percentages of bitumen, the problem of plastic deformation in the infrastructure can occur. To avoid this and to quantify the resistance of the mix at high temperatures, the Marshall test was carried out in accordance with the UNE-EN 12697-34 standard.

Finally, with the results of the aforementioned tests for the different groups of samples, it was possible to observe, graphically and mathematically, the variation of the physical and mechanical properties of the bituminous mixes with increasing bitumen percentage. In this way, the study of the graphical and mathematical models provided an optimum percentage of bitumen emulsion that developed the best physical and mechanical characteristics. This combination is the one that was called optimum, with which all the above-mentioned tests were carried out again to corroborate the mathematically determined properties. These tests for determining the physical properties of the final bituminous mix are: maximum density UNE-EN 12697-5, bulk density UNE-EN 12697-6, and void characteristics UNE-EN

12697-8; and for the mechanical properties: loss of particles without immersion and after immersion UNE-EN 12697-17 and the Marshall test UNE-EN 12697-34.

## 3. Results

### *3.1. Analysis of the Different Waste Dumps in the Mining District of Linares*

The results of the micro-X-ray fluorescence test of the three waste dumps (San Andrés, Arrayanes, and La Cruz) are shown in Table 2.

**Table 2.** Micro-X-ray fluorescence of the waste dumps in study.

| Element | San Andrés, Wt % | Arrayanes, Wt % | La Cruz, Wt % |
|---|---|---|---|
| Si | 20.59 | 19.54 | 18.47 |
| Al | 10.37 | 1.27 | 8.54 |
| Fe | 7.56 | 36.28 | 15.16 |
| Sx | 1.34 | 0.06 | 4.52 |
| Cu | 4.54 | 1.35 | 0.45 |
| Mg | 2.76 | 0.18 | 3.14 |
| K | 2.01 | 0.03 | 3.57 |
| Ca | 0.73 | 0.06 | 2.45 |
| Pb | 1.48 | 0.97 | 2.33 |

The micro-X-ray fluorescence results show that the waste dump with the highest percentage of potentially extractable copper is the San Andrés waste dump, obtaining results of 4.54% copper according to this test. However, since this test was used for a rapid detection of the elements present in the samples without an exhaustive preparation of the sample, the values obtained could be influenced with high probability by the shape of the particles, the excitation of the chemical elements present, as well as by the time of analysis. However, all other things being equal, the sample with the highest percentage of copper could be evaluated, this being the one from the San Andrés waste dump. This sample was the one selected, being analyzed later in greater detail for the evaluation of its chemical composition.

### *3.2. Chemical Characterization of the Selected Waste Dump*

The chemical composition of the waste dump residue determines the percentage of copper in the sample and quantifies the existence of other chemical elements that may impair the leaching process. It is, therefore. essential to perform.

The first of the tests carried out was elemental analysis, and the values are shown in Table 3.

**Table 3.** Elemental analysis of the chemical elements nitrogen, carbon, hydrogen, and sulfur in the sample from the San Andrés waste dump (ESA).

| Sample | Nitrogen, % | Carbon, % | Hydrogen, % | Sulfur, % |
|---|---|---|---|---|
| ESA | $0.000 \pm 0.001$ | $0.843 \pm 0.019$ | $0.410 \pm 0.015$ | $3.122 \pm 0.073$ |

Elemental analysis of the mining waste sample shows a very low percentage of carbon. This low percentage of carbon confirms the low proportion of organic matter and carbonates. The low percentage of hydrogen may be due to the transformation of the hydrated compounds or to unavoidable traces of humidity from the testing process. However, as in the case of carbon, this value is quite low. Finally, it can be observed that there is a percentage of sulfur. The existence of this percentage is obvious, since the sample contains copper sulfides, iron sulfides, lead sulfides, and to a much lesser extent, zinc sulfides. However, it should be noted that the percentage of sulfur determined by elemental analysis is not the total sulfur in the sample, as this test was performed by analyzing the gases produced in the combustion of the sample at $1000 \pm 5$ °C. Subsequently, the percentage of remaining sulfur was evaluated by the X-ray fluorescence method.

The loss-on-ignition test reflects the mass variation in the sample when the sample is subjected to the temperature of 1000 ± 5 °C. The loss on ignition of the sample of the mining waste under study is 4.35 ± 0.10%. This very low loss on ignition is mainly due to the transformation of the chemical compounds. This loss on ignition value is usual and similar to those obtained in tests of this type for mining waste.

X-ray fluorescence determined the percentage of the chemical elements with the highest atomic weight. The elemental composition of the mining waste obtained by X-ray fluorescence is shown in Table 4.

**Table 4.** X-ray fluorescence of the San Andrés waste dump.

| Element | Wt % | Est. Error |
|---|---|---|
| Si | 22.45 | 0.12 |
| Al | 8.02 | 0.09 |
| Fe | 5.85 | 0.10 |
| Sx | 2.29 | 0.05 |
| Cu | 3.32 | 0.08 |
| Mg | 2.49 | 0.06 |
| K | 3.32 | 0.08 |
| Ca | 2.82 | 0.07 |
| Na | 0.522 | 0.026 |
| Ti | 0.379 | 0.019 |
| Pb | 0.257 | 0.013 |
| Mn | 0.115 | 0.0058 |
| Px | 0.0513 | 0.0028 |
| Sn | 0.0477 | 0.0061 |
| Zn | 0.0345 | 0.0019 |
| Cr | 0.0273 | 0.0014 |
| Cl | 0.0318 | 0.0031 |
| V | 0.0137 | 0.0012 |
| Ni | 0.0178 | 0.0012 |
| Zr | 0.0119 | 0.0024 |
| Oxygen | 43.54 | 1.11 |

Table 4 shows the percentage of the different chemical elements analyzed in the sample. This is, therefore, the most reliable method for determining the actual percentage of each of the chemical elements existing in the sample, regardless of their combination in different chemical compounds.

From the results, it can be seen that the percentage of copper, the main element of this study, was 3.32 ± 0.08%. This copper came from the ores of the waste dump, which is the one that wass intended to be extracted by leaching in acidic media at atmospheric pressure and ambient temperature. The percentage of copper is contemplated as a viable percentage for recovery, i.e., it is not a small percentage, but it would present problems for extraction by pyrometallurgical means. This is due to the diversity of existing minerals, their combination, and the existence of some elements that are detrimental to the pyrometallurgical process, which will be detailed later. In short, the percentage of copper present for the development of this new hydrometallurgical technique is correct and to be expected for the material to which it corresponds.

It should be noted that there was a percentage of sulfur in the elemental composition. This is indicative of the existence of some sulfides, probably copper. Therefore, with the use of this low molarity leaching technique, and without the development of a previous treatment, it was difficult to achieve a complete recovery of the existing copper in the waste dump.

In turn, calcium represented an important percentage in the composition, corresponding to the feldspars and mica of the granite, as well as aluminum. It should be remembered that granite is the main rock in which the metal sulfides deposits have formed, so its presence in the waste dump is important. However, calcium and aluminum are not chemical elements that are detrimental to the hydrometallurgical leaching process, so they are not a problem. Similarly, silicon is present in significant percentages as granite is a siliceous rock.

Magnesium and potassium, as in the previous cases, come directly from the granite and are usually found in the percentages detailed in this rock.

The lead comes from galena, a mineral mainly extracted in the mine working of the vein. The percentage of lead is reduced as the waste dumps belong to mine tailings, so the mining process drastically reduced the percentage of lead in the waste.

Zinc, belonging to the blende ore, appeared in low proportion in the composition. Therefore, it was not the main element of extraction by leaching in an acidic media, but it could be extracted at a lower recovery rate after obtaining copper, being also a sought-after element by the industry.

The other chemical elements were found in very low proportions, and wet test methods are needed to quantify them under higher pressure. However, they do not fall within the scope of this study and will not be detrimental to the industrial process. The quality of the waste in terms of arsenic percentages is noteworthy. It is usual to find arsenic sulfides in this type of mining formations that seriously damage the pyrometallurgical process; however, in hydrometallurgy, its influence is much less and the percentage it represents in the mining waste is very small.

In short, and after the analysis of the chemical composition, it can be confirmed that the chemical study of the San Andrés waste dump carried out previously shows a viable copper percentage and reflects the inexistence of chemical elements in high percentages that could damage the process, making possible the subsequent leaching section of the sample in acidic media at atmospheric pressure and ambient temperature, according to hydrometallurgical techniques.

### 3.3. Leaching in Acidic Media and Atmospheric Pressure

The dry sample of the waste dump was milled in the jaw crusher in order to free the copper compounds in the waste dump for direct contact with the solution and, consequently, its leaching. Figure 4 shows the grading curve of the waste dump after the milling process.

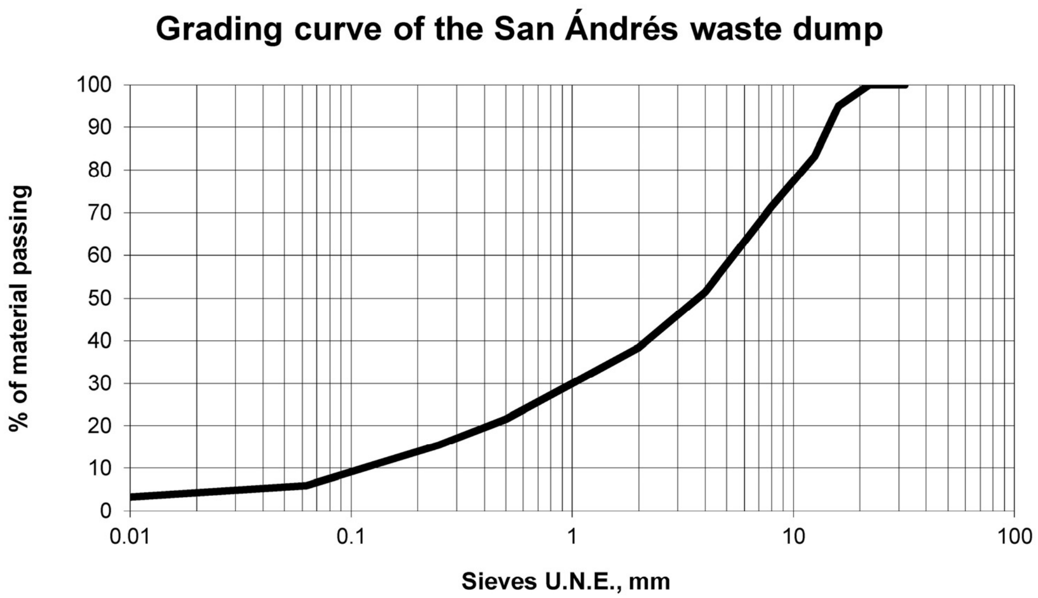


**Figure 4.** Grading curve of the San Andrés waste dump after the milling process.

The grading of the waste dump sample selected coincides with a continuous grading in which the maximum aggregate size is less than 20 mm. It should be noted that this milling process is simple and economical, so it would not increase the cost of treatment and a leaching residue could be obtained that could be used for bituminous mixtures.

Subsequently, the milled mining waste sample was divided into several sub-samples for the leaching process. This process was carried out at ambient temperature (25 ± 1 °C), atmospheric pressure, for 35 days, and with different sulfuric acid solutions: 0.25 molar, 0.50 molar, 1.00 molar, and 2.00 molar.

First, Figure 5 shows the variation of the pH of the leachate as a function of time and according to the concentration of sulfuric acid used.

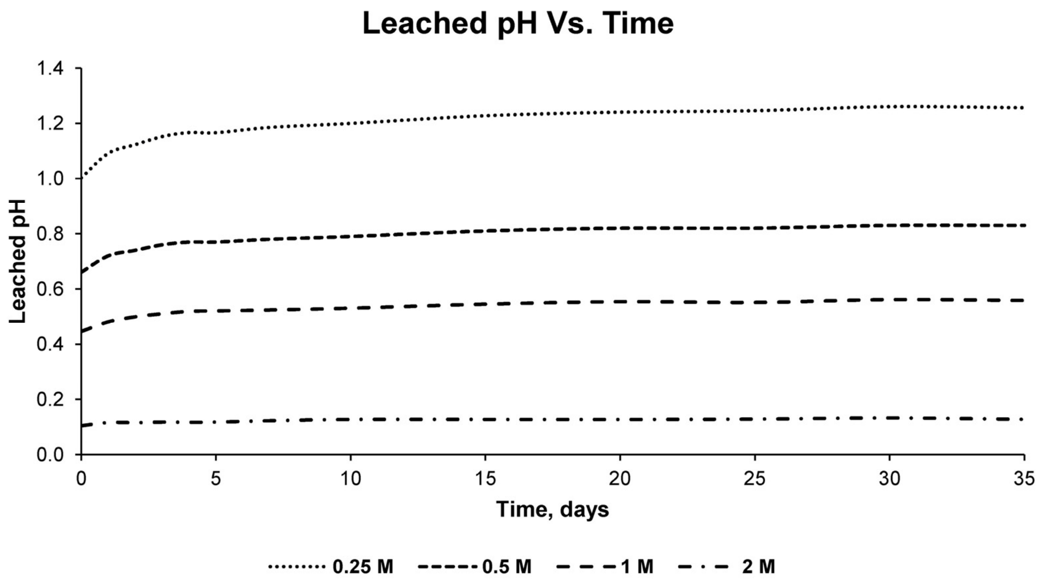


**Figure 5.** Graph of the pH of the leachate, as a function of time, for the 0.25 molar, 0.50 molar, 1.00 molar, and 2.00 molar sulfuric acid solutions.

As can be seen in Figure 5, the pH of the solution was lower the higher the molarity of sulfuric acid, which is to be expected if the activity of this type of acid is taken into account. At the same time, it was observed that, in the first 24 h in all four solutions, there is a higher pH increase than in the following days due to the direct contact of the solution with the mining waste from the landfill.

The 2.0 mol sulfuric acid solution showed a rapid stabilization of the pH after 24 h of the process, producing something similar with the 1.00 mol solution but with a longer leaching time. In contrast, the 0.50 mol and 0.25 mol solutions did not seem to show a stabilization of the pH over the time under study, so it is highly probable that they could represent the need for a longer leaching time to obtain copper concentrations similar to those obtained with higher molarity solutions.

On the other hand, the electrical conductivity of the leachates of the four solutions under study and for different times was measured during the 35 days of testing, reflecting the results shown in Figure 6.

The electrical conductivity of the different solutions at different leaching times clearly showed that the solutions with higher molarity had higher electrical conductivity. This conductivity decreased in contact with the waste dump waste, mainly in the first days. However, the electrical conductivity of the solutions did not seem to stabilize over the days, unlike the pH. This is because this more accurate measure reflects the dissolution of elements in the leachate not only of copper but also of other potentially leachable and less economically interesting elements in the sample. Therefore, this test demonstrates the need to select not only the correct dilution, as in the pH test, but also the correct leaching times. If the correct leaching times were not selected, concentrations of other elements of less economic interest would be produced in the leachate, which would also hinder subsequent hydrometallurgical processes to obtain copper.

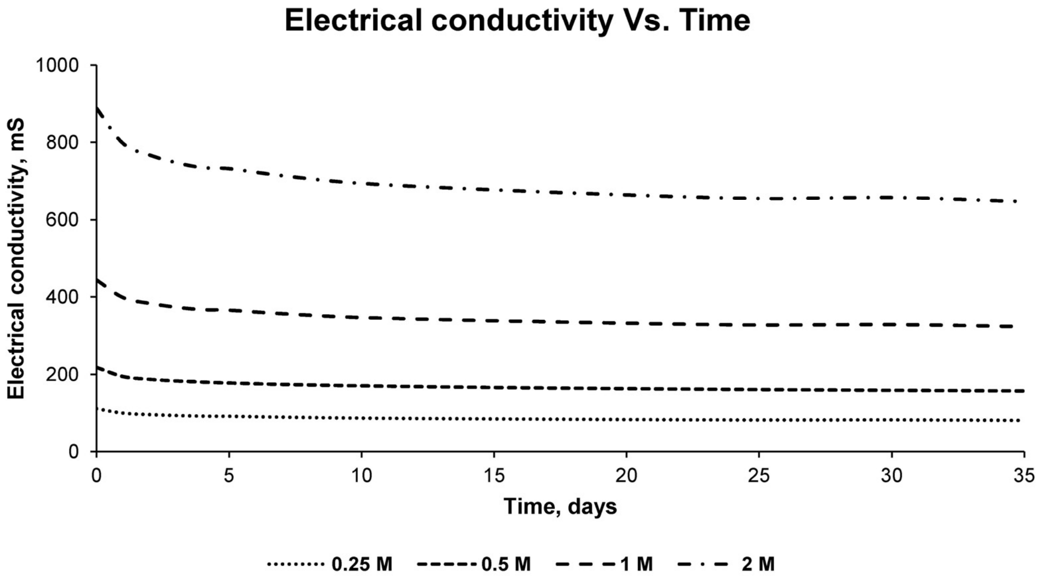


**Figure 6.** Graph of the electrical conductivity of the leachate, as a function of time, for the 0.25 molar, 0.50 mol, 1.00 mol, and 2.00 mol sulfuric acid solutions.

Finally, Figure 7 shows the variation of copper concentration as a function of time and the solution used. The units used are milligrams per gram of sample, with a maximum leachable copper concentration of 33.2 mg/g, according to the X-ray fluorescence test.

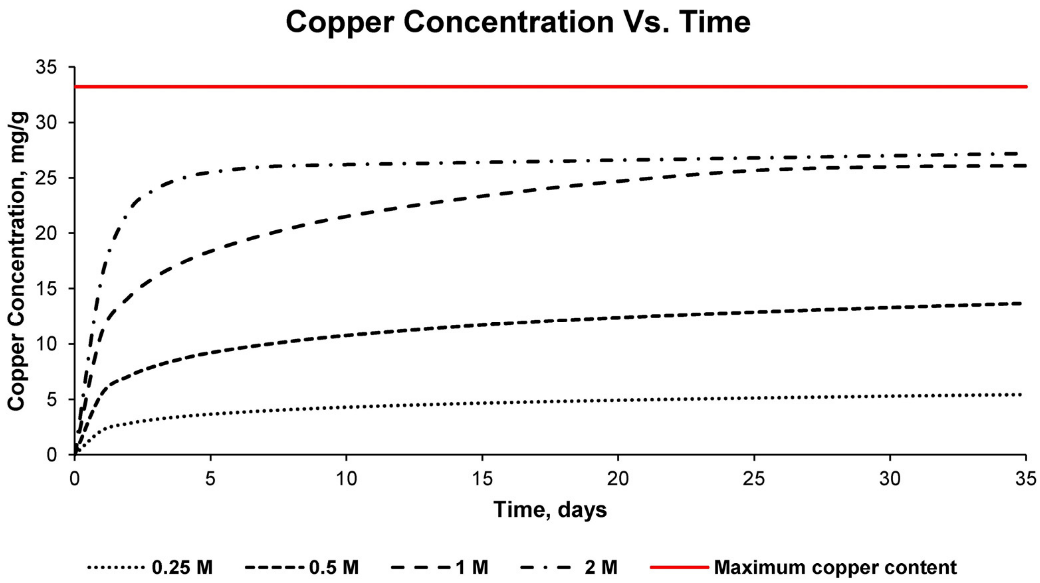


**Figure 7.** Graph of leachate copper concentration as a function of time for 0.25 mol, 0.50 mol, 1.00 mol, and 2.00 mol sulfuric acid solutions.

The graph of copper concentration in the leachate of the four solutions shows how the 0.25 mol sulfuric acid solution produces a reduced concentration of copper in the leachate, which makes its use undesirable. In turn, the 0.5 mol solution shows how the copper concentration increased gradually with time, not reaching a significant copper recovery percentage in the time evaluated and, consequently, needing more time for its recovery. For these detailed reasons, the 0.5 mol solution was also discarded as a possible solution for copper leaching, as the time required would be too long.

The 1.0 molar and 2.0 mol sulfuric acid solutions show that the maximum percentage of copper recovery was approximately 80%, as the 2.0 mol solution reached this maximum and stabilized, not producing higher copper concentrations over time. This is because, as discussed in the chemical analysis of the San Andrés waste dump, there are still copper sulfides in the material that have not been oxidized and are, therefore, very difficult to leach with this hydrometallurgical technique. Therefore, complete leaching of the copper in the sample will be achieved by pre-treating the waste dump material and transforming the copper sulfides into oxides. Since the interest of this research is to obtain an environmentally and economically sustainable process, this pre-treatment was not carried out, and a recovery rate of 80% of the copper in the sample was considered workable.

There are important differences between the 1.0 mol and 2.0 mol sulfuric acid solutions, as the 2.0 mol solution reached stabilization of the copper concentration in the leachate practically 5 days after the start of the process. On the other hand, the 1.0 mol sulfuric acid solution reached stabilization of the copper concentration after 25 days, obtaining similar results to those provided by the 2.0 mol solution. Based on the molarities of the solution, the environmental damage that it can cause, the wear and tear or deterioration of the equipment, as well as the previous activities for the execution of the leaching, in this research, the 1.0 mol solution of sulfuric acid has been taken as the optimum solution for copper recovery, setting a leaching time of 25 days.

### *3.4. Characterization of the Leaching Residue*

The leaching residue obtained after the leaching process at the San Andrés waste dump was recovered for chemical and physical characterization. In this way, it was possible to assess its viability for use in bituminous mixtures.

The test for the evaluation of the viability of using the leaching residue in bituminous mixtures was the leachate test, according to the standard defined in the methodology. This test quantifies the concentrations of the contaminating elements of the leaching residue in the leachate, assessing its suitability for use. The results of the leachate test are shown in Table 5.

**Table 5.** Concentrations of contaminants in the leachate of the leaching residue compared to regulatory maximum limits.

| Element | Leaching Residue, mg/kg | Maximum Limits, mg/kg |
|---|---|---|
| Ba | $0.003 \pm 0.001$ | 17 |
| Cd | $0.001 \pm 0.001$ | 0.009 |
| Cr | $0.003 \pm 0.001$ | 0.5 |
| Mo | $0.002 \pm 0.001$ | 0.5 |
| Ni | $0.007 \pm 0.001$ | 0.4 |
| Pb | $0.165 \pm 0.004$ | 0.5 |
| Se | $0.001 \pm 0.001$ | 0.1 |
| V | $0.026 \pm 0.001$ | 1.3 |
| Zn | $0.017 \pm 0.001$ | 1.2 |
| As | $0.003 \pm 0.001$ | 0.5 |
| Cu | $0.756 \pm 0.019$ | 2 |
| Hg | - | 0.01 |
| Sb | $0.001 \pm 0.001$ | 0.06 |
| Chlorides | $87 \pm 2$ | 800 |
| Sulfate | $267 \pm 6$ | 377 |

The leachates from the leaching residue obtained in the hydrometallurgical process for the extraction of copper comply with the limits set by the regulations. The low concentration of heavy metals is to be highlighted, as well as the acceptable result of sulfates in the leachate. This percentage of sulfates was a critical point for its reuse, as the waste dumps had sulfur and the hydrometallurgical process was carried out with sulfuric acid.

Once the chemical suitability of the leaching residue had been analyzed, the physical properties were determined. These tests are defined in Table 6.

**Table 6.** Physical properties of the leaching residue.

| Test | Standard | Value/Unit |
|---|---|---|
| Particle density | UNE-EN 1097-7 | $2.71 \pm 0.06$ t/m$^3$ |
| Sand Equivalent, % | UNE-EN 933-8 | $77 \pm 2$ |
| Broken surfaces, % | UNE-EN 933-5 | $95 \pm 1$ |
| Flakiness index, % | UNE-EN 933-3 | $8 \pm 1$ |

The physical tests of the leaching residue showed that the density of this material is similar to that of commercial or conventional aggregates, 2.65 t/m$^3$. In turn, the sand equivalent test showed that the percentage of colloidal particles in the residue is adequate, so there should be no subsequent expansivity problems due to clayey particles. The percentage of broken surfaces in the coarse aggregate of the leaching residue, as well as the flakiness index, showed the quality of this material for use in bituminous mixtures, even more so in this type of mixture with discontinuous grading, in which the compressive loads are mainly supported by friction between aggregates.

On the other hand, and due to the fact that the aggregate in the bituminous mix is an essential element for resisting the tensile loads of traffic, the different tests established by the regulations for the quantification of the mechanical properties of the leaching residue were carried out. The mechanical properties tests are listed in Table 7.

**Table 7.** Mechanical properties of the leaching residue.

| Test | Standard | Value/Unit |
|---|---|---|
| Resistance to fragmentation, % | UNE-EN 1097-2 | $18 \pm 1$ |
| Resistance to freezing and thawing, % | UNE-EN 1367-1 | $1.121 \pm 0.016$ |
| Polished stone value | UNE-EN 1097-8 | $57 \pm 1$ |

The resistance to fragmentation test of the leaching residue showed excellent mechanical properties. Therefore, this result ensures that there will be no subsequent breakage of the material in the bituminous mix and, consequently, no undue compaction due to the constant passage of vehicles. On the other hand, the test of resistance to freezing and thawing cycles has shown an excellent resistance of the leaching residue to thermal fatigue, comparable to the results obtained for a high-quality siliceous aggregate. Finally, it should be remembered that the irregular surface of the aggregate must be maintained over time in order to provide the road with sufficient roughness for friction between the tire and the pavement. This characteristic was evaluated through the polished stone value test. This test showed that the leaching residue has a high resistance to the continuous passage of vehicles and that its microtexture characteristics are preserved over time.

Consequently, based on the results of the chemical, physical, and mechanical characterization of the leaching residue, it can be stated that the material has suitable properties for use in bituminous mixtures, even for important traffic roads. This is directly due to the nature of the leaching residue as it is directly derived from a siliceous rock.

### *3.5. Bituminous Mixtures Conforming and Testing*

Once the suitability of the leaching residue for use in bituminous mixtures had been verified, we proceeded to the development of discontinuous grading mixtures with bitumen emulsion. To this end, in the methodology, we defined the grading curve of the bituminous mix, this being the intermediate of the grading envelope detailed in the standards.

First, the compatibility of the medium cationic emulsion (C60BF3 MBA) with the leaching residue was evaluated. For this purpose, a coating or adhesion test was carried out, in which the aggregates with the fixed grading were mixed with the corresponding emulsion percentages. The images of the coating test for the leaching residue in combination with the bitumen emulsion are shown in Figure 8.

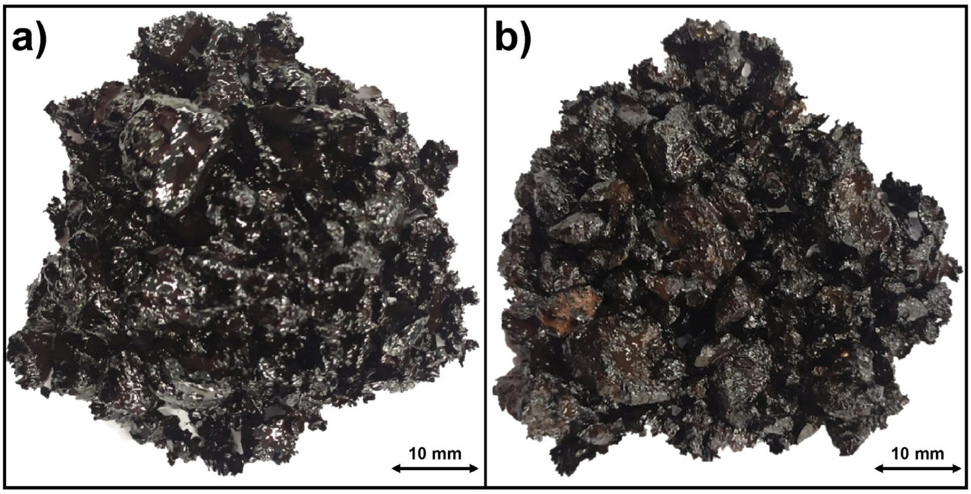


**Figure 8.** Coating test with the leaching residue and the C60BF3 MBA emulsion. (**a**) Dry coating test and (**b**) coating test after water irrigation.

The coating test showed that the coverage of the leaching residue particles by the bitumen emulsion was quite good in all cases. Therefore, it can be stated that the used bitumen emulsion C60BF3 MBA is compatible with the leaching residue and can be used for conforming bituminous mixtures.

After the coating test was performed and the material compatibility was conformed, 12 test samples were manufactured for each emulsion point (5.83%, 6.25%, 6.67%, 7.08%, 7.50%, and 7.92%). The test samples were conformed according to the procedure detailed in the methodology, subsequently, undergoing the curing process and continuously observing that no binder drainage occurred during this time.

In this case, the bituminous mix with an emulsion percentage of 7.92% on aggregate produced binder drainage during the curing process. Consequently, this bituminous mix was rejected for use as this binder drainage manifested the inability of the aggregate to absorb the percentage of emulsion added.

With the test samples of the families of bituminous mixtures manufactured with the viable emulsion percentages (5.83%, 6.25%, 6.67%, 7.08%, and 7.50%), we proceeded to determine the physical properties of the bituminous mixtures. The first of the physical tests was the maximum density of the bituminous mixtures, with the results shown in Figure 9.

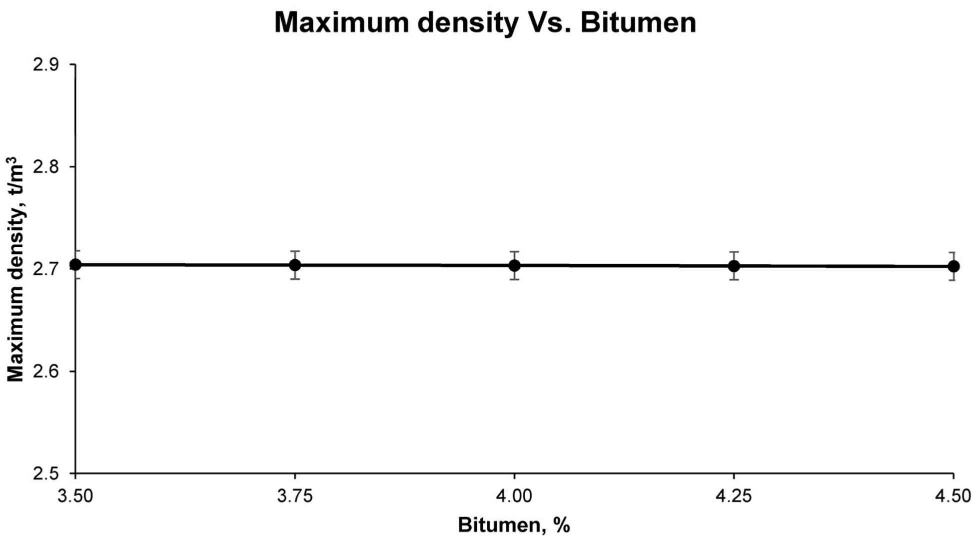


**Figure 9.** Maximum density of bituminous mixtures conforming with leaching residue and increasing percentages of bitumen emulsion.

The maximum density of the different families of bituminous mixes with increasing percentages of bitumen emulsion is approximately similar. However, it can be seen that increasing the percentage of emulsion makes it possible to decrease the maximum density. This is mainly due to the fact that the incorporated binder has a much lower density than the aggregate.

In turn, the bulk density of the conformed bituminous mixtures was calculated according to the standard detailed in the methodology. The results of this test are shown in Figure 10.

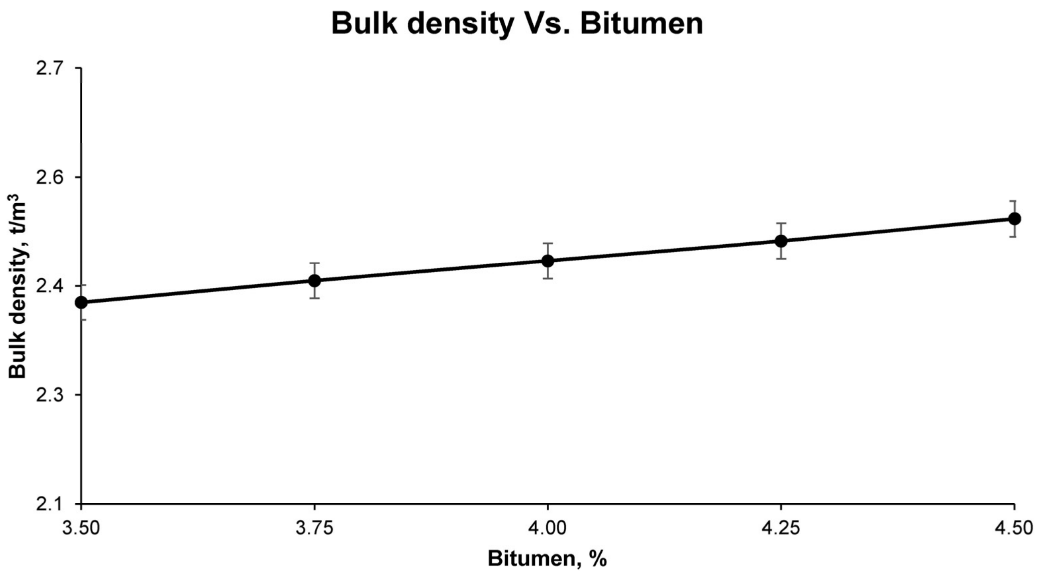


**Figure 10.** Bulk density of bituminous mixtures conforming with leaching residue and increasing percentages of bitumen emulsion.

The bulk density of the different bituminous mixtures, and in contrast to the maximum density, increased as the percentage of bitumen emulsion increased. It should be noted that the bulk density is the density of the bituminous mixture taking into account the internal air void content. Therefore, an increase in bulk density reflects a decrease in voids in the mix, which is to be expected if one considers that a higher percentage of emulsion will provide a higher compactability of the mix.

The last of the physical properties measured in the bituminous mixtures was the voids content. This physical variable, which is essential for the characterization of a bituminous mix, depends directly on the maximum density and bulk density. The void contents of the different families of bituminous mixtures are shown in Figure 11.

The void content in the bituminous mixes, as expected from the results of the bulk density, decreased as the percentage of bitumen emulsion increased. However, in all families of bituminous mixes, a fairly high void content was obtained in the mix, which was capable of providing the bituminous mixes with very interesting properties. In particular, a high void content in the mix is capable of producing good drainage of rainwater from the pavement, thus, preventing vehicles from slipping; it ensures a good macrotexture of the pavement, increasing safety when braking; and it even provides absorption of the noise caused by contact between the tire and the pavement, providing a comfortable and safe road surface.

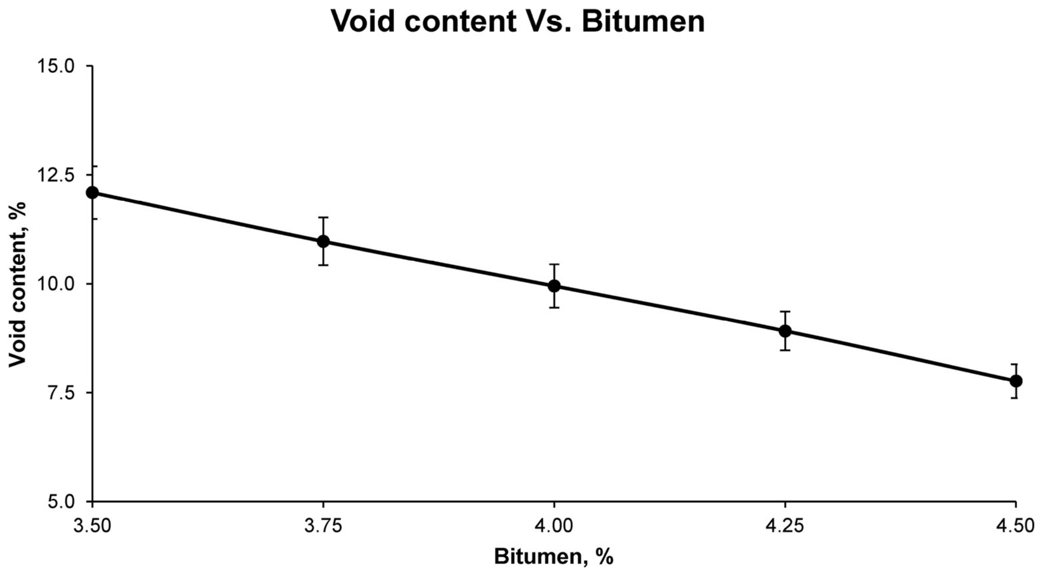


**Figure 11.** Void content of bituminous mixtures conforming with leaching residue and increasing percentages of bitumen emulsion.

Once the physical properties of the bituminous mixes had been analyzed, the mechanical characteristics of the mixes were determined. It should be borne in mind that a high void content in the mix favors beneficial characteristics for the pavement, however, the mastic that surrounds the aggregates must be of sufficient quality to prevent the bituminous mix from fracturing due to tensile loads or even the aggregates being torn out. Therefore, the test that best assesses the behavior of the bituminous mix and the quality of the mastic to hold the aggregates together is the particle loss test. This test was carried out in this research with and without immersion in water in order to evaluate the effect of water on the bituminous mixes, with the results shown in Figure 12.

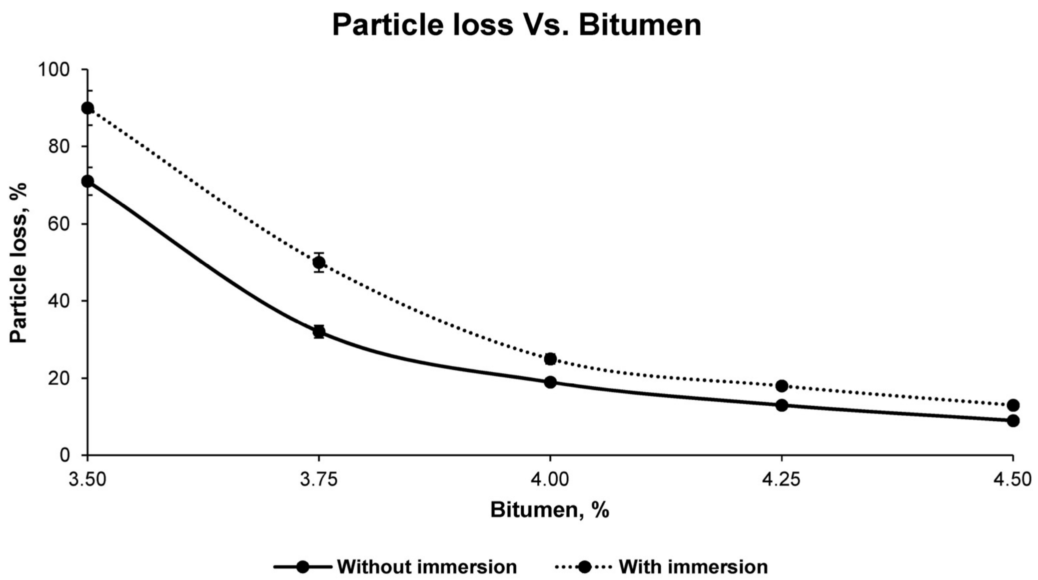


**Figure 12.** Particle loss test with and without water immersion of bituminous mixtures conforming with leaching residue and increasing percentages of bitumen emulsion.

The particle loss test showed a higher wear of the bituminous mixes with water immersion, which is to be expected from developing under extreme conditions. However, the difference between the wear of the mixes with and without immersion decreased as the percentage of emulsion increased. This reflects the fact that a higher quality mastic is being formed as the percentage of residual bitumen increases. It should also be noted that Spanish regulations set a maximum percentage of particle loss of 25% without immersion. Therefore, bituminous mixtures with residual bitumen percentages of 3.5% and 3.75% do not comply with the established limitations and are considered to be rejectable. The rest of the families comply with the requirements of the standard, even for test samples with water immersion.

It should be noted that a high percentage of emulsion will create a high percentage of residual bitumen after curing, therefore the mastic developed will be able to better wrap the aggregates and hold them together. However, a high percentage of bitumen can develop plastic deformations at high temperatures, i.e., variations in the physical properties of the bituminous mixes. This defect renders the infrastructure completely unusable for use, as subsidence, bleeding, etc. can occur on the pavement. It must, therefore, be monitored and controlled to ensure that this high percentage of bitumen, which is so necessary for maintaining the joint between the particles, does not develop plastic deformations. The evaluation of this problem was carried out with the Marshall test. The results of the Marshall test for conformed bituminous mixtures are shown in Figure 13.

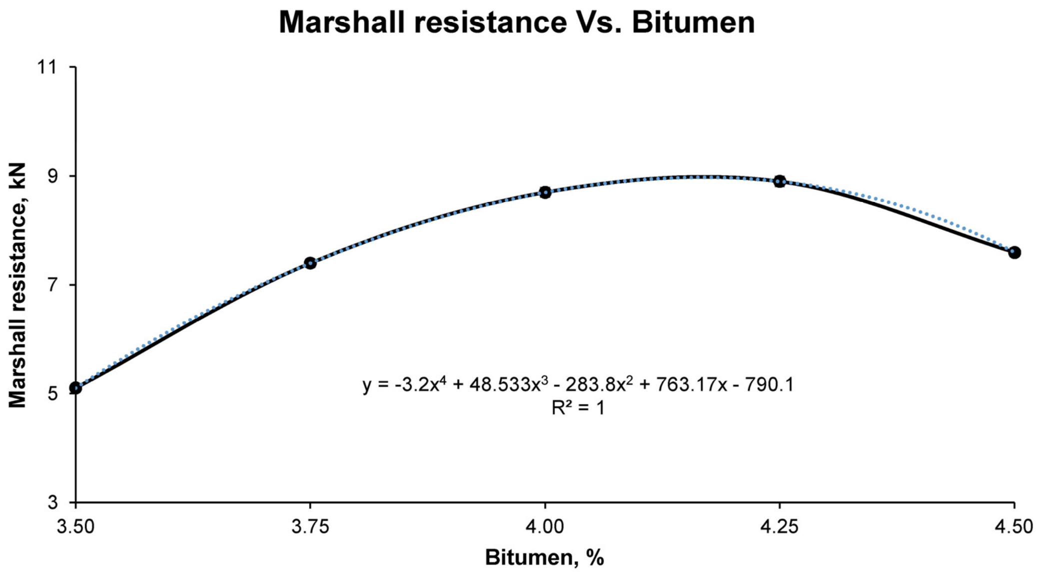


**Figure 13.** Marshall resistance of bituminous mixtures conforming with leaching residue and increasing percentages of bitumen emulsion.

The Marshall resistance as shown in the figure above increased up to a maximum and then decreased for the maximum percentage of residual bitumen, 4.5%. Spanish regulations stipulate that Marshall resistance must be higher than 7.5 kN; therefore, bituminous mixes with residual bitumen percentages of 4%, 4.25%, and 4.5% are acceptable, the others being rejected by this test.

It should be noted that the Marshall test results clearly show a maximum between the residual bitumen percentage of 4% and 4.25%. This maximum percentage of Marshall resistance was calculated mathematically through the expression shown in the figure, obtaining the percentage of residual bitumen and bitumen emulsion that developed this maximum stability. This percentage of emulsion will be considered as optimum, provided that the results of the other tests mentioned are acceptable according to the regulations.

In order to verify the properties and characteristics of the optimum bitumen emulsion corresponding to the maximum Marshall stability, test samples with the determined grading and this percentage of emulsion were carried out again, with the results shown in Table 8.

**Table 8.** Results of the physical and mechanical tests of the test samples conforming with the optimum percentage of bitumen emulsion.

| Test | Standard | Value/Unit |
|---|---|---|
| Residual bitumen, % | - | 4.17 |
| Bitumen emulsion, % | - | 6.95 |
| Maximum density, t/m$^3$ | UNE-EN 12697-5 | 2.703 ± 0.069 |
| Bulk density, t/m$^3$ | UNE-EN 12697-6 | 2.452 ± 0.062 |
| Void content, % | UNE-EN 12697-8 | 9.27 ± 0.23 |
| Particle loss without immersion, % | UNE-EN 12697-17 | 14 ± 1 |
| Particle loss with immersion, % | UNE-EN 12697-17 / NLT-362/92 | 18 ± 1 |
| Marshall stability, kN | UNE-EN 12697-34 | 8.99 ± 0.23 |

The results of the AF12 bituminous mix with discontinuous grading with bitumen emulsion conformed with leaching residue and with the optimum percentage of emulsion according to the Marshall test showed very suitable properties for medium traffic roads. The high void content in the mixture will be able to provide a comfortable and safe road surface, and the particle loss and Marshall resistance values show the mechanical strength of the mixture conformed with a high percentage of waste.

## 4. Conclusions

The tests mentioned in the methodology allowed us to obtain a series of partial conclusions that lead to the verification of the initial hypothesis of this research.

On the one hand, it should be pointed out that the element copper was present in the three waste dumps analyzed, the San Andrés waste dump being the one with the highest percentage. The detailed waste dump was leached with different sulphuric acid solutions after milling, demonstrating that the highest percentage of copper recovery produced was 80%, with the 1 and 2 mol sulphuric acid solutions. At the same time, the leaching waste was chemically characterized, determining its usefulness for use in bituminous mixtures according to the regulations. The bituminous mixture formed with the leaching waste and a bitumen emulsion percentage of 6.95% was the one with the best mechanical properties, with a residual bitumen percentage of 4.17%. This bituminous mix had a Marshall stability of 8.99 KN and a particle loss before and after immersion of 14% and 18%. Therefore, this bituminous mixture has physical and mechanical properties suitable for use on medium and low traffic roads.

Consequently, and according to the detailed partial conclusions, it can be stated that the San Andrés waste dump has an interesting material for the extraction of copper by means of hydrometallurgical techniques carried out at atmospheric pressure, ambient temperature, and acidic media, recovering a high percentage of the copper existing in it. In addition, the leaching residue after the hydrometallurgical process showed physical, chemical, and mechanical properties suitable for use as an aggregate in bituminous mixtures of discontinuous grading and bitumen emulsion. In short, this research has developed a new industrial process from a waste product with no use or value at present, in which economically interesting elements such as copper and aggregates for construction are obtained. In this way, a new environmental hydrometallurgy is developed for the rehabilitation, strengthening, and development of the city of Linares, based on circular engineering.

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