Construction and Building Materials, vol. 190 (2018), pp. 427-438.
https://doi.org/10.1016/j.conbuildmat.2018.09.120
http://www.sciencedirect.com/science/article/pii/S0950061818322980

The use of copper slags as an aggregate replacement in asphalt mixes with RAP: physical-chemical and mechanical behavioural analysis

A.C. Raposeiras[a], D. Movilla-Quesada[a,*], R. Bilbao-Novoa[a], C. Cifuentes[a], G. Ferrer-Norambuena[a], D. Castro-Fresno[b]

[a] *Dept. of Civil Engineering, College of Engineering Sciences, Austral University of Chile, Valdivia, Chile*
[b] *Dept. of Transport and Technology of Projects and Processes, University of Cantabria, Santander, Spain*

ABSTRACT

Copper slag (CS) is a derivative of copper production that is mainly composed of heavy metals. The large amount of this material accumulated around the world entails a serious environmental danger. Its use as a replacement of mineral aggregate in asphalt mixtures would allow to increase the durability and resistance, taking advantage of its physical-chemical properties. In this research, physicochemical analyses of different combinations of CS, reclaimed asphalt pavements (RAP), asphalt cement and aggregates by X-Ray Diffraction (XRD) and Fourier-Transform InfraRed spectroscopy (FT-IR) were developed. Subsequently, Marshall stiffness ratio, indirect tensile strength (IDT) and resilient modulus tests were performed to determine their implication in mechanical behaviour. Asphalt mixes with ranges from 45 to 55% of recycled material have improved stability, Marshall Flow and Stiffness ratio, obtaining values comparable with those from a conventional mixture. At the same time, its resilient modulus and IDT values increased by 35% compared to conventional mixes. To maintain values similar to conventional mixes, when the amount of RAP decreases the amount of CS should be increased, with a maximum value of 35%. This behaviour is explained by the presence of fayalite and magnetite in CS, which are hard, dense and hydrophobic components that produce increased elastic deformation of the binder before breaking.

Keywords: *Copper Slag; Reclaimed Asphalt Pavement; Physical-chemical characterization; Marshall Stiffness; Indirect Tensile Strength; Resilient Modulus*

1. Introduction

Close to 19 million tons of copper are produced annually worldwide. When this primary material is obtained at a concentration between 2 and 2.5 tons of copper slag (CS) per ton of produced copper, this translates into an estimated annual production of close to 42 million tons of copper slag [1, 2]. Due to the origin and formation of this waste, which contains heavy metals such as iron, aluminium, copper, nickel or lead, all in their metallic or oxide form, it is classified as dangerous with a high environmental risk, especially when taking into consideration its leaching potential [3, 4].

This waste currently has minimal industrial use, therefore, it is necessary to transform this sub-product into a useful element for different construction areas, reducing its build-up and treating it to avoid contamination associated to leaching. This also reduces the use of new aggregates and the exploitation of natural resources. The CS has properties even superior to traditional aggregates if it is adequately processed, cooled to the air and crushed, with high angularity, resistance to wear, high density and hydrophobic properties [2, 5], which converts it into an adequate option as an added substitute to improve the mechanical properties both of concrete and asphalt pavements. Its viability as an aggregate has been proven in high resistance concretes, improving their mechanical performance and durability at incorporations of 20% [6–9]. Its use as cement has also been studied, obtaining favourable results for incorporations between 5% and 10% [10].

Some studies have evaluated the use of CS in asphalt mixtures, using the fine size of this material as an aggregate replacement [5, 11, 12]. The results show a decrease in the resilient modulus, a reduction in indirect tensile strength (IDT) but an increase in the tensile-strength ratio and its fatigue life, making its use favourable in asphalt mixes. Due to the characteristics of CS, the decrease of the resilient modulus and IDT can be compensated through the use of copper slags of a larger size, due to the edges that are generated after the last crushing process of the material [13]. In these studies it was also shown that including slags into the mixes covers this in an asphalt binder, eliminating contamination associated to leaching.

Asphalt mixtures with CS as aggregate in all sizes would have a mechanical behaviour similar to that obtained with steel slags, because the most of the chemical components are identical, presenting good values of IDT, resilient modulus or Marshall stability, improving the resistance when compared to traditional mixtures [14–17]. However, the expansive problem associated with steel slag would be avoided due to the low content of calcium present in the copper slag, which would reduce the appearance of cracks in humid environments and prevent the excess rigidity provided by the steel slag.

Another sub-product that helps reduce consumption of primary materials in the making of asphalt mixes is Reclaimed Asphalt Pavement (RAP). The use of RAP reduces manufacturing costs up to 25%, compared to a mixture that requires new primary materials, as a result of the reduced need for new aggregates and the decrease in the consumption of asphalt binders between 25% and 50%, depending on the amount of RAP used [18, 19].

However, the use of RAP is influenced by the binder included in this material, which is found in an aged state and has lost some of its properties. Adding the RAP in its natural state increases the rigidity of the mixtures, being more evident when the amounts of RAP exceed 20%, but satisfactory results have been obtained in asphalt mixes with a RAP content between 10% and 70% if RAP fractions are adequately controlled, and their variability is avoided [19–22]. These investigations show improvements concerning rutting (1 to 2 mm reduction) and moisture damage (increase between 15 and 25 points), but stiffness increases are observed in tests of resilient and dynamic modulus [22]. Adding rejuvenating additives recovers part of the RAP aged binder properties, similar to using softer modified binder that allows improved adhesiveness and penetration of materials, balancing RAP binder stiffness and obtaining a behaviour similar to a conventional mixture [23, 24]. It was observed that in mixtures with 20% RAP and selecting the appropriate rejuvenator the values of Marshall stability, TSR conserved resistance, fatigue life and resilient modulus are increased, and at the same time the rutting and permanent deformation by creep test is reduced in 1 mm and in 20% respectively [25]. In the same way, if an analysis is made for mixtures with 100% RAP and vegetable or petroleum rejuvenators are used, with a 12% addition rate, it is observed that the RAP fulfils the SUPERPAVE requirements regarding to fatigue life and workability, considerably reducing its rigidity and thermal cracking, but the workability does not reach levels of a conventional mixture [24].

There are other investigations where the reactivation of the binder included in the RAP was evaluated through the addition of other materials such as cement or fly ash [25, 26]. The degree of activation generated in the material by the fly ash was determined by X-ray fluorescence (XRF), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) tests, considering that this material includes NaOH and Ca (OH) 2. It was obtained that these existing compounds in the ashes react with the RAP binder, increasing its resistance and modifying the mastic due to its pozzolanic nature [26]. In the case of the addition of cement, an increase in the resistance and the resilient modulus was observed after performing IDT, triaxial and bending tests, which implies an increase in the rigidity of mixtures with RAP [27]. In both cases, an opposite effect to the desired one is obtained due to the limestone component of the materials added, increasing the rigidity of the mixtures with RAP. But it highlights the reactivation of the binder, which means that adding other materials with reduced proportions of limestone components can reactivate the binder without increasing the rigidity in the mix, with no need to use rejuvenators. Precisely the behaviour generated by CS can resolve problems of excessive rigidness associated to the use of RAP in asphalt mixtures, considering that its natural properties can generate characteristics similar or superior to those of a common mixture, without incorporating additives or modified asphalt cements. The presence of iron oxide and silicon dioxide in the CS helps to reduce the rigidity provided by the RAP binder, reducing the hardening of the mastic.

2. Methodology

The tests of this study are divided into two parts, one for the physical-chemical analysis and another for the mechanical analysis. The physical-chemical analysis that allows to determine the components present in the CS, RAP, aggregates and asphalt cement, and to evaluate the chemical interaction and the reactions that take place between the materials to be analysed. X-Ray Diffraction (XRD) tests were carried out to identify the crystalline phases present in the mixture and determine if there are new elements due to some chemical interaction between the materials. Fourier-Transform InfraRed spectroscopy (FT-IR) was also performed to obtain the functional groups and the intensity of these, being able to determine the interaction that exists between the materials analysed. 11 combinations of CS, RAP, aggregates and asphalt cement were carried out for the physical-chemical tests (Table 1), with which the test samples were made, on which a minimum of 4 measurements was made to corroborate the results.

The most usual tests in asphalt mixtures for the mechanical analysis were selected, and at the same time those in which information on the modification in the adhesiveness, rigidity and elastic behaviour of the mixtures is obtained. While there are tests that provide more information on the real durability that these solutions may have, such as fatigue and rutting tests, those that are required by regulations and that in turn are easily replicable were selected, in addition to providing the most information on the effect of the CS on the properties that are sought to be modified.

Marshall stability and flow tests were carried out to determine the maximum compressive strength and its deformability under the effect of water and temperature, since the characteristics of the CS and RAP binder, the combination of these conditions are the most unfavourable. This test was selected as it continues to be considered as a requirement in many regulations worldwide. At the same time, indirect tensile tests (IDT) were carried out, since it allows to evaluate the cohesive capacity of the mixture and the adhesiveness present between materials. Finally, resilient modulus tests were carried out to determine the effect of copper slag on the original rigidity of the RAP, to establish the degree of influence of the copper slag in this parameter. Sixteen material combinations were analysed (Table 2), using 64 test samples for Marshall stability/flow tests and another 64 test samples for the resilient modulus and indirect tensile tests.

2.1. Materials

The materials used are aggregate (AG), RAP, CS and asphalt cement (AC) AC-30 according to the ASTM D3381/D3381M classification. The aggregate used comes from the alluvial deposit, the RAP was obtained from the milling of an asphalt surface layer of a pavement, and the CS came from the CS landfill and was crushed in the sizes required for the research. The company that supplies the CS reported that it was air cooled and that the slags have been accumulated in the landfill for over a year. A previous analysis of the CS was performed to discover their compositions and concentration of heavy metals (Table 3). The highest concentrations obtained correspond to oxides of iron, silicon, zinc, calcium, aluminium and copper, highlighting the elevated concentrations of iron oxide (68.85%) and silicon oxide (19.08%).

Physical characterization of the three aggregates was also performed. No significant differences were observed between AR and RAP, with a density close to 2.700 g/cm3, water absorption of 1.2% and wear of 15.5%. In CS, densities of 3.700 g/cm3, water absorption of less than 0.3%, and wear of 21%, was slightly higher than that obtained for the remaining materials. These differences are explained by the amount of oxide iron, the crystalline structure and the elevated amount of fractured faces that the material present after crushing. The values of the three aggregates meet the requirements to be used as an asphalt mixture for surface layer [28].

There are two types of binder used in this research: the virgin one used as raw material for the sample preparation; and the binder included in the RAP portion. The RAP used included 3.8% of binder for sizes larger than 3/8", 5.2 % for sizes from sieve N8 to N4, and 9.1% for sizes lower than sieve N30. Both binders are AC-30 with the same original characteristics, but the one included in the RAP has lost part of its viscoelastic properties due to the aging during the life service. This aging produced a hardening of the binder and a reduction of the penetration value. The original asphalt cement AC-30 used had a viscosity of 3305 Poise at 60°C, a penetration of 53dmm, a density of 1.029 g/cm3 and its softening point was 50.2°C.

2.2. Manufacture and test assays

For the manufacture of samples for physical-chemical tests, aggregate sizes of approximately 0.06 mm were used, to obtain a homogenous mixture and observe its effects under the microscope. A manual mixture was made in hot conditions for each combination and once each mixture was homogenized, this was extended over a smooth and inert surface to ensure the elimination of any external agents. Samples with a diameter of 20 mm and a width of 2 mm were prepared and then analysed by XRD and FT-IR.

To obtain the mineralogical phases from the sample by XRD, Ni filters of copper K-alpha radiations (30 kV and 10 mA), with ventilation and anti-scattering slots of 1 mm respectively were used and, the diffraction patterns were performed in a range of 5-45° theta degrees, 5 seconds per 0.01° pass. To determine the functional groups and identify the organic compounds in the samples by FT-IR, spectrograms between 550 and 4000 cm-1 were performed.

Marshall samples for the mechanical tests were made by volume dosage of the aggregates due to the difference in CS densities with the remaining materials The percentages shown in Table 2 correspond to 100% of the aggregate volume used, but not to 100% of the volume of sample materials, since this depends on the CS percentage that should be added to the mixture.

To make Marshall samples, a gradation curve of the semi-dense type IV-A-12 mixture was used following the Chilean Road Manual [28], equivalent to a D-4 dense mixture according to the ASTM D3515 regulation. RAP particle size and CS was maintained with the original gradation (Table 4) by using all of the materials retained in each sieve and adding AG to adjust the three materials to the selected mixture gradation curve, taking advantage of all the reused materials. RAP was added to all sieves of the gradation curve meanwhile the slags used were between 9.50 and 0.15 mm.

Asphalt cement AC-30 should be added to all the aggregates previously mentioned, incorporated in its optimum calculated amount according to the Marshall method stipulated by the ASTM D6927, considering the amount of binder provided by the RAP.

Four samples of 101, 6 mm diameter and 63 mm high were prepared for each combination of Marshall stability/flow, IDT and Resilient Modulus. Manually mixing was used, maintaining a temperature of 155 ºC. Both the AG and the CS were heated to 175 ° C while the binder was heated to 155 ° C and the RAP to 80 ° C to prevent over-ageing of the existing binder. For Marshall stability/flow, samples were conditioned at 60°C during 30 minutes in a water bath, according to the ASTM D6927 standard. In the case of IDT, samples were conditioned in dry conditions during 6 hours at 25°C, according to ASTM D6931. To determine the Resilient Modulus samples were conditioned at 15°C during the 24 hours previous to the tests, following the ASTM D7369 standard.

3. Results

3.1. Physical-chemical tests

Once the samples are made with the required dimensions, physical-chemical tests were performed. Firstly, the combinations were analysed by XRD (Fig. 1). The XRD patterns indicate that the CS used (Fig. 1.A) has iron and silica based oxide minerals, such as magnetite (Fe_3O_4) and fayalite (Fe_2SiO_4), compounds that have a high density and are hard (Table 5) [29,30]. The results are similar to those obtained in other researches, except that in this case there is no significant presence of calcium components [31].

The XRD pattern of the AG sample (Fig. 1.B) presented quartz (SiO_2), albite ($NaAlSi_3O_8$), and muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$) as the main phases. Quartz and albite are harder than muscovite, however, the three phases have a low density compared to the minerals in the CS (Table 5).

The XRD pattern of the AC-30 (Fig. 1.C) is identified only with the asphalt element, and the RAP sample (Fig. 1.D) has a combination of the elements present in the AR and AC-30 samples, since this material is a mixture of both, therefore, this type of analysis cannot distinguish differences between the base components and the AC-30.

In the samples with combinations of the different materials (Fig. 2) the obtained elements are the sum of the individual elements in each material in an individual manner. This indicates that a chemical interaction is not produced between elements; therefore, the adherence between them is mechanic.

Through the FT-IR analysis, the functional groups for each material and combinations were identified (Fig. 3). In all the materials the presence of humidity resulted in stretching of the OH- from the water molecule between 3450 and 1625 cm-1 [32]. The spectrograms performed for each of the CS samples (Fig. 3.A) showed peaks in the bands 875 and 566 cm-1, corresponding to Si-O stretching and Si-O distortion of the u3 mode in SiO_4, respectively [33]. Vibrations associated to u4 (O–Si–O) in the range of 600 and 500 cm-1 were identified, which indicated that CS vibrations are related to the Si-O bonds [34]. The high presence of Si-O bonds agrees with what was obtained in other researches [31], which indicates that the CS will have a behaviour similar to acidic siliceous aggregates.

Vibrations were identified in spectrograms, where AG and/or RAP were used, (Fig. 3.B, C) between the bands 900 and 1200 cm-1 which represent stretching in the Si-O, reaffirming the presence of silicates and aluminosilicate in the mixtures. In the bands 2920, 2852 and 1458 cm-1, stretching between carbons and hydrogens was observed, elements that belong to hydrocarbons, compounds that form part of the structure of petrol, identifying the presence of AC-30 (Fig. 3D). All the combinations with AC-30 (Fig.

4) had phenol groups, hydrocarbons and carbonyl groups, which have great strength within their bonds, working as a binder and providing structural properties to the mixture.

3.2. Mechanical tests

For mechanical tests, Marshall samples were made with the optimal percentage of binder, according to the ASTM D6927 standard, considering the amount of binder provided by the RAP. Marshall stability and flow, Indirect Tensile Strength (IDT) and resilient modulus were measured.

Fig. 5 shows the results of Marshall stability for all the combinations. All of them exceed 9.0 kN, which is the minimum value set according to the normative for the tread layer. In mixes that only included AG and RAP, the values of maximum stability increase in percentages that vary from 40 to 80% as the amount of RAP increases. Stability values between 16 and 23 kN were obtained, with a similar behaviour observed in previous studies, where these values were between 15 and 18kN for mixtures between 40% and 60% RAP [19].

However, when adding CS, variable results for Marshall stability were obtained. In mixes without RAP, the CS increases to maximum resistance at higher CS levels, passing from 12 kN in the conventional mixture to 15 kN in mixes with 35%. This is due to the elevated stiffness and shape of the CS and its affinity with the binder, which increases the final resistance of the mixture.

In samples where both materials take action, the increases in resistance were compensated. For mixes with 20% RAP, the highest Marshall stability values were obtained with CS of 15%, but the results closest to the conventional mixtures were obtained with a 35% CS. In mixes with 30% RAP, the results obtained with 25% CS were similar to a conventional mixture, meanwhile the rest of the CS amounts increased mixture stability values. In regards to mixtures with a RAP of 40%, adding 15% CS achieves resistances higher than a conventional mixture; meanwhile the remaining CS proportions increases the parameter to values between 16 and 18 kN.

In these cases, the CS is affected by aging of the binder provided by RAP. Although it was not possible to obtain the penetration of binder included in the RAP nor its viscosity, its workability was lower compared to the virgin binder AC-30 used. The CS does not cover itself properly in the aged binder, showing higher affinity with the virgin binder, decreasing the final resistance of the mixture. The virgin binder had a high viscosity and greater workability, suitably coating the CS. This effect becomes more evident as the amount of RAP increases and the amount of new binder decreases. However, the resistances obtained are superior to the conventional mixture, decreasing the stiffness of RAP mixtures.

The flow results show behaviours that correlate with the previous (Fig. 6). The conventional mixture has expected values, located halfway within the interval required by regulation, between 2 and 4 mm of deformation. In mixtures that only RAP is included, as the amount of RAP increases deformation also increases, obtaining values close to the maximum deformation limit for mixtures with 40% RAP, but always within the permitted values. These values are slightly higher than those obtained in other studies where flow was maintained at values below 3 mm [19], which could be explained by the difference in the binders used and the degree of ageing of them.

Adding CS varies the behaviour of the mixture. In mixtures without RAP, adding CS increases mixture flow, increasing deformation to values close to the maximum limit, therefore, in these cases the best result is obtained at CS concentrations of 15%. This is due to the fact that CS, as a result of their hydrophobic characteristics, do not absorb part of the mixture binder unlike traditional aggregate, but rather adheres to the surface, allowing deformation of the binder before rupture of the mixture. This deformation is also affected by the conditioning temperature (60°C), which increases viscous behaviour and avoids fragile rupture of the binder.

By combining the RAP and the CS, the properties of both materials compensate and stabilise the deformations (flow) that are formed in the mixture. When 20% RAP is used, it is only appropriate to include 35% CS, obtaining values similar to the conventional mixture, while the rest of the amounts of CS exceed the allowed deformation values.

For mixtures with 30% RAP, adding CS also reduces flow, but in this case, all CS quantities comply with the regulations and resemble the conventional mixture. As in the previous case, when the amount of CS is increased, the deformation in the mixture is reduced.

Finally, in mixtures with 40% RAP, it is only possible to add the lowest CS dosage (15%), since the rest of the quantities exceed the permitted flow values. Using 15% CS, values similar to a conventional mixture are again obtained.

In these cases, increased deformation is due to the decrease of new binder, which provokes a higher increase of freedom of movement in the mixture aggregates due to the lack of adhesiveness. The reduction in deformation provoked by CS is due to the particles of the material that anchor to the rest of the aggregates due to their fracture surfaces.

Fig. 7 shows the Marshall stiffness index, where stability and flow of the Marshall tests are related. The conventional mixture shows an index close to 4.0 kN/mm, lower than the usual one (6.5 kN/mm) [19] , but higher than the recommended minimum, which stands at 3.0 kN/mm. These results are caused by low stability values, which is due to a poor affinity of the aggregate and the binder.

Mixtures that only include RAP have a higher index, with values between 4.5 and 5.5 kN/mm, and closer to those obtained in previous researches [19]. When CS is incorporated, the stiffness index varies always following the same trend, with an initial increase in stiffness when using 15% CS, a subsequent decrease when using 25% EC, and a new increase to include 35% CS. The trend is lower marked in the case of 40% RAP, due to the greater variability found in the results. It is observed that this behaviour is inversely related to the flow increase that the mixtures suffer.

The Marshall Stiffness ratio showed that the best flow relation is obtained for values between 25% and 35% for any amount to RAP, obtaining relations similar to a conventional mixture, and close to 4.0 kN/mm (Fig. 7). However, in the case of 40% RAP the results of the flow test should be taken into consideration, employing only 15% CS, obtaining values with high Marshall Stiffness with this provision, between 5.0 and 5.5 kN/mm, appropriate for their use in projects. In all the analysed cases the adequate stiffness values were obtained for their use in surface layers, since their index is situated below 8.0 kN/mm established as a maximum limit that does not compromise durability when mixtures are prepared with RAP [19].

The results of IDT tests present behaviour complementary to the previous (Fig. 8). In mixes without CS, when adding RAP the IDT value increases due to the increase of stiffness provided by the aged binder. This behaviour is expected based on previous researches where the same phenomenon happened [19, 22]. In mixtures without RAP, the use of CS does not affect its IDT parameters, remaining at values close to those of the conventional mixture for any of the CS provisions used

The combination of both materials reduces the IDT values, maintaining above the values obtained for a conventional mixture. Adding 35% CS in mixtures with 20% RAP does not modify the behaviour, however lower provisions of CS reduce resistance. In mixtures with 30% RAP resistance is reduced with 35% CS, and the resistance for the remaining provisions increases. The resistance in mixtures with 40% RAP increases with 15% CS and the remaining resources decrease their resistance.

When analysing the results of the resilient modulus the same behaviour was observed (Fig. 9), with increases in the resilient modulus in mixtures without CS as the amount of RAP increased, and no variations were found to the module when CS is added to mixtures without RAP; with reductions in this parameter when both materials were combined.

This behaviour, both in IDT assays and in the resilient modulus, is a result of the new binder that adheres with more strength to the aggregate covered by aged binder that included RAP than to the rest of the materials, and this adhesiveness does not present significant differences between aggregate and CS. However, when both are combined, the new binder, due to its increased affinity to RAP, reduces its affinity with CS, allowing increased movement in this type of mixture. This indicates that adding CS reduces IDT resistance and resilient modulus, but is always within the permitted parameters and higher than in conventional mixtures.

4. Analysis of the results

An analysis of the correlation between variables was performed to determine their statistic influence on the materials analysed in the results section, obtained in the different tests (Table 6). Also, based on the previous analysis of the results, the effect of the combination of both materials in the mixture was included in the analysis. The analysis shows that RAP has a direct influence on the results of all the tests, except for the flow assay. This relation implies that as RAP increases, the values obtained in the test also increase, becoming more evident in IDT and resilient modulus tests, where the relation is close to 0.80. This verifies the observations in graphs, where modifications to behaviour induced by RAP can be observed, similar to that obtained in previous studies.

On the other hand, the CS has a minor influence on the behaviour of the mixture, since only a high correlation is observed in Marshall flow and stiffness, while in the rest of the tests the correlation is lost. It is observed that the values of correlation are low, always lower than 0.32 and with inverse relation, except the flow test. This behaviour shows that as the amount of CS increases the Marshall stability and stiffness, IDT and resilient modulus values are reduced, which indicates that the CS has little effect on the mixture but compression results are more affected than tensile results.

The combinations of CS+RAP show a high significance, especially in IDT, resilient modulus and Marshall stability tests. A high correlation is observed in indirect tensile strength tests, with values higher than 0.50. The combination of materials shows that as the amount of replacement material (RAP+CS) is increased the strength but also the elasticity of the mixture increases.

These results indicate that the CS by itself does not generate the desired positive effect, but the combination of this material with RAP does produce an increase in resistance while reducing the stiffness added by the RAP.

To obtain a more detailed analysis on the influence of each material, a particle size analysis of the aggregates was performed, dividing each one of them in a fine and a coarse fraction, separated by the amount of material retained in the N°30 sieve, considering fine aggregates below the N°30 sieve and coarse aggregates above this size. At the same time, the relative contribution of both the fine and coarse component was calculated for each material in different mixtures. A normality test was performed to determine the relation between assay results with the particle size of each aggregate (fine and coarse fraction). Additionally a correlation between the behaviour characteristics, previously mentioned, with the percentage of total binder of each sample was obtained (Table 7).

Stability, IDT and resilient modulus correlate with RAP in both fractions and with fine aggregate but not with CS and coarse aggregate, increasing the RAP parameter and decreasing the fine aggregate as its proportion increases in the mixture. The percentage of binder used also affects this value, decreasing as the percentage increases. Both fractions of RAP are the ones that most affect these results, with Pearson correlation values between 0.50 and 0.60. The increase in the amounts of RAP causes a noticeable increase in the strength of the mixture both tensile and compression, due to the hardening of the mixture, but also increases stiffness. This behaviour is the opposite of that observed with the fine aggregate.

Flow is affected by CS, aggregate and binder, but RAP is not related to this parameter. Both CS sizes have a direct relation with flow, like the binder. However, the aggregate has an inverse relation, with an increased influence on fine aggregate. The most important material in the flow of the mixture is the amount of binder. As this material increases, the deformation of the sample increases, mainly associated with the greater area affected by the water and the temperature at which the test is carried out (60 ºC), which softens the material and directly affects the flow.

In regards to Marshall stiffness, all the materials influenced on this parameter, except for aggregate. The same analysis of the graphs was performed, observing increased influence of RAP, which has a direct and positive affect, meanwhile the binder and CS also present an elevated but inverse relation, independent of the size of the material. The aggregate has a low relation, especially in coarse aggregate, which does not affect stiffness. The RAP and the amount of binder generate the most significant modification of this parameter. These results are explained because of the increase in Marshall stability, and the greater increase in flow generated by the binder, which is reflected in the Marshall stiffness index, as it is a relationship of the stability and flow parameters.

By performing a controlled partial correlation of RAP, no significant relationships between CS, AR and binder with IDT or resilient modulus were found. This suggests that RAP has a stronger influence on these characteristics of the asphalt mixture. This partial correlation allowed the identification of coarse aggregates that positively correlate with stability, which was not observed with fine aggregates (Table 8). Also, a positive relation was obtained, significant between the presence of fine and coarse CS, the fine AR and the percentage of binder in regards to flow, which indicates that these materials directly affect this property independently of the presence of RAP in the mixture. However, it is observed that again this property depends mainly on the binder, increasing the flow values when the binder dosage increases, as it was observed in Table 7.

The analysis of the results shows that it is finally the RAP that directly affects the resistance, but also increases the stiffness of the mixture. The combination of materials CS+RAP helps to reduce that stiffness while maintaining adequate resistance values resistance. Regarding the Marshall flow and softening of the mixture, this is affected mainly by the amount of binder, and since these properties are not related to the amount of RAP, it can be deduced that it does not influence whether the binder is aged or not.

5. Conclusions

The following conclusions can be made on the effect of CS and RAP in asphalt mixtures:

A general chemical reaction between the different analysed materials in the asphalt mixtures is not produced, generating adhesiveness between these materials only in a mechanical manner. The resistance of the mixture depends on the stiffness of the materials and the cohesive bonds present in the binder.

RAP present in the mixture increases all the resistance values, both Marshall Stability and IDT, thanks to the affinity of the new binder with the existing RAP.

The presence of CS controls Marshall Stability and excessive IDT provided by RAP, reducing values to those similar to a conventional mixture.

CS reduces flow and resilient modulus values in mixes with RAP to values similar to a conventional mixture thanks to the shape of the material. If the combination between RAP and CS is not adequate, both parameters will increase due to the high amount of binder bounded to RAP.

The use of CS is beneficial to mixtures with RAP when the combination of these materials is located in the range between 45 and 55% over the total aggregate volume of the mixture. The use of CS in mixtures without RAP does not modify its behaviour in a sensible way, but its use must be limited to low concentrations.

The size of RAP or CS does not affect behaviour of the mixture; the amount of material is more influential than its size. However, the amount of fine AR does affect the properties of the asphalt mixture, worsening the behaviour as its proportion with the rest of the materials increases.

It is necessary to carry out moisture damage, fatigue and rutting tests in the future to establish the overall behaviour of the analysed mixtures and evaluate their durability. These tests allow determining the effect of water in the mixture, its behaviour against plastic deformations and its durability under repetition of loads at different temperatures and load frequencies.

Acknowledgements

These results are part of a project funded by: the Universidad Austral de Chile [DID S-2014-27]; and a CONICYT-Chile project [FONDECYT Initiation into Research No. 11140889]. The authors also would like to thank BITUMIX S.A. and its CDI, GIMACH LTDA. and the Regional Laboratory of Transportation of the Ministry of Public Works of Valdivia for the material donations and facilitation of their dependencies.

References

[1] Davenport, W.G., King, M.J., Schlesinger, M.E., Biswas, A.K., Extractive metallurgy of copper, Elsevier, 2002.
[2] Gorai, B., Jana, R.K., Characteristics and utilisation of copper slag—a review, Resources, Conservation and Recycling. 39 (2003) 299–313. doi:http://dx.doi.org/10.1016/S0921-3449(02)00171-4.
[3] Alp, I., Deveci, H., Süngün, H., Utilization of flotation wastes of copper slag as raw material in cement production, Journal of Hazardous Materials. 159 (2008) 390–395. doi:http://dx.doi.org/10.1016/j.jhazmat.2008.02.056.
[4] Vítková, M., Ettler, V., Mihaljevič, M., Šebek, O., Effect of sample preparation on contaminant leaching from copper smelting slag, Journal of Hazardous Materials. 197 (2011) 417–423. doi:http://dx.doi.org/10.1016/j.jhazmat.2011.09.102.
[5] Dhir, R.K., Brito, J. de, Mangabhai, R., Lye, C.Q., 3 - Production and Properties of Copper Slag, in: R.K. Dhir, J. de Brito, R. Mangabhai, C.Q.B.T.-S.C.M.C.S. Lye (Eds.), Woodhead Publishing, 2017: pp. 27–86. doi:https://doi.org/10.1016/B978-0-08-100986-4.00003-1.
[6] Al-Jabri, K.S., Taha, R.A., Al-Hashmi, A., Al-Harthy, A.S., Effect of copper slag and cement by-pass dust addition on mechanical properties of concrete, Construction and Building Materials. 20 (2006) 322–331. doi:http://dx.doi.org/10.1016/j.conbuildmat.2005.01.020.
[7] Al-Jabri, K.S., Al-Saidy, A.H., Taha, R., Effect of copper slag as a fine aggregate on the properties of cement mortars and concrete, Construction and Building Materials. 25 (2011) 933–938. doi:http://dx.doi.org/10.1016/j.conbuildmat.2010.06.090.
[8] Moura, W.A., Gonçalves, J.P., Lima, M.B.L., Copper slag waste as a supplementary cementing material to concrete, Journal of Materials Science. 42 (2007) 2226–2230. doi:http://dx.doi.org/10.1007/s10853-006-0997-4.
[9] Khanzadi, M., Behnood, A., Mechanical properties of high-strength concrete incorporating copper slag as coarse aggregate, Construction and Building Materials. 23 (2009) 2183–2188. doi:http://dx.doi.org/10.1016/j.conbuildmat.2008.12.005.
[10] Zain, M.F.M., Islam, M.N., Radin, S.S., Yap, S.G., Cement-based solidification for the safe disposal of blasted copper slag, Cement and Concrete Composites. 26 (2004) 845–851. doi:http://dx.doi.org/10.1016/j.cemconcomp.2003.08.002.
[11] Chesner, W.H., Collins, R.J., MacKay, M.H., User guidelines for waste and by-product materials in pavement construction (No. FHWA-RD-97-148), 1998.

[12] Hassan, H.F., Al-Jabri, K., Laboratory Evaluation of Hot-Mix Asphalt Concrete Containing Copper Slag Aggregate, Journal of Materials in Civil Engineering. 23 (2010) 879–885. doi:http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0000246.

[13] Behnood, A., Gharehveran, M.M., Asl, F.G., Ameri, M., Effects of copper slag and recycled concrete aggregate on the properties of CIR mixes with bitumen emulsion, rice husk ash, Portland cement and fly ash, Construction and Building Materials. 96 (2015) 172–180. doi:http://dx.doi.org/10.1016/j.conbuildmat.2015.08.021.

[14] Chen, J.-S., Wei, S.-H., Engineering properties and performance of asphalt mixtures incorporating steel slag, Construction and Building Materials. 128 (2016) 148–153. doi:https://doi.org/10.1016/j.conbuildmat.2016.10.027.

[15] Masoudi, S., Abtahi, S.M., Goli, A., Evaluation of electric arc furnace steel slag coarse aggregate in warm mix asphalt subjected to long-term aging, Construction and Building Materials. 135 (2017) 260–266. doi:https://doi.org/10.1016/j.conbuildmat.2016.12.177.

[16] Ahmedzade, P., Sengoz, B., Evaluation of steel slag coarse aggregate in hot mix asphalt concrete, Journal of Hazardous Materials. 165 (2009) 300–305. doi:https://doi.org/10.1016/j.jhazmat.2008.09.105.

[17] Amelian, S., Manian, M., Abtahi, S.M., Goli, A., Moisture sensitivity and mechanical performance assessment of warm mix asphalt containing by-product steel slag, Journal of Cleaner Production. 176 (2018) 329–337. doi:https://doi.org/10.1016/j.jclepro.2017.12.120.

[18] Copeland, A., Reclaimed asphalt pavement in asphalt mixtures: state of the practice (No. FHWA-HRT-11-021), 2011.

[19] Valdés, G., Pérez-Jiménez, F., Miró, R., Martínez, A., Botella, R., Experimental study of recycled asphalt mixtures with high percentages of reclaimed asphalt pavement (RAP), Construction and Building Materials. 25 (2011) 1289–1297. doi:http://dx.doi.org/10.1016/j.conbuildmat.2010.09.016.

[20] Kim, W., Lim, J., Labuz, J.F., Cyclic triaxial testing of recycled asphalt pavement and aggregate base, in: Transportation Research Board 88th Annual Meeting, 2009.

[21] Geng, L., Ren, R., Wang, L., Wang, P., Experimental study of recycled asphalt mixtures containing high rates of reclaimed asphalt pavement, Advances in Civil Engineering and Building Materials. (2012) 473.

[22] Colbert, B., You, Z., The determination of mechanical performance of laboratory produced hot mix asphalt mixtures using controlled RAP and virgin aggregate size fractions, Construction and Building Materials. 26 (2012) 655–662. doi:10.1016/J.CONBUILDMAT.2011.06.068.

[23] Shen, J., Amirkhanian, S., Tang, B., Effects of rejuvenator on performance-based properties of rejuvenated asphalt binder and mixtures, Construction and Building Materials. 21 (2007) 958–964. doi:http://dx.doi.org/10.1016/j.conbuildmat.2006.03.006.

[24] Zaumanis, M., Mallick, R.B., Poulikakos, L., Frank, R., Influence of six rejuvenators on the performance properties of Reclaimed Asphalt Pavement (RAP) binder and 100% recycled asphalt mixtures, Construction and Building Materials. 71 (2014) 538–550. doi:http://dx.doi.org/10.1016/j.conbuildmat.2014.08.073.

[25] Pradyumna, T.A., Mittal, A., Jain, P.K., Characterization of Reclaimed Asphalt Pavement (RAP) for Use in Bituminous Road Construction, Procedia - Social and Behavioral Sciences. 104 (2013) 1149–1157. doi:https://doi.org/10.1016/j.sbspro.2013.11.211.

[26] Saride, S., Avirneni, D., Challapalli, S., Micro-mechanical interaction of activated fly ash mortar and reclaimed asphalt pavement materials, Construction and Building Materials. 123 (2016) 424–435. doi:https://doi.org/10.1016/j.conbuildmat.2016.07.016.

[27] Fedrigo, W., Núñez, W.P., Castañeda López, M.A., Kleinert, T.R., Ceratti, J.A.P., A study on the resilient modulus of cement-treated mixtures of RAP and aggregates using indirect tensile, triaxial and flexural tests, Construction and Building Materials. 171 (2018) 161–169. doi:https://doi.org/10.1016/j.conbuildmat.2018.03.119.

[28] Department of Public Works of Chile, Highway Manual of Chile. Construction general technical specifications. Volume 5. ("Manual de Carreteras de Chile. Especificaciones técnicas generales de construcción. Volumen 5"), (2016).

[29] Blaney, L., Magnetite (Fe3O4): Properties, synthesis, and applications, The Lehigh Review. 15 (2007) 33–81.

[30] Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C., Handbook of mineralogy, Chantilly, VA, 20151-1110, USA, 2011. http://www.handbookofmineralogy.org/.

[31] Nazer, A., Payá, J., Borrachero, M.V., Monzó, J., Use of ancient copper slags in Portland cement and alkali activated cement matrices, Journal of Environmental Management. 167 (2016) 115–123. doi:https://doi.org/10.1016/j.jenvman.2015.11.024.

[32] Darder, M., Gonzalez-Alfaro, Y., Aranda, P., Ruiz-Hitzky, E., Silicate-based multifunctional nanostructured materials with magnetite and Prussian blue: application to cesium uptake, RSC Advances. 4 (2014) 35415–35421. doi:http://dx.doi.org/10.1039/C4RA06023G.

[33] Mihailova, I., Mehandjiev, D., Characterization of fayalite from copper slags, Journal of the University of Chemical Technology and Metallurgy. 45 (2010) 317–326.

[34] Jiménez, A.M.F., Alkaline activated slag cements: influence of variables and process modeling (Cementos de escorias activadas alcalinamente: influencia de las variables y modelización del proceso), Universidad Autónoma de Madrid, 2000.

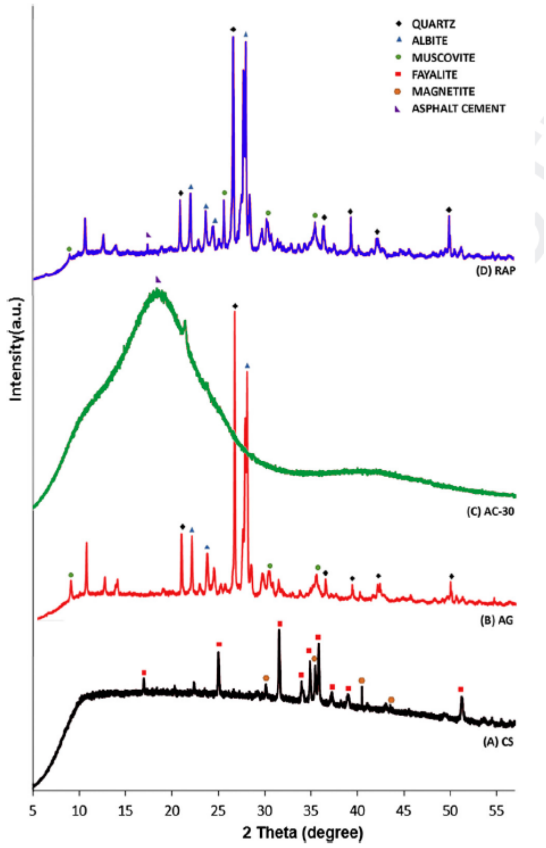

Fig. 1. Individual materials XRD analysis: A, Copper Slag (CS); B, Aggregate (AG); C, Binder (AC-30); D, Reclaimed Asphalt Pavement (RAP).

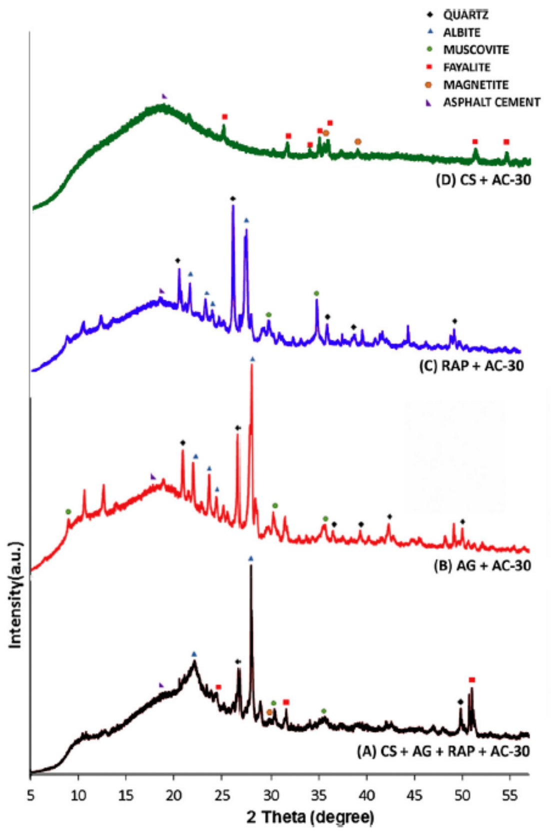

Fig. 2. Materials combinations XRD analysis: A, CS + AG + RAP + AC30; B, AG + AC30; C, RAP + AC30; D, CS + AC30.

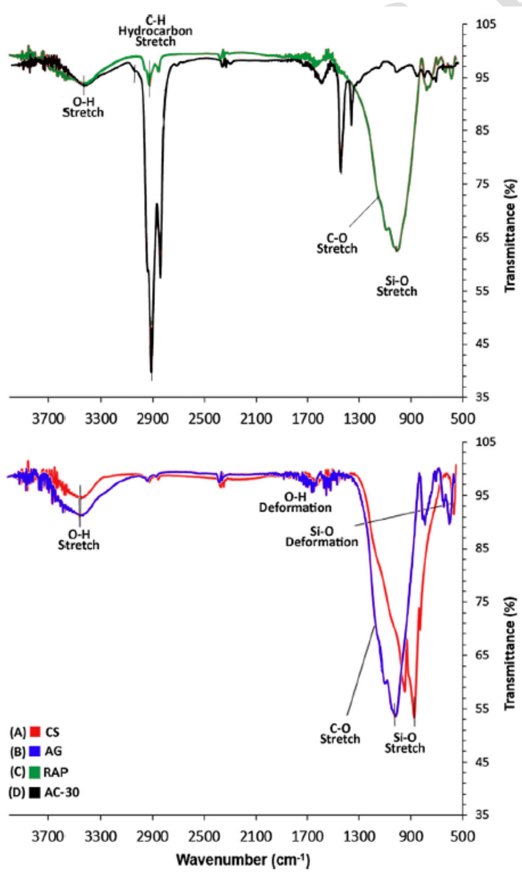

Fig. 3. Individual materials FT-IR analysis: A, Copper Slag (CS); B, Aggregate (AG); C, Reclaimed Asphalt Pavement (RAP); D, Binder (AC-30).

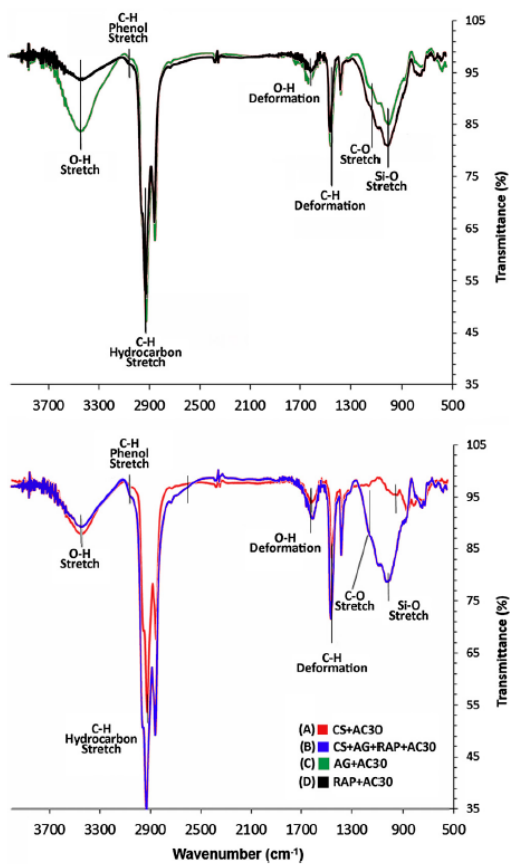

Fig. 4. Materials combinations FT-IR analysis: A, CS + AC30; B, CS + AG + RAP + AC30; C, AG + AC30; D, RAP + AC30.

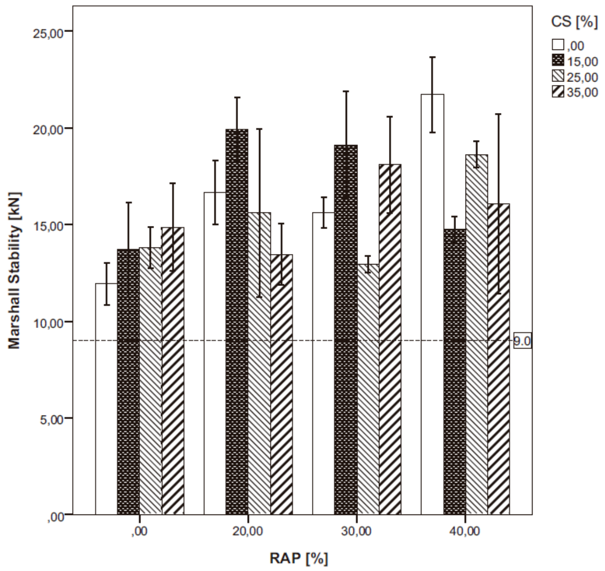

Fig. 5. Marshall stability.

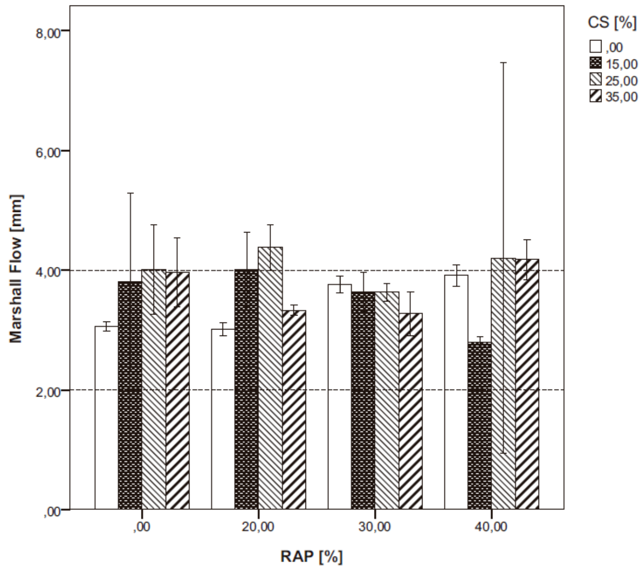

Fig. 6. Marshall flow.

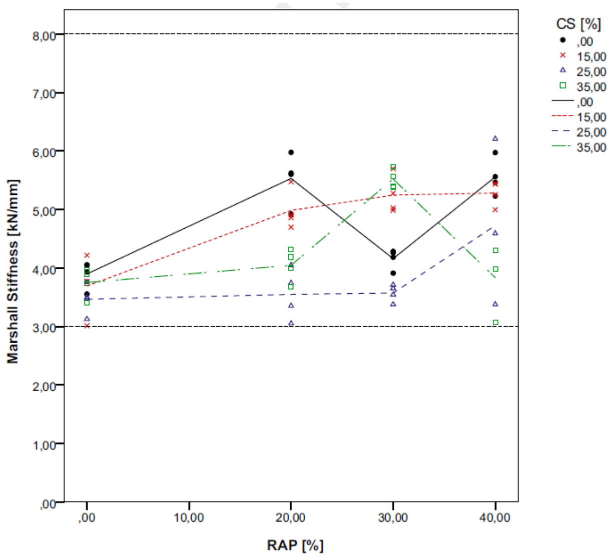

Fig. 7. Marshall stiffness.

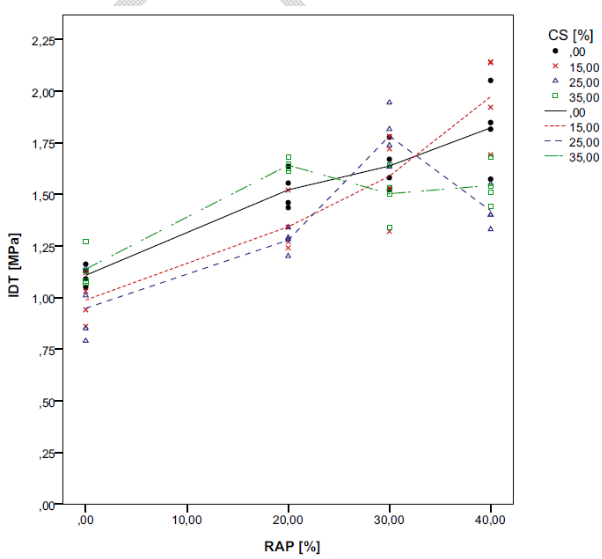

Fig. 8. IDT.

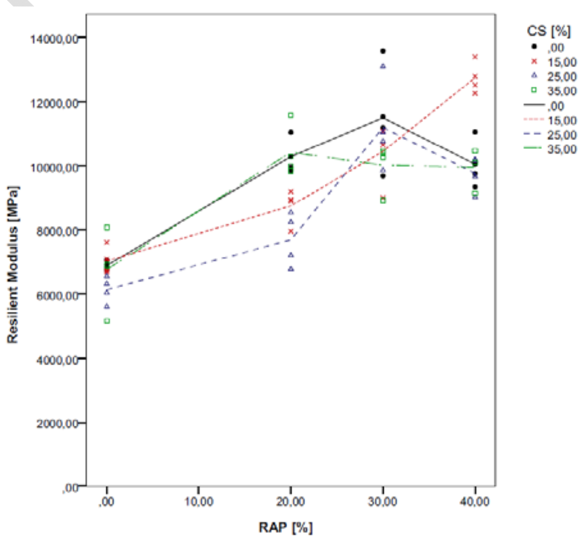

Fig. 9. Resilient modulus.

Table 1
Material combination for physical-chemical tests.

Sample	Material combination	Sample	Material combination
1	CS	7	AC30 + CS + RAP + AG
2	AG	8	AC30 + CS + AG
3	RAP	9	AC30 + AG
4	AC30	10	AC30 + AG + RAP
5	AC30 + CS	11	AC30 + RAP
6	AC30 + CS + RAP		

Table 2
Material combination for mechanical tests.

Material dosages			
Sample	%RAP	%CS	%AG
M1	–	–	100
M2	20	25	55
M3	30	15	55
M4	40	35	25
M5	20	15	65
M6	30	35	35
M7	40	25	35
M8	–	15	85
M9	–	25	75
M10	–	35	65
M11	40	15	45
M12	30	25	45
M13	20	35	45
M14	40	–	60
M15	30	–	70
M16	20	–	80

Table 3
CS composition.

Element	Concentration [%]	Oxide	Concentration [%]
Fe	48.16	Fe_2O_3	68.85
O	34.76	–	–
Si	8.92	SiO_2	19.08
Zn	1.82	ZnO	2.26
Ca	1.48	CaO	2.07
Al	1.37	Al_2O_3	2.59
Cu	0.86	CuO	1.08
Mg	0.57	MgO	0.95
Na	0.55	Na_2O	0.75
K	0.46	K_2O	0.55
S	0.29	SO_3	0.73
Ti	0.18	TiO_2	0.31
Pb	0.10	PbO_2	0.12
Co	0.09	CoO	0.12
Ba	0.07	BaO	0.07
Mn	0.07	MnO_2	0.11
Mo	0.06	MoO_3	0.09
Cr	0.03	Cr_2O_3	0.05
Sb	0.03	Sb_2O_5	0.04
Ni	0.02	NiO	0.03
P	0.02	P_2O_5	0.06
Sn	0.01	SnO_2	0.02
Zr	0.01	ZrO_2	0.02
Sr	0.01	SrO	0.01

Table 4
CS, RAP and IV-A-12 gradations.

	CS		RAP		IV-A-12	
Sieve size	% absolute	% passing	% absolute	% passing	% absolute	% passing
3/4″				100		100
1/2″			5	95	5	95
3/8″		100	13	82	13	82
N4	37	63	30	52	30	52
N8	26	37	15	37	15	37
N30	25	12	23	14	23	14
N50	9	3	8	6	8	6
N100	3	0	4	2	4	2
N200			1	1	1	1
<N200			1	0	1	0

Table 5
Elements mineralogical properties [20,21].

Element	Chemical formula	Hardness [mohs]	Density [G/CM^3]
Magnetite	Fe_3O_4	5.5	5.18
Fayalite	Fe_2SiO_4	6.5–7.0	4.39
Quartz	SiO_2	7.0	2.65
Albite	$NaAlSi_3O_8$	6.0–6.5	2.60–2.65
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	2.5	2.77–2.88

Table 6
Correlations for materials v/s mechanical tests results.

		Marshall Stability [kN]	Marshall Flow [mm]	Marshall Stiffness [kN/mm]	IDT [MPa]	Resilient Modulus [MPa]
RAP [%]	Pearson correl.	0.498	−0.015	0.487	0.794	0.784
	Bilateral signif.	0.000	0.909	0.000	0.000	0.000
	N	64	64	64	64	64
CS [%]	Pearson correl.	−0.160	0.244	−0.319*	−0.119	−0.123
	Bilateral signif.	0.212	0.053	0.011	0.349	0.333
	N	64	64	64	64	64
RAP + CS [%]	Pearson correl.	0.269	0.151	0.154	0.520	0.509
	Bilateral signif.	0.033	0.236	0.227	0.000	0.000
	N	64	64	64	64	64

Table 7
Correlations for materials particle size v/s mechanical tests results.

		Marshall stability [kN]	Marshall flow [mm]	Marshall stiffness [kN/mm]	IDT [MPa]	Resilient modulus [MPa]
RAP Fine [%]	Pearson correl.	0.589	0.076	0.498	0.424	0.501
	Bilateral signif.	0.000	0.543	0.000	0.000	0.000
	N	64	64	64	64	64
RAP Coarse [%]	Pearson correl.	0.591	0.076	0.499	0.423	0.501
	Bilateral signif.	0.000	0.541	0.000	0.000	0.000
	N	64	64	64	64	64
CS Fine [%]	Pearson correl.	−0.099	0.240	−0.246	0.087	0.069
	Bilateral signif.	0.427	0.050	0.045	0.481	0.576
	N	64	64	64	64	64
CS Coarse [%]	Pearson correl.	−0.096	0.249	−0.251	0.086	0.068
	Bilateral signif.	0.438	0.042	0.040	0.488	0.581
	N	64	64	64	64	64
AG Fine [%]	Pearson correl.	−0.345	−0.220	−0.178	−0.356	−0.399
	Bilateral signif.	0.004	0.074	0.149	0.003	0.001
	N	64	64	64	64	64
AG Coarse [%]	Pearson correl.	−0.091	−0.140	−0.025	−0.222	−0.293
	Bilateral signif.	0.462	0.260	0.839	0.069	0.015
	N	64	64	64	64	64
Binder [%]	Pearson correl.	−0.233	0.300	−0.440	−0.282	−0.295
	Bilateral signif.	0.058	0.013	0.000	0.020	0.014
	N	64	64	64	64	64

Table 8
Partial correlations controlled for RAP percentage.

		Marshall stability [kN]	Marshall flow [mm]	Marshall stiffness [kN/mm]	IDT [MPa]	Resilient modulus [MPa]
CS Fine [%]	Pearson correl.	−0.197	0.234	−0.343	0.040	0.009
	Bilateral signif.	0.113	0.059	0.005	0.748	0.945
	N	64	64	64	64	64
CS Coarse [%]	Pearson correl.	−0.205	0.242	−0.358	0.031	−0.002
	Bilateral signif.	0.099	0.050	0.003	0.803	0.990
	N	64	64	64	64	64
AG Fine [%]	Pearson correl.	0.155	−0.262	0.330	−0.046	−0.005
	Bilateral signif.	0.215	0.034	0.007	0.713	0.971
	N	64	64	64	64	64
AG Coarse [%]	Pearson correl.	0.263	−0.120	0.280	−0.005	−0.043
	Bilateral signif.	0.033	0.336	0.023	0.966	0.735
	N	64	64	64	64	64
Binder [%]	Pearson correl.	0.008	0.370	−0.297	−0.118	−0.095
	Bilateral signif.	0.947	0.002	0.015	0.347	0.448
	N	64	64	64	64	64