



## Production of asphalt mixes with copper industry wastes: Use of copper slag as raw material replacement

Aitor C. Raposeiras<sup>a,b,\*</sup>, Diana Movilla-Quesada<sup>c,a</sup>, Osvaldo Muñoz-Cáceres<sup>a</sup>, Valerio C. Andrés-Valeri<sup>a</sup>, Manuel Lagos-Varas<sup>a</sup>

<sup>a</sup> *G<sup>2</sup>V Research Group, Institute of Civil Engineering, Faculty of Engineering Sciences, University Austral of Chile, General Lagos St. #2060, Of. 11.302, 5090000, Valdivia, Chile*

<sup>b</sup> *Departamento de Ingeniería Mecánica, Escuela Politécnica Superior de Zamora, Universidad de Salamanca, Av. Requejo #33, 49022, Zamora, España*

<sup>c</sup> *Departamento de Construcción y Agronomía, Escuela Politécnica Superior de Zamora, Universidad de Salamanca, Av. Requejo #33, 49022, Zamora, España*

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### ABSTRACT

Copper slag is a waste obtained from copper production and it has a limited use, being mainly accumulated in landfills on a massive scale. This material presents a high hardness and it has hydrophobic properties, so it can be used as aggregate replacement in the production of asphalt mixtures. However, each size of copper slag behaves differently when used in asphalt mixes, especially under changing conditions of moisture or temperature. Precisely these climatic factors directly affect the service life of asphalt pavements. In this research, semi-dense graded asphalt mixtures were produced with copper slag as replacement of aggregates, varying the particle sizes used in the range from 2.5 to 0.08 mm to determine the size of copper slag with the best performance. Indirect tensile strength tests were used to analyze samples subjected to different moisture and temperature conditions and ageing degrees. The results show that copper slag can be used as aggregate replacement in asphalt mixes when the proper size is selected. The strength of the asphalt mixture increased as the size of the copper slag increased, especially under variable moisture and ageing conditions. Superior behaviour compared to a reference mixture was obtained when replacing the size of aggregate No. 8 with copper slag, increasing its indirect tensile strength and retained strength, reducing its stiffness under all the ageing periods, and being equally effective at the different temperatures, which results in mixtures with improved durability and delayed cracking. Furthermore, it would help to reduce between 15 and 20% of the virgin aggregate needed to produce asphalt mixes and it would also allow reducing the accumulated volume of this waste, decreasing the environmental impact of both industries.

### 1. Introduction

The road infrastructure has increased prominently worldwide during the last century, in order to provide adequate road infrastructure for transportation services both for goods and population. In the particular case of Chile, the extension of the road infrastructure during the last two decades was increased nearly ten times, asphalt mixtures being the most commonly used road material in the road infrastructure. The expected population and economic growth in Chile, and therefore the growth of the traffic over the existing infrastructure as well as the necessity of new infrastructure to fulfill the needs of a growing economy lead to the necessity of looking for alternative sources of raw materials to be used in the production of asphalt pavements.

Looking for alternative and environmentally friendly aggregate sources for use in asphalt mixtures is an important factor that can help to mitigate both the environmental impact of asphalt mixtures and the production costs (Jahanbakhsh et al., 2020). There are different residues and industrial by-products that were studied as potential replacements of virgin aggregates in asphalt mixtures, highlighting reclaimed asphalt pavements (RAP) (Botella et al., 2016; Hidalgo et al., 2020; Miró et al., 2011; Mogawer et al., 2012; Pradyumna et al., 2013; Valdés et al., 2011) or by-products from steel production (Chen and Wei, 2016; Fakhri and Ahmadi, 2017; Masoudi et al., 2017; Moreno-Navarro et al., 2016), among others. These materials showed to provide good mechanical characteristics to asphalt mixtures when used correctly, and hence were highlighted as good alternatives for virgin aggregate replacement in

\* Corresponding author.

E-mail addresses: [aitor.raposeiras@uach.cl](mailto:aitor.raposeiras@uach.cl), [araposeiras@usal.es](mailto:araposeiras@usal.es) (A.C. Raposeiras).

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areas where they are available.

Chile is the world's principal producer of copper with 30% of global production. The predominance of this raw material generates an economic base that represents about 80% of the industrial activity in Chile (Atienza et al., 2018). A lot of wastes and by-products are generated in the process of obtaining copper. 2.2–3.0 tons of metallurgic slag are generated for each ton of copper, leading to a total yearly production of 4.5 million tons of this waste with an accumulated volume of 50 million tons (Gorai and Jana, 2003; Nazer et al., 2016). This situation generates the necessity of finding solutions to reuse it in order to reduce the stored volume of waste and/or to reduce the quantity that has to be placed in landfills (Chen and Wei, 2016; Gorai and Jana, 2003; Shi et al., 2008).

Studies performed on copper slag (CS) obtained from landfills of copper mining industries in the region of Atacama (Chile) indicate that this material has bonding properties that can be interesting for construction purposes (Nazer et al., 2016). In particular, the chemical composition of CS depends on the source of copper extraction and manufacture, but they normally consist of oxides such as iron (FeO: 30–40%), silicon (SiO<sub>2</sub>: 35–40%), aluminum (Al<sub>2</sub>O<sub>3</sub>: 0–10%) and calcium (CaO: 0–10%) (Gorai and Jana, 2003; Lemouagna et al., 2020). In spite of the components existing in this material, previous studies have shown no evidence of leaching hazards associated with the use of copper slag, being classified as a non-hazardous material (Alter, 2005; Lori et al., 2019; Modarres and Bengar, 2019).

Additionally, CS has shown to have good physicochemical characteristics such as good wear resistance, hydrophobic properties and high cohesion, angularity and density, suggesting that this material can be suitable for virgin aggregate replacement in the production of both concrete and asphalt mixtures as well as base and sub-base layers for pavement construction (Dos Anjos et al., 2017; Lidelöw et al., 2017; Nazer et al., 2016; Sharifi et al., 2020; Shi and Qian, 2000). These properties of CS indicate that it can increase mixture adhesion and the interlocking of aggregate particles in asphalt mixes, hence reducing their damage caused by the effects of water, temperature and ageing.

CS is found forming large layers of material in its natural state after the cooling process, so it must be crushed and graded before it can be used as an aggregate replacement. This process is similar to that used for the preparation of natural aggregate, but CS has a higher hardness than aggregate so the crushing process can be more expensive than for conventional aggregate.

The commonly used sizes of CS are smaller than 1 mm, as this material is mainly used in ship hull cleaning (Gorai and Jana, 2003). Therefore, previous research has focused on sizes smaller than this value. However, the use of larger sizes can facilitate the crushing process of the material, and at the same time find applications that allow to increase the amount of CS used and improve the mechanical properties of the material to be modified.

Previous research of asphalt mixtures which incorporate RAP and CS showed a beneficial effect of the inclusion of both materials in dense graded asphalt mixtures in terms of thermal susceptibility and ageing (Raposeiras et al., 2016, 2018). Although CS does not modify the behaviour of the binder and its rheological characteristics at different temperatures, it can help to keep the mix more stable against these changes in pavement temperature due to its thermal behaviour, reducing the variability of durability as a function of temperature variation. In these same studies it could be observed that the properties of the CS varied depending on the particle size, which together with certain siliceous components in its composition, showed that the behavior of the mixture with CS depended on the amount of CS used and the relationship between the proportion and particle size of this material.

The use of CS with a 20% replacement of the mineral skeleton in asphalt mixes improves the results of mechanical resistance to creep, resilient modulus, cracking and water resistance (Ziari et al., 2019). This improvement in the mechanical capacity is achieved without increasing leaching toxicity (Behnood et al., 2015; Lidelöw et al., 2017; Modarres

and Bengar, 2019). In other studies, it has shown that the addition of 5% CS in asphalt mixes increases the resistance to rutting failure by 68% (Abdelfattah et al., 2018). However, the use of a different stabilising agent can also use to reduce the amount of material required to achieve the required strength (Ziari et al., 2016). For dynamic loads, the addition of CS demonstrates a reduction in strength as CS added for the reduced frequencies of the master curves (Hassan and Al-Jabri, 2011). In the case of fine material replacement, the use of CS as a filler in asphalt mixtures improves performance by up to 20% compared to Indirect Tensile Test, resilience modulus and fatigue tests (Choudhary et al., 2018; Modarres and Bengar, 2019). The use of CS material generates more excellent bonding between the larger mineral aggregates in particular (Pundhir et al., 2005), for 17–32% replacement in creep, indirect tension, dynamic modulus and moisture sensitivity tests, better performance is obtained compared to a conventional mix (Havanagi et al., 2007).

All previous studies that include CS in asphalt mixes use the material in the same way as a conventional AG, without any difference in the conditioning, mixing or compaction process, which facilitates its use in asphalt mixing plants. Despite the good results shown in these studies, it was observed that the best behavior is obtained by the coarse sizes when all the sizes of copper slag are used. Therefore, it is necessary to check that using coarse CS sizes improves the properties of the mixture even more than fine sizes of CS. The overall objective of this research is to analyse the influence of CS particle size on different moisture, temperature and ageing conditions to determine the optimum sizes to be used as an aggregate replacement in an asphalt mix.

## 2. Materials and methods

### 2.1. Materials and test plan

For the development of the research, a total of 300 Marshall samples were produced, to be distributed in the tests of moisture damage (36 samples), ageing (120 samples) and thermal susceptibility (144 samples) which are detailed below. Compaction of 75 blows per side were used for the production of the samples, except for moisture damage samples, where 50 blows per side were used. Five different dosages were carried out with replacement of 100% of the volume of aggregate for CS for the sieves from No. 8 to No. 200, together with a series of reference mixture samples manufactured with 100% aggregate (AG). The asphalt mixtures correspond to a semi-dense graded asphalt mixture type IV-A-12 (Table 1), which is equivalent to an AC16S mixture in European classification and serves both as a surface and an intermediate layer according to the Chilean Road Manual.

In addition, an analysis of the heat capacity of both materials (AG and CS) was performed for the different sizes analysed in the research, in order to complement the results obtained in the mechanical tests on asphalt mix samples.

The properties of the materials used are obtained before manufacturing the samples, which are also used to calculate the amount in grams of aggregate and CS to be incorporated in each mixture (Table 2). The CS used is copper smelting slag, which is a residue from

**Table 1**  
Semi-dense gradation IV-A-12.

Sieve size		Percentage passing (%)
mm	ASTM	
20.000	3/4"	100.0
12.500	1/2"	87.5
10.000	3/8"	77.5
5.000	No. 4	50.5
2.500	No. 8	35.0
0.630	No. 30	18.5
0.315	No. 50	12.5
0.160	No. 100	9.0
0.080	No. 200	6.0

**Table 2**  
Properties of AG, CS and asphalt binder CA-24.

	AG	CS		CA-24
Bulk density (g/cm <sup>3</sup> )	2.719	2.803	Penetration at 25 °C (0.1 mm)	59
Water absorption (%)	1.17	0.25	Softening point R&B (°C)	50
Los Angeles wear loss (%)	15.54	12.64	Absolute viscosity 60 °C (Pa·s)	360
Crushed particles (%)	89.21	100.00	Ductility 25 °C (cm)	>150

copper production in central Chile. This material was obtained from slag accumulation areas (dumps) in areas near the smelting plants after the cooling process, where there is a large accumulation of this environmental liability. The slag is cooled in the open air, resulting in slag with glassy characteristics and low water absorption (Table 2). Table 3 shows the components present in the CS used, where the main contents correspond to Fe<sub>2</sub>O<sub>3</sub> y SiO<sub>2</sub>.

For the manufacture of the asphalt mix samples, the CS and conventional AG were conditioned in the same way prior to the mixing process: the materials were heated in an oven at 180 °C for 4 h to remove moisture and raise their temperature.

In this study, the asphalt binder used is CA-24, which is the most widely used in asphalt paving in Chile and it is similar to a B50/70 asphalt binder according to the European classification. This binder was supplied by the company PROBISA, and its physical properties are summarized in Table 2 with the essential characteristics and specifications.

By substituting 100% of the aggregate volume of each sieve, the CS varies between 3.0% and 16.5% depending on the size replaced (Table 4). Since the dosage is done by volume due to the difference in bulk density between the materials, the same percentage of optimum binder obtained for the conventional mixture is used for the manufacture of all the test samples and combinations. The CA-24 binder was heated in an oven to 155 °C in the manufacturing process of the asphalt mixes. The optimal binder content used is 5.2% of binder referred to mixture, which generates 5% of air voids in the mixture. This binder percentage is the one used in previous studies that used the same materials in the reference mix and it was obtained through the Marshall Design (EN 12697-34:2013), evaluating percentages from 4 to 6%, with 0.5% steps. The optimum binder percentage is associated with the amount of binder in which 5% of voids is obtained, which ensures an adequate behavior of the mixture under the usual field conditions according to previous experiences, especially when tested under moisture conditions and permanent deformation.

## 2.2. Moisture damage

Six identical Marshall-type test samples were produced for each combination mentioned, compacted at 50 blows per side, making a total of 36 samples, which were subdivided into two groups of similar mean densities (three test samples per group). One group of samples was kept dry, at a temperature of 15 °C in a controlled environment, while the other group was conditioned wet with saturation and vacuum processes

**Table 3**  
CS composition.

Oxide	Concentration [%]	Oxide	Concentration [%]
Fe <sub>2</sub> O <sub>3</sub>	68.85	K <sub>2</sub> O	0.55
SiO <sub>2</sub>	19.08	SO <sub>3</sub>	0.73
ZnO	2.26	TiO <sub>2</sub>	0.31
CaO	2.07	PbO <sub>2</sub>	0.12
Al <sub>2</sub> O <sub>3</sub>	2.59	CoO	0.12
CuO	1.08	MnO <sub>2</sub>	0.11
MgO	0.95	MoO <sub>3</sub>	0.09
Na <sub>2</sub> O	0.75	Other	<0.09

**Table 4**  
Materials combination by volume.

Combination	Sieve size		CS (% vol.)	Aggregate (%vol.)
	mm	ASTM		
M1	–	–	0.0	100.0
M2	2.500	No. 8	15.5	84.5
M3	0.630	No. 30	16.5	83.5
M4	0.315	No. 50	6.0	94.0
M5	0.160	No. 100	3.5	96.5
M6	0.080	No. 200	3.0	97.0

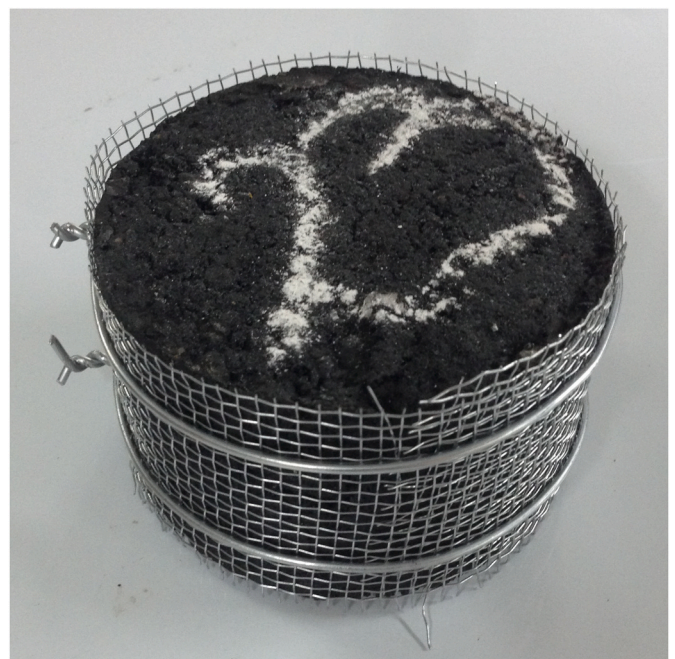
at a pressure of 50 mmHg, subsequent immersion at a temperature of 40 °C for 72 h, and finally wet conditioning at a temperature of 15 °C, to finally perform indirect tensile strength (IDT) tests on each sample and establish the retained strength ratio in percentage. The water absorption of the samples was determined after the vacuum process of the samples and before introducing them into the water bath at 40 °C, comparing the variation in volume before and after vacuum conditioning.

## 2.3. Accelerated ageing

A total of 120 Marshall-type samples were manufactured, with 20 samples for each combination, considering periods of 0, 5, 20, 40 and 72 h and four identical samples for the combination and ageing period. The samples were subjected to an accelerated thermal ageing process once the manufacturing process was finished, introducing them into an oven with forced ventilation at a constant temperature of 163 °C. For this purpose, the samples had to be prepared by wrapping them laterally with a metal mesh (Fig. 1) to prevent them from crumbling due to the high temperature to which they were exposed. Once the ageing period had elapsed, they were removed from the oven, then they were left to rest for a period of 24–48 h and subsequently the indirect tensile test was made to obtain their IDT values.

## 2.4. Thermal susceptibility

144 Marshall samples were produced for this test. Each sample was thermally conditioned for 6 h. Conditioning temperatures of –30 °C, –10 °C, 10 °C, 25 °C, 40 °C and 60 °C were analysed, and four identical



**Fig. 1.** Sample preparation for accelerated ageing.

Marshall samples were used for each combination and temperature previously mentioned. The indirect tensile test was carried out right after the 6 h of conditioning, to determine the resistance of the samples and their behaviour under thermal variations.

### 2.5. Heat capacity

A thermal study was carried out by subjecting aggregate (AG) and copper slag (CS) samples of different sizes to two thermal cycles: a cooling cycle in a cold chamber at  $-25\text{ }^{\circ}\text{C}$ ; and a heating cycle in a forced-ventilated oven at  $170\text{ }^{\circ}\text{C}$ . Samples of 1000 g were generated for each material (AG and CS), with particle sizes from 5000 to 2500 mm (ASTM No. 8), from 2500 mm–0.315 mm (ASTM No. 30+No. 50) and from 0.315 mm to 0.080 mm (ASTM No. 100+No. 200), resulting in a total of 6 analysed combinations.

Temperature control was performed with a Hti model HT-18 thermographic camera (thermal sensitivity  $0.07\text{ }^{\circ}\text{C}$ ), measuring the temperature every 15 min in the initial stage, until the first 100 min or until the stable temperature (cooling or heating) was reached. Subsequently, the samples were left at this temperature for another 60 min, and finally left at room temperature until reaching again the thermal equilibrium at a temperature of approximately  $24\text{ }^{\circ}\text{C}$ , controlling its temperature every 15 min in this phase. It was considered that the sample reached its stable temperature when there was a difference less than or equal to  $0.2\text{ }^{\circ}\text{C}$  in consecutive measurements.

## 3. Results and discussion

### 3.1. Moisture damage test

The water absorption results of each combination were analysed in the first phase of the test, evaluating the variation in volume of the vacuum-conditioned samples. The values obtained show that water absorption is reduced in mixtures with CS compared to the reference mixture (Table 5). The absorption values decrease as the size of the CS decreases, reaching values close to 1%. This reduction in absorption is produced because the AG has a higher binder absorption than the CS and causes a small increase in the effective air void percentage of the mixture.

Once the rest of the conditioning process was completed, the IDT test was carried out (Fig. 2). The results show that the reference mixture obtains an adequate value under dry conditioning, but its IDT strength under moisture conditions decreases markedly. The siliceous aggregate used shows poor water behaviour, with low adhesiveness, due to the acid nature of the aggregates used.

The behaviour of the mixture varies when using CS to replace the aggregate. The smaller sizes of CS analysed have low adhesion with the binder, and reduce the IDT strength in both dry and wet conditions. CS has an acidic character due to its composition (Raposeiras et al., 2018), similar to the aggregate character in the reference samples, and the CS also has slightly rough faces, which accentuate the loss of adhesiveness, especially when dealing with the smallest particles in the mixture.

However, the behaviour of the mixture improves as the size of the CS increases and the aggregate is reoccupied in the smaller sizes, increasing its strength in both dry and wet conditions. Smaller sizes of CS cause less

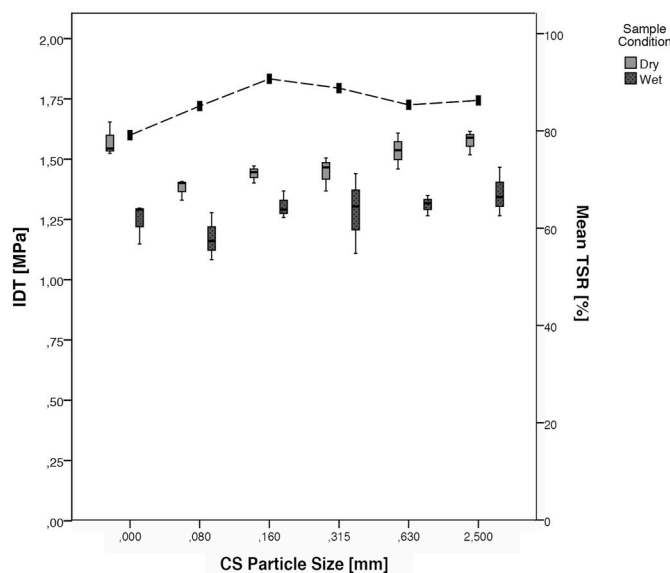


Fig. 2. IDT and TSR for moisture damage test.

adhesiveness in the mastic asphalt, which reduces the strength of the mix in wet conditions, while large particles of CS reinforce the skeleton of the mix. In this case, the characteristics of high hardness and high number of fracture faces help to increase the particle interlocking of the mineral skeleton of the mixture, increasing the resistance, both in dry and wet conditions, while adhesiveness is provided by the smaller AG particles.

According to Spanish regulations, it must be obtained a retained strength ratio (TSR) value greater than 85% in order for a mixture to be used as a surface layer, while it must exceed the TSR value of 80% for its use as a base or intermediate layer. The lower TSR value is obtained in the reference mixture, due to the low results obtained in wet conditions, causing it not to be used in any of the asphalt layers of the pavement. This behavior is mainly due to the low adhesiveness provided by the fine aggregate.

It is also observed that all mixtures with CS obtain TSR values higher than 85%, which indicates a more balanced behavior in the mixture in comparison with the AG. Based on the IDT strength absolute results and the TSR values, the large size of CS shows better behaviour against moisture.

Using CS as a replacement for aggregate in intermediate and coarse sizes, from 0.630 mm to 2.500 mm, improves the performance of the mixtures against adhesiveness tests in comparison to conventional mixtures manufactured with 100% siliceous aggregates, since the IDT dry strength values are maintained but the loss of adhesiveness and strength caused by the water in the mixture is reduced. The finer particles of CS reduce the dry strength of the mixture due to its low affinity with the binder and its slightly rough surface, and under wet conditions do not improve the behaviour of siliceous aggregates. Even so, all mixtures with CS as an aggregate replacement improve the TSR values of the reference mixture analysed, meeting the requirements to be used as a surface layer.

When performing variance and correlation analyses controlled by type of conditioning, it is verified that the size of CS is directly related to the IDT strength obtained in dry conditions (Table 6). It can also be observed that the CS size has a lower influence on wet conditioning ( $\text{sig} = 0.360$ ), as shown in Fig. 2, and these adhesiveness losses can be associated to the acidic character of the CS and its interaction with the binder under moisture conditions.

Table 5  
Water absorption.

Combination	Absorption (%)
M1	8.49
M2	4.44
M3	2.80
M4	2.21
M5	1.36
M6	1.77

**Table 6**  
Partial correlations and ANOVA for IDT and TRS vs. CS particle size controlled by sample condition.

		IDT [MPa]			TRS [%]	
CS Particle Size [mm]	Pearson Correlation	0.530			-0.284	
	Sig. (2-tailed)	0.003			0.136	
	N	27			27	
	Sum of Squares	<b>df</b>	<b>Mean square</b>	<b>F</b>	<b>Sig.</b>	
Dry	Between Groups	0.098	5	0.020	5.598	0.007
	Within Groups	0.042	12	0.004		
	Total	0.141	17			
Wet	Between Groups	0.060	5	0.012	1.214	0.360
	Within Groups	0.119	12	0.010		
	Total	0.180	17			

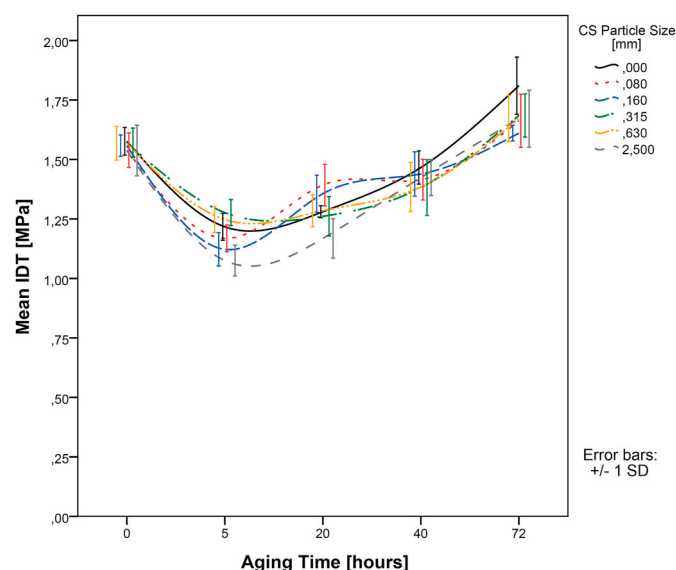
a. Predictors: (Constant), CS Particle Size [mm]rowhead  
b. Dependent Variable: IDT [MPa]rowhead

**3.2. Accelerated ageing test**

The ageing results are shown in Fig. 3. The IDT strength of the samples at 0 h of ageing is practically the same for both the sample with 100% AG and the samples with CS. However, when ageing begins, they tend to lower their strength in a first phase, and then increase it as the ageing hours increase. This is explained by the fact that ageing produces a hardening effect on the samples. The same trend is observed in all mixtures, where the softening of the binder occurs in the first hours, making the sample less resistant, and the strength increases as the hours of ageing increase, due to the hardening produced by the oxidation of the binder and the loss of its volatile components.

The lowest strengths are obtained at 5 and 20 h of ageing, because the greatest volatilization of binder elements is generated in those periods due to the high temperature, so it is losing its properties, causing the aggregates to be less bonded throughout the asphalt mastic. The mixture with the coarsest CS size (M2) also has the largest amount of this material and has the least strength in the short aging periods. The CS used has lower porosity than the AG so the binder flows faster. For this reason, the ageing process in the short term is greater in mixtures with CS due to the greater contact surface of the free binder with air and heat, which is accentuated more in the coarsest size.

The binder solidifies and hardens as the ageing time increases, again



**Fig. 3.** IDT for ageing test.

reducing the exposed surface, and the metallic components of the CS retain more heat in this case, preventing the rest of the components (aggregates and binder) from excessively increasing their temperature, which generates less stiffness and less ageing. All the samples containing CS were kept below the strength of the reference sample during the longest ageing times (40 and 72 h), which indicates that an asphalt pavement with CS will have less stiffness during the useful life than one made only with siliceous aggregate, and therefore, it will have less risk of having a fragile failure and it will take longer to present fatigue failures.

All mixtures with CS reduce the stiffness of the mixture under long-term ageing conditions compared to mixtures manufactured with the siliceous aggregates analysed. Finer CS sizes suffer faster ageing in the short term, but maintain their more gradual ageing in the long term, while coarser CS sizes reduce the stiffness of the mixture over the whole range of ageing periods. Using CS as a replacement for siliceous aggregate in the analysed sizes extends the useful life of the mixture by reducing stiffness, resulting in more ductile behavior over a longer period of time.

The findings in the graphs are validated when performing a correlation analysis (Table 7), since the greatest influence on the IDT strength results is determined by the ageing time (Sig. = 0.000). However, a certain degree of influence can be observed on the size of the CS (Sig. = 0.266). Table 7 also shows the ANOVA for the different aging periods, where it can be noticed that the variation in the CS sizes has the greatest influence in the short aging (5 and 20 h) and in the long term aging (72 h), as shown in Fig. 3.

**3.3. Thermal susceptibility test**

Thermal susceptibility is shown in Fig. 4. The results are mainly ordered based on the conditioning temperature, independent of the quantity and size of the CS used, with maximum strength values for the samples at temperatures of -10 °C and minimum values at temperatures of 60 °C. The differences in behaviour between the different

**Table 7**  
Correlations and ANOVA for IDT vs. CS particle size and ageing time.

		CS Particle Size [mm]		Ageing Time [hours]		
IDT [MPa]rowhead	Pearson Correlation	-0.115		0.472**		
	Sig. (2-tailed)	0.266		0.000		
	N	96		96		
	Sum of Squares	<b>df</b>	<b>Mean square</b>	<b>F</b>	<b>Sig.</b>	
0	Between Groups	0.006	5	0.001	0.216	0.951
	Within Groups	0.092	18	0.005		
	Total	0.098	23			
5	Between Groups	0.108	5	0.022	5.974	0.003
	Within Groups	0.058	16	0.004		
	Total	0.166	21			
20	Between Groups	0.112	5	0.022	4.003	0.015
	Within Groups	0.089	16	0.006		
	Total	0.201	21			
40	Between Groups	0.018	5	0.004	0.454	0.804
	Within Groups	0.129	16	0.008		
	Total	0.147	21			
72	Between Groups	0.088	5	0.018	1.756	0.173
	Within Groups	0.180	18	0.010		
	Total	0.268	23			

a. Predictors: (Constant), CS Particle Size [mm]  
b. Dependent Variable: IDT [MPa]

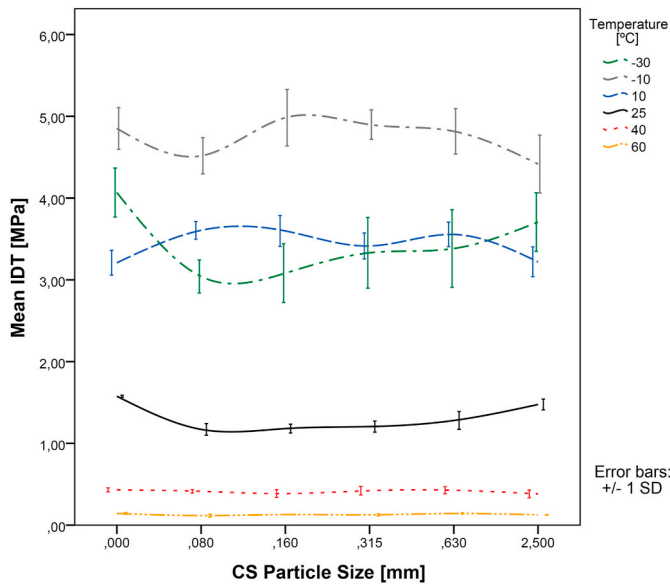


Fig. 4. IDT for thermal susceptibility.

combinations are minimal when the conditioning temperatures are high (40 and 60 °C), since at these temperatures the behaviour is delimited by the reduced strength provided by the softened binder.

Greater differences between combinations begin to appear from 25 °C onwards. The greater strength is presented by the reference mixture at this temperature, and the strength values increase as the size of the CS increases, reaching values similar to the reference mixture. This behavior was expected, since a similar tendency was observed in the moisture damage test in dry conditioned samples.

The stiffness of the mixture increases as the temperature decreases, moving from viscoelastic to elastic behaviour (Lagos-Varas et al., 2019). Once again, the greatest influence on the behaviour will be given by the binder, but differences are beginning to be appreciated between the combinations analysed in this case. There is a noticeable change in stiffness in the reference mixture when the barrier drops below 10 °C. The reference mixture has a low stiffness at this temperature compared to the rest of the combinations, but its behaviour becomes fragile as soon as the temperature decreases, and the greater resistance is obtained due to an excess of stiffness, generating a more fragile break in the mixture. The most balanced behaviour at these temperatures is obtained by combinations with large sizes of CS, since they reduce the stiffness of the mixture but maintain an adequate strength. This behaviour is due to the high hardness of the CS together with less porous fracture faces of the material, allowing a certain degree of creep of the material before generating the break.

CS decreases the stiffness of the mixture at low temperatures when increasing the particle size. However, the behaviour of mixtures at different temperatures is mainly marked by the behaviour of the binder, with the type of aggregate having a much lower incidence. This result is demonstrated by performing the correlation analysis between variables (Table 8), since even with a partial correlation controlled by temperature, the significance of the CS particle size in the sample strength is negligible (Sig. = 0.921). As shown in the ANOVA analysis (Table 8), the influence of CS size at different temperatures is high, especially at room temperature (10–25 °C) and at extreme temperatures (–30 and 60 °C).

### 3.4. Heat capacity test

Figs. 5 and 6 show the thermal conditioning curves of CS and AG samples in the size range analysed in the mechanical tests on asphalt mixtures. These curves present an S-shape with a first part of conditioning up to the limit temperature and a subsequent gradual initial

Table 8

Partial correlations and ANOVA for IDT vs. CS particle size controlled by temperature.

CS Particle Size [mm]		IDT [MPa]				
rowhead		Pearson Correlation	0.009			
		Sig. (2-tailed)	0.921			
		N	117			
		Sum of Squares	df	Mean square	F	Sig.
–30	Between Groups	3.069	5	0.614	4.593	0.007
	Within Groups	2.406	18	0.134		
	Total	5.474	23			
–10	Between Groups	1.028	5	0.206	2.637	0.059
	Within Groups	1.404	18	0.078		
	Total	2.432	23			
10	Between Groups	0.670	5	0.134	5.293	0.004
	Within Groups	0.456	18	0.025		
	Total	1.126	23			
25	Between Groups	0.584	5	0.117	24.298	0.000
	Within Groups	0.087	18	0.005		
	Total	0.671	23			
40	Between Groups	0.009	5	0.002	1.047	0.421
	Within Groups	0.031	18	0.002		
	Total	0.040	23			
60	Between Groups	0.002	5	0.000	3.616	0.019
	Within Groups	0.002	18	0.000		
	Total	0.004	23			

- a. Predictors: (Constant), CS Particle Size [mm]
- b. Dependent Variable: IDT [MPa]

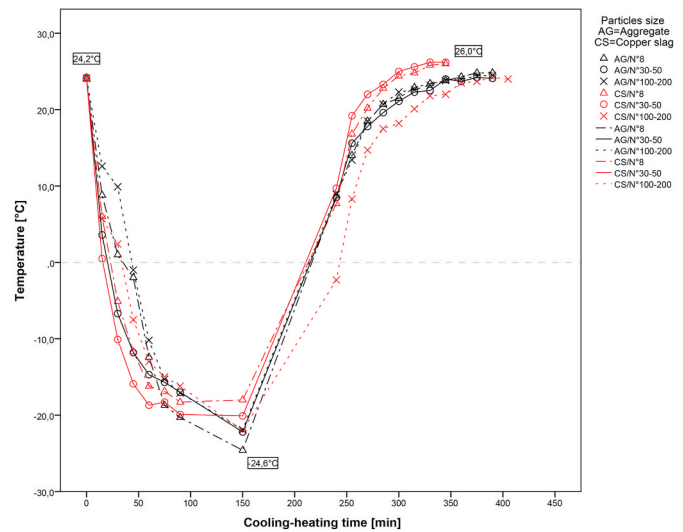


Fig. 5. Cooling cycle for each material and size.

temperature recovery. CS particles with size 0.315 to 0.080 mm present higher temperatures than larger CS particles in the first part of the cooling curve (Fig. 5). Similarly, these small-sized CS particles also present the lowest temperatures in the first part of the heating curve (Fig. 6). This trend changes in the second part of both curves when the system starts its stabilization at room temperature (approx. 24 °C). This difference in amplitude between the CS curves of different sizes shows that CS particles with smaller sizes present a higher thermal inertia than larger particles, generating a steeper S-curve and showing higher resistance to the change of their internal temperature.

This trend is not so clear in AG particles, where the temperature curves for the different particle sizes are similar, except for the boundary cooling zone in Fig. 5. Although the curves obtained for AG and CS particles are similar, less heat energy is required to generate changes in the temperature of CS compared to AG, showing a lower volumetric thermal capacity of this material. This can be observed by analysing the

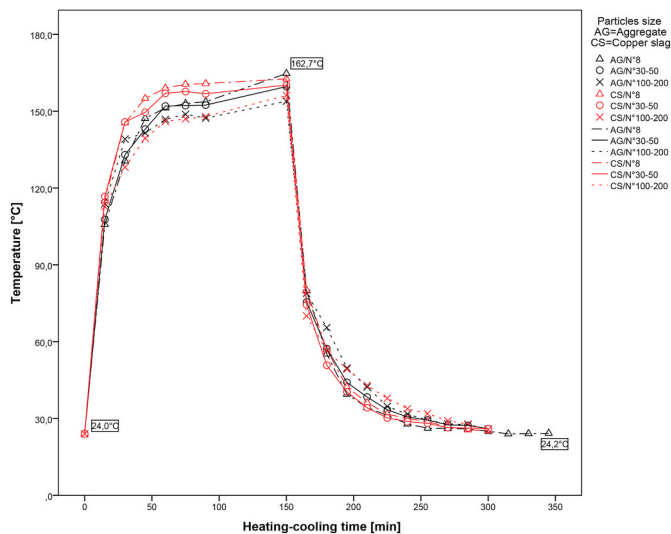


Fig. 6. Heating cycle for each material and size.

temperature changes between particles at consecutive times, in which the same amount of energy has been applied.

These behaviors are related to the results obtained in the ageing (Fig. 3) and thermal susceptibility (Fig. 4) tests. The mixtures with CS presented lower stiffness in both thermal ageing and thermal susceptibility conditions, especially in large CS sizes, due to their higher thermal retention capacity. This thermal capacity of CS can also be observed at the extremes of the curves in Figs. 5 and 6, where this material required less time to reach thermal equilibrium at room temperature. This effect causes the CS to absorb temperature changes faster than the AG, reducing and delaying the thermal change in the asphalt binder, which is reflected in a later stiffening of the latter.

#### 4. Conclusions

Semi-dense graded asphalt mixture incorporating different sizes of CS as partial replacement for the mineral aggregate in the mix have been manufactured and tested. The results obtained indicate that the CS size used influences the strength and durability of the mix. Only some of the sizes analysed allow improving the performance of the mix while others present similar behaviour to silica type aggregates. The following specific conclusions are drawn:

- CS in coarse and medium sizes improves the performance of the mixes compared to conventional mixes. These CS sizes absorb more rapidly the thermal changes that the mixture may suffer and delay the temperature change in the binder, especially in the aggregate-binder bonding zone. Coarse CS sizes reduce both the moisture damage of the mix and medium- and long-term ageing, and the mix exhibits lower stiffness under temperature changes, especially at low temperatures. This CS size is recommended for all types of applications, especially in areas with high temperatures and thermal gradients.
- Fine CS sizes perform poorly against water, with worse results than those obtained with aggregate, even if it is of siliceous type. However, its performance against ageing and thermal changes is slightly better than siliceous aggregate, so this size of CS could be considered if the paving area has no or minimal rainfall.
- CS should be considered as a siliceous aggregate with improved thermal characteristics, being beneficial its use in coarse and medium sizes, and combining it with limestone aggregates in fine sizes. A balanced behavior between ageing, stiffness and adhesiveness can be achieved with this combination of materials, resulting in an increase in durability with respect to conventional mixes.

- Based on the thermal behavior of the coarse and medium sizes of CS, it is estimated that the energy consumption in the production of asphalt mixtures with CS should be lower due to the shorter time required to raise the temperature of the material. In future research, it is proposed to analyze the emission cycle of mixtures with this material as well as durability analysis against fatigue and rutting, in order to establish the environmental impact of these mixtures and their life cycle analysis (LCA).

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#### Credit author statement

A.C. Raposeiras: Conceptualization, Methodology, Formal analysis, Writing – original draft, Project administration; D. Movilla-Quesada: Methodology, Formal analysis, Writing – original draft, Resources; O. Muñoz-Cáceres: Supervision, Data curation, Writing – review & editing; V.C. Andres-Valeri: Formal analysis, Validation, Data curation; M. Lagos-Varas: Supervision, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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