Moisture Sensitivity of Hot Mix Asphalt Modified with Micronized Calcium Carbonate

Gholam Hossein Hamedi[1*], Fereidoon Moghadas Nejad[2]

[1] Department of Civil Engineering, Faculty of Engineering, University of Guilan, P. O. B. 3756, Rasht, Iran
[2] Department of Civil and Environmental Engineering, Amirkabir University of Technology, P. O. B. 1619, Tehran, Iran
* Corresponding author, e-mail: hamedi@guilan.ac.ir

Abstract

Moisture sensitivity in an HMA refers to the loss of mastic cohesion and durability between the bitumen and aggregates due to water presence. Various methods exist to mitigate this type of sensitivity, with one of the most important approaches being the incorporation of anti-stripping agents into either the bitumen or aggregate materials. Based on this premise, the current study investigates the impact of using micronized calcium carbonate powder (MCCP or $CaCo_3$) as a modifier for bitumen on moisture sensitivity in HMA. Three types of aggregates with different mineralogical properties (limestone, granite, and quartzite), and PG 64–16 bitumen (along with 2% and 4% MCCP based on the mass of the bitumen) were utilized. The modified Lottman test was performed under 1 to 5 freeze-thaw cycles while measuring surface free energy (SFE) elements for both bitumens and aggregates with Wilhelmy Plate (WP) and Universal Sorption Device (USD), respectively. The results of the moisture sensitivity test on the asphalt mixtures used in this study demonstrate that the addition of MCCP in the modified samples has led to a reduction in the sensitivity of the asphalt mixtures, particularly in multiple freeze-thaw cycles, compared to the control samples. Furthermore, findings from SFE analysis demonstrated that MCCP enhanced cohesion free energy (CFE) which subsequently reduced rupture probability within the bitumen membrane. Additionally, it improved adhesion between acidic aggregates susceptible to moisture-induced sensitivity and bitumens.

Keywords

HMA, micronized calcium carbonate powder, moisture sensitivity, indirect tensile strength, surface free energy

1 Introduction

Water is commonly found in road pavement layers, especially in unbound granular layers such as subgrades and subbase layers. However, the presence of water within and between bound layers, specifically asphalt layers, is a relatively recent understanding within the professional community [1]. The bond quality between bitumen-aggregates has a considerable influence on the durability of HMA against moisture sensitivity [2].

The percentage and properties of materials used in HMA play a significant role in their failure [3]. Moisture sensitivity of HMA can occur through two mechanisms: loss of adhesion, loss of cohesion, or a combination. When water penetrates into the HMA, it affects the ability to coat aggregates. The higher affinity of aggregates for water compared to the bitumen leads to the separation of the bitumen from the surface of aggregates, resulting in reduced adhesion or stripping [4]. Anti-stripping agents can be divided into polymeric materials, liquid anti-stripping materials, metal

nanomaterials, and mineral nanomaterials [5]. A new category of anti-stripping agents that have been used over the last two decades is metal nanomaterials.

Hamedi et al. [6], for instance, studied the effect of nano-zinc oxide (ZnO) on the moisture sensitivity of hot-mix asphalt (HMA) using the dynamic method and SFE concept. Their results indicated that the use of these materials improves the adhesion of bitumen and aggregates and decreases the moisture sensitivity potential of the resulting mixture due to the alteration in SFE elements. Hamedi [7] examined the effect of nano- AL_2O_3 and nano- Fe_2O_3 as bitumen modifiers on the performance of HMA against moisture and concluded that these agents play a significant role in reducing the moisture sensitivity of HMA by decreasing separation energy. The results of dynamic experiments also confirmed this conclusion. Fakhri and Shahriyari investigated [8] the impact of Nano Zinc Oxide (ZnO) and Nano Reduced Graphene Oxide (RGO) on the

moisture sensitivity resistance of Stone Mastic Asphalt. It was observed that these nanomaterials improved the bitumen coating on aggregates within Stone Mastic Asphalt. The calculated moisture sensitivity indices based on the aforementioned tests indicated a significant improvement in the resistance of stone mastic HMA against moisture damage when incorporating Nano ZnO and Nano RGO as additives. Singh et al. [9] explored the impact of a liquid nanobased namely Zycotherm on the properties of HMA. The study involved adding Zycotherm in varying proportions to the mix and subsequently examining the characteristics of the HMA. The obtained results were then compared and analyzed to draw conclusions regarding the influence of Zycotherm on the performance of HMA. The findings and comparisons derived from these tests are presented in this study providing valuable insights into how incorporating Zycotherm as a warm mix agent can affect key properties of HMA concerning their resistance to moisture sensitivity.

Hydrated lime is one of the minerals that has been used in various forms to reduce the moisture sensitivity in HMA and has shown positive results. In 2013, Moghadas Nejad et al. [10] employed hydrated lime in the surface coating of aggregates. The results of the modified Lottman dynamic test and the study of SFE elements of the samples revealed that this agent has a significant effect on increasing the resistance of HMA against moisture. Sakanlou et al. [11] evaluated stone powder, portland cement, hydrated lime, and sedimentary calcium carbonate fillers on the moisture potential of HMA made with various bitumen-aggregate combinations using thermodynamic concepts and the modified Lottman mechanical method. The results obtained from the analysis of thermodynamic parameters indicate that only the addition of stone powder filler leads to an increase in bitumen-aggregate AFE. On the other hand, the incorporation of other types of fillers has shown a reduction in AFE between bitumen and aggregates.

The nanotechnology industry's growth has sparked increased interest in the utilization of nano-sized mineral additives. In this context, a study investigated the effect of nano $CaCO_3$ and nano ZnO, as modifiers for bitumen on moisture sensitivity in HMA. The results obtained from the thermodynamic parameters revealed that these nanomaterials enhance the wettability of bitumen on aggregates and improve adhesion between bitumen and aggregates. This suggests that incorporating such nanomaterials can positively influence the moisture resistance properties of HMA [12]. In a separate study, the impact of utilizing nano $CaCO_3$ as an antistrip agent on the moisture sensitivity of HMA was investigated. Multiple freeze-thaw cycles were employed

to examine the effect of these modifiers. The findings from the modified Lottman test indicated that mixtures containing nanomaterials exhibited higher indirect tensile strength ratio compared to control samples. Moreover, incorporating nanomaterials resulted in a decrease in the acid SFE element and an increase in the base SFE element of bitumen. This effect led to improved adhesion between bitumen-aggregates.

The calcium carbonate powder is also an appropriate aggregate surface modifier for decreasing the moisture sensitivity of HMA. Hamedi et al. [13] studied the effect of using nanocoating, namely nano calcium carbonate ($CaCO_3$) and nano zinc oxide (ZnO), on the surface of aggregates on moisture sensitivity of HMA using thermodynamic and dynamical methods. The results of this study indicate that the tensile strength ratio of samples utilizing modified aggregates has increased compared to the control samples. Sohrabi et al. [14] examined the impact of using micronized calcium carbonate as an anti-stripping material by covering the surface of aggregates. These findings suggest that incorporating micronized calcium carbonate as a surface treatment for aggregates can enhance adhesion energy and reduce debonding energy, thereby potentially improving resistance against stripping-related issues in HMA.

2 Statement of the present study and objectives

The application of anti-stripping agents is one of the most effective ways to increase the strength of HMA against moisture sensitivity. So far, many additives have been taken into consideration in the feasibility process and have undergone initial tests. The key factors such as strengthening HMA against moisture, lack of deficiencies in other engineering properties of the resulting mixture, and executive, low cost, and environmental considerations have always been influential factors in this regard. The material used in the present study was micronized calcium carbonate powder (MCCP), micronized using new superfine technology, and offering more advantages compared to systems that use only a separator or mill. Consequently, the primary objectives of the present study are summarized as follows:

- Evaluation of the moisture performance of the HMA containing MCCP using the modified Lottman mechanical method
- Investigating the SFE elements of aggregates and the MCCP-modified bitumen
- Calculation of thermodynamic parameters based on the SFE elements of bitumen and aggregates
- Comparison of the results of moisture sensitivity mechanical tests with thermodynamic parameters based on the SFE method

- Introduction of an accessible and affordable agent with efficient performance against moisture sensitivity as a suitable alternative to hydrated lime with similar effects and fewer executive problems.

3 Materials and methods

Fig. 1 illustrates the algorithm of the laboratory experimental program used in this research. The tests described were conducted on every individual sample, with each test being replicated three times. To ensure the reliability of the findings, multiple samples were prepared for each combination of aggregate blend and bitumen, with a minimum of three separate samples being generated to evaluate result reproducibility.

In the present study, three types of aggregate, including limestone, granite, and quartzite, were utilized, with characteristics presented in Table 1. These aggregates were employed after sieving in accordance with the continuous grading of AASHTO M323 standard. The aggregate distribution curve of these materials is illustrated in Fig. 2. The nominal maximum aggregate size is 12.5 mm. The filler used to make these mixtures was also produced from the same aggregates.

The characteristics of the bitumen as one of the main elements of HMA have a significant effect on their properties [15]. The choice of the PG 64–16 bitumen for this study was made considering the typical climatic conditions in the region (Iran). The specifications of this bitumen supplied from Pasargad Oil Company, Iran, are given in Table 2. It is worth mentioning that the fatigue parameter ($G^*Sin\delta$) for long term aged bitumen is applicable when the criteria for high temperature ($G^*/Sin\delta$) and low temperature S and m-value) of the bitumen are met.

Precipitated calcium carbonate (PCC) is a unique

product derived from lime that finds application in various industries. PCC is produced by hydrating high-calcium quicklime and then reacting the resulting slurry, often referred to as "milk-of-lime," with carbon dioxide. This process yields precipitated calcium carbonate, which possesses distinct properties and offers versatile uses across different industrial sectors. PCC can be used as a filler in HMA. The use of this powder as a bitumen modifier requires crushing using other methods. Accordingly, in this study, an attempt has been made to use a cheaper and more efficient way to produce calcium carbonate.

The ball mill crusher is the primary apparatus for pulverizing calcium carbonate rock. By rotating the mill, the steel pellets inside the apparatus cause calcium carbonate to be crushed. When the calcium carbonate stone is crushed, it is transferred to the classifier shield by an elevator. This device separates the coarse-grained rocks from the powder so that these coarse-grained stones can be re-ground in the ball mill. The powders separated by the classifier enter the cyclones and are divided into two types of granulations by the centrifugal fan. Cyclone devices are centrifugal particle collection systems that use a round air effect to separate dust particles from gas. Cyclonic collection systems are commonly used as precursors to reduce the amount of dust reaching the final separator. These separators are great for collecting medium to large size particles. Calcium carbonate powder with a mesh of 100 to 1000 is removed from the cyclone discharge hopper and packaged by a bag filling machine. Adjusting the rotational speed of the centrifuge allows accurate control over the size of the powder particles. Using this system, the maximum tolerance of ±10% is obtained compared to the desired size. In this system, unlike sedimentary crushing systems, calcium carbonate is crushed by a mechanical method. Consequently, the use of this crushing system not only has better control over the size distribution of the powder particles but also preserves the properties of the main rock.

Literatures show that the size and chemical properties of agents affect the performance of resulted mixture. MCCP with the chemical formula of $CaCO_3$ and the size of 40 microns was utilized as an anti-stripping agent in this study because of its basic characteristics and availability. This powder is a white and odorless solid substance used in various industries such as plastics, foods, pharmaceuticals, paper making, cosmetics, and agriculture. MCCP has a melting point of 825 °C, a density of 2.71 g/cm³, and minimal solubility in water. The chemical compounds of this anti-stripping additive supplied from Azadi Powder Makers Co., Iran, are presented in Table 3.
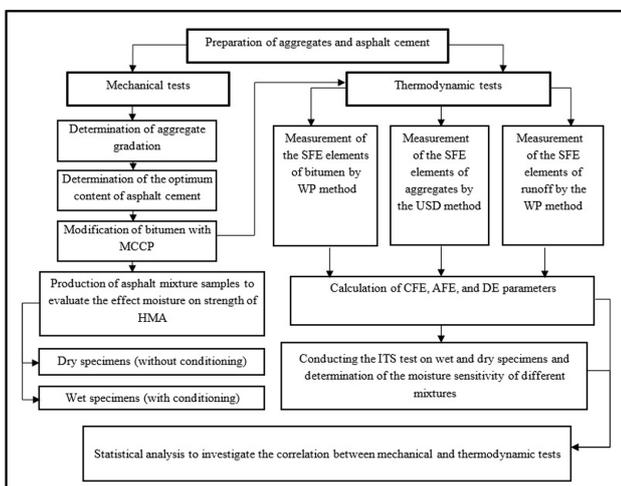

Fig. 1 The test design algorithm

Table 1 Properties of aggregates

Test	Specification	Requirements	Limestone	Granite	Quartzite
Fine aggregates					
Bulk specific gravity	ASTM C128		2.568	2.598	2.462
SSD specific gravity			2.583	2.624	2.477
Apparent specific gravity			2.614	2.646	2.490
Maximum water absorption (%)	ASTM C128		0.8	1.2	1.7
Specific gravity (filler)	ASTM D854	--	2.56	2.55	2.44
Sodium sulfate soundness (%)	ASTM C88	Max 12	2	4	7
Coarse aggregates					
Bulk specific gravity	ASTM C127	--	2.593	2.609	2.476
SSD specific gravity			2.598	2.634	2.494
Apparent specific gravity			2.623	2.653	2.518
Maximum water absorption (%)	ASTM C127	Max 2.5	0.8	1.2	1.7
Abrasion loss (Los Angeles) (%)	ASTM C131	Max 25	27	19	26
Flat and elongated particles (%)	ASTM D4791	Max 15	3	9	6
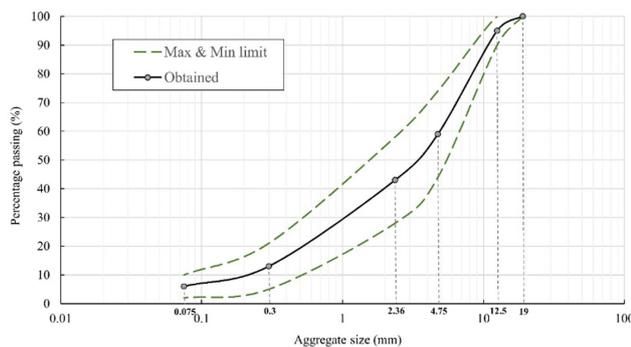
Fig. 2 The size distribution of used aggregates

3.1 Sample preparation

In the present research, the bitumen was initially modified with 2 and 4% of MCCP by weight of the bitumen, and then the modified bitumen was employed to prepare HMA samples. Bitumen modification was performed with the help of a high-shear mixer at the speed of 8000 rpm in 20 min. For this purpose, the bitumen was first heated to 160 °C, and MCCP was gradually added to it to ensure the homogeneous distribution of the agent in the bitumen. Bitumen temperature was maintained at 160 °C during the mixing process. According to previous studies, it is necessary to apply the same modification conditions (including the blending of bitumen, temperature, and mixing duration) to the control bitumen samples as well. This is to ensure that aging does not introduce any confusion or misinterpretation of the results during the analysis [16]. Accordingly, this condition was simulated for the virgin bitumen to ignore the effect of bitumen aging during the mixing process on the results. To control the homogeneity and uniform distribution of MCCP in bitumen, samples were taken from the upper one-third and lower one-third of the bitumen container. The penetration grade and softening point tests were performed on these samples. The results of this investigation indicate that the percentage of variations is below 5%, which is statistically acceptable. To examine how MCCP are dispersed in the bitumen, the mixture of the base bitumen and MCCP was analyzed using scanning electronic microscope to observe the resulting composition (Fig. 3).

3.2 Laboratory studies
3.2.1 Mix design

In this particular study, the Marshall mix design method, as specified by MS-2 asphalt institute manual, was employed to determine the optimal bitumen content (OBC). At first, the OBC for HMA samples was determined using the Marshall method and following the MS-2 specification of the Asphalt Institute. Subsequently, modified samples were produced using the OBC and subjected to the modified Lottman test.

3.2.2 Modified Lottman test

In this study, wet conditioning is employed according to the AASHTO T 283 with three replications on the samples subjected to 1, 3, and 5 freeze-thaw cycles to increase the accuracy. The test was conducted at a loading rate of 5.08 cm/min (2 in/min). The amount of force applied to the sample was recorded at the moment of failure, and the ITS of the specimens was determined using Eq. 1.

$$\text{ITS} = \frac{2000F}{t\pi d}. \tag{1}$$

Table 2 Properties of PG 64-16 bitumen

Bitumen	Row	Property/test	Unit	Test temperature (°C)	Result	Limits		Standard
				Base bitumen				
	1	Flash point	°C	-	308	230	-	ASTM D92
	2	Viscosity	Pa.s	135	0.358	-	3	ASTM D4402
	3	G^*	kPa	64	1.79	-	-	ASTM D7175
		δ	Degree		82.3	-	-	
		Dynamic shear ($G^*/Sin\delta$)	kPa		1.81	1.00	-	
				Bitumen rolling thin-film oven (short term aged)				
Aging temperature				163	-	--	-	ASTM D2872
	4	Mass loss	Percentage	163	0.08	-	1.00	ASTM D2872
	5	G^*	kPa	64	3.59	-	-	ASTM D7175
		δ	Degree		79.4	-	-	
		Dynamic shear ($G^*/Sin\delta$)	kPa		3.65	2.2	-	
				Bitumen pressure aging vessel test (long term aged)				
Aging temperature				100	-	--	-	ASTM D6521
	6	G^*	kPa	28	4013	-	-	ASTM D7175
		δ	Degree		42.5	-	-	
		Dynamic shear ($G^*Sin\delta$)	kPa		2710	-	5000	
	7	Creep stiffness (S)	MPa	−6	109	-	300	ASTM D6448
	8	m-value	-	−6	0.365	0.300	-	ASTM D6648

Table 3 Chemical compounds of the anti-stripping agent

Constituent elements	(%)
CaO	56.82
MgO	0.26
SiO_2	0.14
P_2O_5	0.08
Al_2O_3	0.07
Na_2O	0.06
Fe_2O_3	0.02
K_2O	0.01
L.O.I	42.54

Fig. 3 The distribution of MCCP in bitumen

Where, ITS is the ITS (kPa), F is the maximum load (N), t is the sample thickness (mm), and d is the sample diameter (mm).

After calculating the ITS of wet and dry samples, the indirect tensile strength ratio (TSR) for the samples was also calculated. The TSR, defined in Eq. 2 is a criterion for assessing the performance of HMA against moisture sensitivity.

$$TSR = \left(\frac{ITS_{wet.}}{ITS_{dry}} \right) \times 100 . \qquad (2)$$

Where, ITS_{Wet} and ITS_{Dry} denote the average tensile strength of the samples under wet and dry conditions (kPa), respectively.
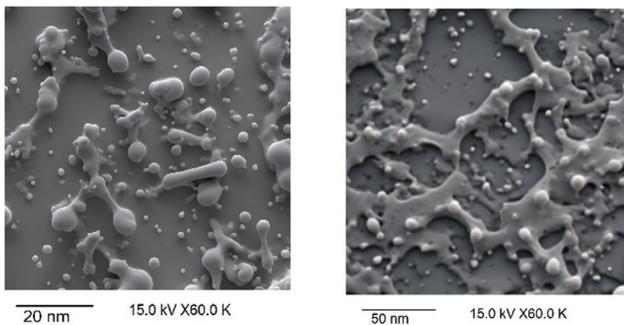
3.2.3 SFE theory

According to the acid-base theory, the SFE of any material, defined as Eq. 3, is formed of three elements: the *LW* or non-polar, the Lewis acidic, and the Lewis base elements based on the type of forces among the surface molecules [17].

$$\Gamma = \Gamma^{LW} + \Gamma^{AB} = \Gamma^{LW} + 2\sqrt{\Gamma^+ \Gamma^-} . \qquad (3)$$

Where, Γ indicates the total SFE of material, ΓLW denotes the non-polar element of SFE, ΓAB represents the polar element of SFE, including acid element (Γ^+), and base element (Γ^-).

The cohesion SFE (ΔGic) is thermodynamically defined as the energy required to create a crack with the unit area in a material. Based on the SFE definition, the total work

of cohesion for various materials can be shown in eq. 4, in which ΓA is the total SFE of the intended material.

$$W^{AC} = 2\Gamma^A .\qquad(4)$$

The adhesion SFE (ΔGia), which indicates the amount of external force necessary to separate the two materials at their contact surface in vacuum conditions, also includes two main elements: the polar or acid-base, and the non-polar or the LW elements. Eq. 5 is used to determine the adhesion SFE of bitumen and aggregates.

$$\Delta G_i^a = \Delta G_i^{aLW} + \Delta G_i^{aAB} = 2\left[\begin{array}{c}\left(\sqrt{\Gamma_2^{LW}\Gamma_1^{LW}}\right) + \left(\sqrt{\Gamma_2^+\Gamma_1^-}\right)\\ +\left(\sqrt{\Gamma_2^-\Gamma_1^+}\right)\end{array}\right].\qquad(5)$$

In which ΔGia is the adhesion SFE; ΔGiaLW is the non-polar element, and ΔGiaAB is the polar element of adhesion SFE; Γ1LW, Γ1+, and Γ1− are the SFE elements of the bitumen; and Γ2LW, Γ2+, and Γ2− are aggregate SFE elements.

Eq. 6 is applied to calculate the adhesion between bitumen and aggregate in the presence of water. The 1, 2, and 3 subscripts in this equation indicate the elements of bitumen, aggregates, and water, respectively. The negative values of adhesion SFE demonstrate the tendency of the two materials to stick to each other, and the higher the negative value, the greater this tendency is [18].

$$\Delta G_{132}^a = \Gamma_{12} - \Gamma_{13} - \Gamma_{23} .\qquad(6)$$

3.2.4 SFE measurements

Various theories have been proposed to describe the SFE of materials based on their molecular structure. One prominent theory is the acid-base theory, commonly employed to define the SFE elements of substances. According to this theory, the overall SFE of a substance can be divided into three elements based on the types of intermolecular forces at its surface: Lifshitz-van der Waals (LW) element or non-polar element, Lewis acid element, and Lewis base element.

SFE is the energy needed to make a new unit area of substances in the free space. If the bond between two materials is not the same, the SFE is called AFE, and if the bond between two materials is the same, the SFE is called CFE. Based on the SFE theory, thermodynamic changes in the SFE cause a failure in bitumen or at the boundary between aggregate and bitumen [19].

Since the intermolecular non-polar forces such as LW and acid-base forces create the adhesion and cohesion between HMA elements, any change in the amount of SFE can alter these bonds. Therefore, the resistance of bitumen and HMA against rupture can be evaluated by measuring the SFE, the work of adhesion, and the work of cohesion.

In this research, the USD developed by Little and Bhasin [19] was utilized to determine the SFE elements of aggregates. Water, methyl propyl ketone (MPK), and normal hexane (n-Hexane) with the determined SFE elements were selected to perform this test (Table 4).

By determining the work of adhesion based on three types of liquid vapor (Fig. 4), a set of three linear relationships (Eq. (7)) was created and utilized to obtain the three SFE elements of aggregates. Here, the coefficient matrix (Aij) is the double square root of the used liquid SFE elements, the matrix of answers (X) is related to the work of adhesion between aggregates and three types of used liquids, and the matrix of unknowns (Y) is the square root of aggregates' SFE elements [19].

$$\begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix}\begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} = \begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \end{bmatrix}\qquad(7)$$

WP is a common method for measuring the SFE elements of not only bitumen (in the solid form) but also aggregates with low SFE elements. Considering that the aggregates in this study had high SFE elements, this method was applied only to determine the SFE elements of the bitumen. The contact angles of the various test

Table 4 SFE elements of the liquids used to determine SFE elements of aggregates (ergs/cm²)

Solvent Liquids	Γ^+	Γ^-	Γ^{AB}	Γ^{LW}	Γ^{Total}
Water	25.5	25.5	51	21.8	72.8
MPK	0	19.6	0	24.7	24.7
n-Hexane	0	0	0	18.4	18.4

Fig. 4 Placing the sample of aggregate materials in the chamber of the USD test

liquids droplets formed on the flat horizontal surface of the bitumen were obtained by analyzing the images and utilized to determine the SFE elements of bitumen using the work of adhesion relationships (Eq. 8).

$$\Gamma_L(1+\cos\theta)=2\left[\left(\sqrt{\Gamma_L^{lw}\Gamma_S^{lw}}\right)+\left(\sqrt{\Gamma_L^+\Gamma_S^-}\right)+\left(\sqrt{\Gamma_L^-\Gamma_S^+}\right)\right] \quad (8)$$

Where, the L index represents the SFE elements of the test liquid, θ is the contact angle obtained from the sessile drop test, and the S index denotes the three SFE elements of bitumen obtained by solving three equations and three unknowns.

Three liquids, including water, methylene iodide, and ethylene glycol, whose SFE elements are presented in Table 5, were incorporated in this study. Three samples were tested for each liquid, and their averages were recorded as the contact angle. These tests resulted in three equations and three unknowns. The SFE elements of the bitumen were obtained by simultaneously solving these equations. Fig. 5 depicts the image taken from the droplet of test liquid formed on the surface of the sample.

Fig. 5 illustrates the immersion process of a glass surface coated with asphalt. The calculation of the contact angle is determined based on the required force to move the pseudo-static plate, the medium surrounding the plate, fluid density, and plate area entering into water. According to the Pythagorean theorem method, this value is then inserted into Eq. 8.

After determining the SFE elements of aggregates and bitumen, an appropriate assessment can be made for the resistance of the HMA to moisture sensitivity. The three derived terms based on the SFE related to the moisture sensitivity of HMA are as follows:

1. Work of adhesion between the bitumen and aggregates (W_{AB})
2. Work of debonding or reduction in the free energy of the system when water displaces the bitumen from a bitumen-aggregate interface (W_{ABW}^{wet})
3. Cohesive bond energy of the bitumen (W_{BB}).

Table 5 SFE elements of the liquids used to determine SFE elements of aggregates (ergs/cm²)

Solvent Liquids	Γ^+	Γ^-	Γ^{AB}	Γ^{LW}	Γ^{Total}
Water	25.5	25.5	51	21.8	72.8
Methylene iodide	0	0	0	50.8	50.8
Ethylene glycol	3	31	19.29	29	48.29
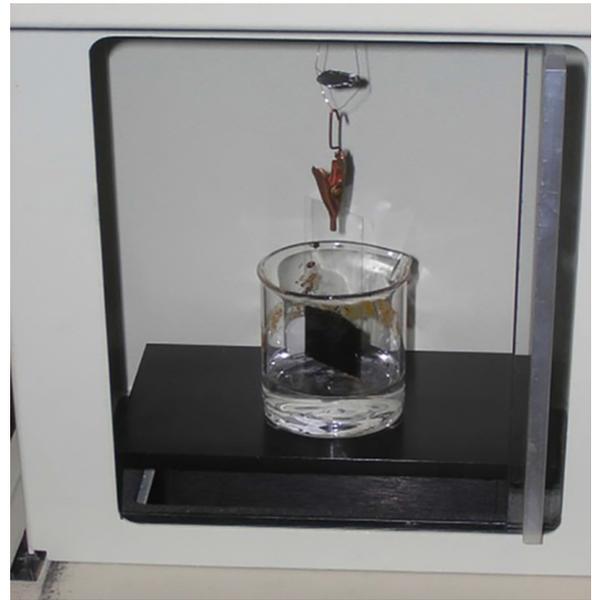
Fig. 5 Immersing the asphalt-coated surface and removing it in the WP

The ER_1 and ER_2 bond energy parameters were computed using the terms obtained from the SFE experiments and Eqs. 9 and 10. These parameters provide a complete assessment of the moisture sensitivity of the samples by combining the SFE elements of bitumen and aggregates. The higher the value of these parameters, the less likely to moisture sensitivity due to the reduced thermodynamic potential [19].

$$ER_1=\left|\frac{W_{AB}}{W_{ABW}^{wet}}\right| \quad (9)$$

$$ER_2=\left|\frac{W_{AB}-W_{BB}}{W_{ABW}^{wet}}\right| \quad (10)$$

4 Results and discussions
4.1 Mix design results
In this study, Marshall mix design based on the Asphalt Institute MS-2 was employed to determine the OBC. Since different bitumen percentages in controlled and modified samples can cause an error in the analysis of results, the OBC obtained in controlled samples has also been used for modified ones. The OBC based on Asphalt Institute MS-2 was obtained from the average of three bitumen content corresponding to the maximum specific gravity, maximum Marshall stability, and 4% air void (AV). Other parameters such as voids in mineral aggregates (VMA), voids filled with bitumen (VFA), and Marshall flow were controlled by the values of the MS-2 manual. The OBC in control samples made with limestone, granite, and quartzite aggregates were found to be 6, 5.6, and 5.3%, respectively.

4.2 Modified Lottman test

The results of the ITS test on the samples made with different aggregates are presented in Figs. 6–8. The use of MCCP in samples made with all three types of aggregates improved the ITS of the modified specimens compared to the control samples. The reason for this is the improvement in the adhesion of samples made with the modified bitumen, making it daunting to remove bitumen from aggregates. The stiffness of bitumen is another factor playing a significant role in this regard. The use of MCCP in bitumen increased its stiffness and enhanced the strength of the resulting mixture against adhesion rupture. The ITS of samples in dry conditions in the specimens made with granite aggregate were better than ones with limestone and quartzite aggregates. The use of MCCP has caused the amount of increase in the ITS of limestone HMA to be higher than samples made with granite and quartzite aggregates. Moreover, the results of mechanical strength in samples made with limestone aggregate under wet conditions showed that this parameter had increased significantly in the samples under the freeze-thaw cycles. Accordingly, it can be said that the addition of MCCP does
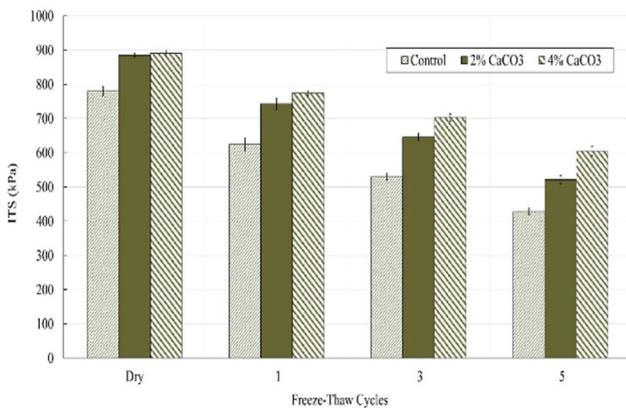

Fig. 6 Results of the ITS test on the modified HMA containing limestone aggregates
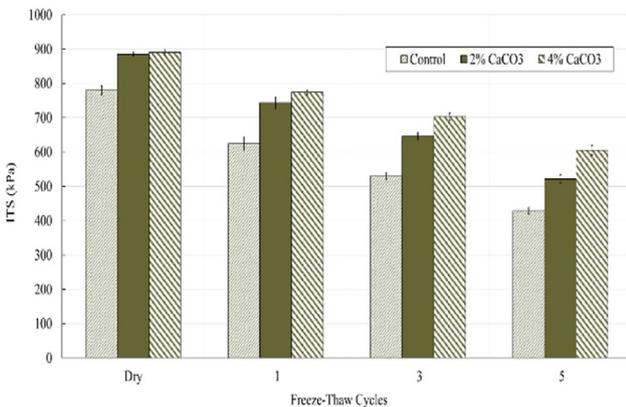

Fig. 7 Results of the ITS test on the modified HMA containing granite aggregates
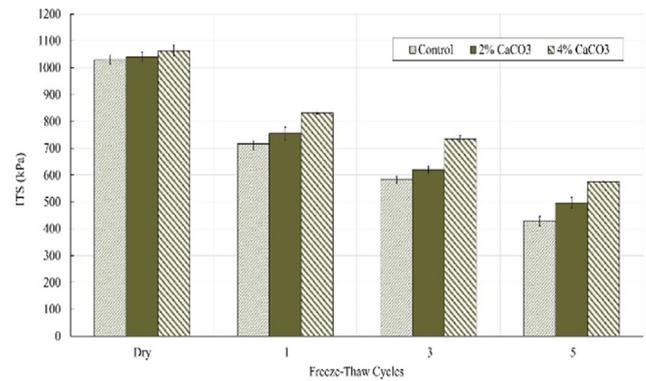

Fig. 8 Results of the ITS test on the modified HMA containing quartzite aggregates

not affect the bitumen-aggregate adhesion in the samples of this group. However, its main effect has been on increasing the stiffness and cohesion of mastic, which increases the strength of the mixture in both dry and wet conditions. Furthermore, the results of ITS on the granite and quartzite aggregate samples showed that the resistance of HMA in the samples under wet conditions had increased significantly. In contrast, it has not improved under dry conditions. Hence, it can be concluded that the use of MCCP increases the adhesion and forms strong non-polar bonds that do not easily disappear in the presence of water.

Since the ITS is not an appropriate index for determining the moisture sensitivity of samples alone, the TSR parameter was utilized as a measure to evaluate the moisture performance of the modified HMA. These values are given in Fig. 9. Evidently, with increasing the number of freeze-thaw cycles, the TSR value for all samples decreased. The main reason for this is that the specimens were subjected to more severe conditions, and multiple freeze-thaw cycles caused the bitumen-aggregate adhesion and bitumen cohesion to decrease further. This reduction was higher in the control sample and had a slower trend in the samples containing MCCP.

In fact, the use of MCCP creates stronger bonds between the bitumen and aggregate, especially non-polar bonds, which do not easily disintegrate in the presence of water. In addition, in a specific number of freeze-thaw cycles, the use of MCCP improved the moisture performance of the HMA and increased their tensile strength. For instance, in the samples made with quartzite aggregates under five freeze-thaw cycles, the application of 2 and 4% MCCP enhanced the TSR by 4 and 16%, respectively. The main reason for this is that MCCP has alkaline properties, and its use reduces the acidic properties of bitumen and strengthens its alkaline properties. These changes improve the adhesion between the bitumen
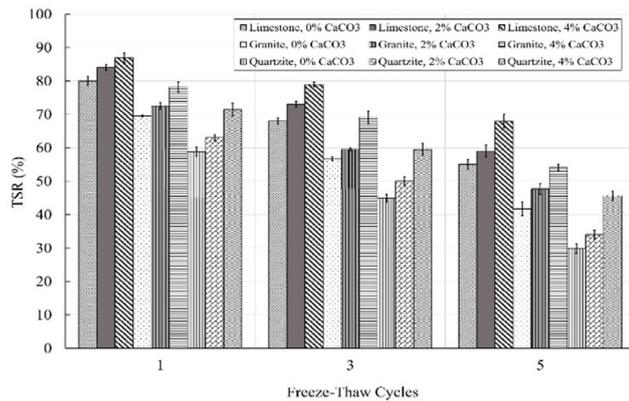
Fig. 9 TSR parameters of different HMA samples

and acidic aggregates, which are prone to moisture sensitivity. In fact, the use of MCCP improves both bitumen cohesion and bitumen-aggregate adhesion.

However, in samples made with alkaline aggregates such as limestone, the use of MCCP does not have a significant effect on adhesion and mainly has a positive effect on the bond strength of bitumen. This difference makes the use of MCCP more effective on samples made with acidic aggregates. This is desirable from the executive point of view because the moisture sensitivity occurs chiefly in asphalt layers made with acidic aggregates.

In addition to improving the adhesion and cohesion properties of the modified bitumen, MCCP improves the coating properties of aggregates by the bitumen by forming molecular layers on the surface of aggregates and plays a vital role in increasing the strength of the samples against moisture. The type of aggregates is another factor influencing the strength of the samples against moisture sensitivity. According to the mentioned results, samples manufactured with quartzite aggregates had the highest moisture sensitivity from among these aggregates, and limestone had better resistance to moisture. Various factors affect the occurrence of moisture sensitivity and resistance of a mixture against it, with the structure of minerals which form aggregates being one of the most important ones. Two minerals, SiO_2 and CaO (or $CaCO_3$), induce a substantial change in the hydrophilic or hydrophobic properties of HMA. The higher the percentage of SiO_2 in aggregates, the more hydrophilic it will be. On the contrary, CaO is an indicator of the hydrophobicity of aggregates, and as the minerals increase in the aggregates, their resistance to moisture is improved.

The different percentages of MCCP can have a significant impact on the performance of asphalt mixtures against moisture damage. Higher percentages of MCCP can increase the resistance of the mixture against water penetration and help maintain its structural integrity. This can result in a noticeable improvement in the service life of the

asphalt mixture against moisture damage. Similarly, lower percentages of MCCP may have a lesser effect on the resistance of the mixture against water penetration and result in a shorter service life against moisture damage. Therefore, the selection of an appropriate percentage of MCCP should be based on the specific needs and conditions of the project to achieve the desired improvement in the performance of the asphalt mixture against moisture damage.

The results indicate that the use of lower percentages of MCCP additives has not significantly improved the performance of asphalt mixtures against moisture. The main reason for this is that these additives have been dispersed sporadically within the bitumen structure. As this percentage increases, a homogeneous network can be considered throughout the volume of the bitumen, which enhances its stiffness and improves its stability, especially against cohesive failure.

The resistance of asphalt mixtures against moisture damage is influenced by the bitumen's cohesion and the bitumen-aggregate's adhesion. The use of MCCP additives improves the cohesion energy of the bitumen (Table 6), reducing the likelihood of cohesive failure in the bitumen phase. MCCP additives also increase the alkanik characteristics of the bitumen and reduce its acidity. This is particularly beneficial for granite and quartzite aggregates, as these aggregates have acidic characteristics, and their adhesion to modified bitumen with reduced acidity is enhanced. However, this is not desirable for limestone aggregates, which have alkanik characteristics. Therefore, the positive effect of MCCP additives is less pronounced for mixtures made with limestone aggregates.

The type of aggregates used in asphalt mixtures can indeed have an influence on the effectiveness of MCCP additive. The specific characteristics of different aggregates can lead to variations in performance when antistripping additives are utilized. One key factor is the surface chemistry of the aggregates. Aggregates with higher surface energy tend to have better adhesion with the asphalt binder, which can enhance the effectiveness of antistripping additives in promoting a strong bond between the binder and the aggregates. On the other hand, aggregates with lower surface energy may exhibit reduced adhesion and may be more prone to stripping, even with the use of antistripping additives.

Furthermore, the mineralogical composition of aggregates can impact their susceptibility to moisture damage and stripping. Some minerals may be more prone to moisture-induced distress and may require more effective antistripping additives to mitigate the potential for stripping. It is important to consider these variations in

Table 6 Cohesion, Adhesion, and debonding SFE terms of modified HMA (ergs/cm^2)

Mixture	Bitumen type	Aggregate type	W_{BB}	W_{AB}	W_{ABW}^{wet}
1	PG 64–16		57.2	131.0	−131.6
2	PG 64–16 + 2% CaCO$_3$	Limestone	65.1	141.5	−129.0
3	PG 64–16 + 4% CaCO$_3$		69.6	147.7	−127.3
4	PG 64–16		57.2	134.8	−145.6
5	PG 64–16 + 2% CaCO$_3$	Granite	65.1	145.6	−142.7
6	PG 64–16 + 4% CaCO$_3$		69.6	152.1	−140.8
7	PG 64–16		57.2	131.8	−152.6
8	PG 64–16 + 2% CaCO$_3$	Quartzite	65.1	141.6	−150.7
9	PG 64–16 + 4% CaCO$_3$		69.6	147.6	−149.2

Table 7 The results of XRF analysis

Compound	Limestone	Granite	Quartzite
SiO$_2$	16.58	52.19	66.96
Al$_2$O$_3$	4.84	6.05	13.67
Fe$_2$O$_3$	3.87	7.08	4.09
MgO	2.24	2.93	1.76
CaO	72.47	31.75	13.53

aggregate characteristics during the selection and dosage of antistripping additives. Conducting laboratory tests and field evaluations using different aggregates can help assess the performance and effectiveness of antistripping additives under specific aggregate conditions.

An X-ray fluorescence (XRF) test was conducted to determine the mineral structure of aggregates. The mineral elements of the three types of aggregates used in this study were measured by this test, with results presented in Table 7. It is clear that SiO$_2$ formed a large part of granite and quartzite aggregates, resulting in strong acidic properties, especially in quartzite aggregates. In terms of the two types of aggregates, their composition reveals a significant difference in the percentage of SiO$_2$ and CaO, with the acidic portion being more predominant than the strong basic portion (e.g., calcium oxide or CaO). It is important to note that while granite and quartzite aggregates both possess acidic properties, they differ considerably due to variations in their mineral structure data. On the surface of acidic aggregates like granite and quartzite, hydroxyl groups (OH) are present. These OH groups form hydrogen bonds with carboxylic acid groups found in bitumens, thereby playing a crucial role in adhesion between bitumen and acidic aggregates. However, these hydrogen bonds are prone to breakage when exposed to water. As a result, the OH groups on aggregate separate from the carboxylic acid groups and instead form hydrogen bonds with water molecules. This preference for bonding with water molecules over bonding between aggregate's OH groups (SiOH) and

bitumen's carboxylic acid groups (COOH) leads to bond rupture. Furthermore, it should be noted that limestone aggregates have significantly lower SiO$_2$ content compared to CaO. The primary reason for strong adhesion resistance between bitumen and limestone aggregates lies in the formation of water-insoluble covalent bonds resulting from physical reactions between calcium present on aggregate surfaces and specific functional groups within bitumens.

The mineral structure of aggregates affects the adhesion properties of the asphalt mixture. The CaO minerals have better adhesion with asphalt binder, resulting in improved resistance to moisture damage. On the other hand, certain minerals (SiO$_2$) have poor adhesion, leading to reduced adhesion and increased susceptibility to moisture-induced distress. Based on this, aggregates such as limestone (Table 7) that have a high percentage of the mineral CaO are called hydrophobic aggregates, while aggregates such as granite and quartzite that have a high percentage of SiO$_2$ (Table 7) are referred to as hydrophilic aggregates.

Adhesion of materials can be classified into two types: physical adhesion and chemical adhesion. The difference between physical and chemical adhesion lies in the type and mechanism of bonding between two different surfaces. One of the influential factors in physical adhesion is the surface texture of the substrate, on which the adhesive or the bitumen is applied, and a portion of the bitumen penetrates into the fissures and voids of the substrate. Accordingly, the surface texture of aggregates is an additional factor that impacts the extent of moisture sensitivity. If the surface texture is more porous, the amount of force required for failure increases, reducing the stripping potential. In this study, granite aggregates have weaker performance than limestone aggregates despite having a higher AFE in dry conditions.

The most important reason for this occurrence is the surface texture of limestone compared with granite aggregates. The surface texture of limestone aggregate has a high degree of porosity, causing the bitumen to penetrate into them and providing a more effective adhesion between bitumen and aggregates.

In addition to the degree of porosity, its size should also be appropriate for the penetration of bitumen. If the

size of voids and fractures in aggregates is very small, there is no possibility for bitumen to penetrate them, and therefore it does not have any effect on the physical adhesion of bitumen to the aggregates.

On the other hand, the presence of voids and fractures with a large size causes a reduction in the effective volume of bitumen that is supposed to be placed between the aggregates, leading to inadequate adhesion.

To assess the significance of the modified Lottman test results (Tables 8–10), a *t*-test was conducted on the TSR. In Tables (8–10), two lines of results are provided based on the outcome of Levene's test, which determines if the variances between the two samples are equal. If Levene's test indicates equal variances, then the first line of results is used. However, if it suggests unequal variances, then the second line of results should be considered.

For these particular samples, with a sig. value greater than 0.05 for Levene's test, it can be concluded that both samples have equal variances. In conclusion, the first rows of Tables 8–10 are used for all samples. Since the sig. values of the *t*-test for all samples are < 0.05, the use of both percentages of MCCP significantly affects the TSR parameter as a measure to evaluate the moisture sensitivity of HMA and improves their performance against moisture. The results of this analysis indicate that the use of 4% of the additive MCCP has led to a significant improvement in moisture sensitivity results as the *p*-values are less than 0.05. This analysis shows that the *p*-values in samples made with granite and quartzite aggregates are closer to zero in the first cycle. This suggests that the use of the additive is more effective in samples made with these two types of aggregates.

Additionally, the results show that the *p*-values for comparing samples with 4% MCCP additive to control samples are closer to zero compared to samples with 2% MCCP additive to control samples. This indicates that the use of 4% MCCP additive improves the performance of asphalt mixtures against moisture damage more effectively.

4.3 SFE theory
The SFE values for the aggregates are provided in Table 11. Evidently, the acidic SFE element of quartzite aggregates is larger than that of granite and limestone aggregates. The same trend is true for the basic SFE elements of these aggregates. In addition, quartzite aggregates are more polarized than the other two aggregates due to their larger polar SFE element. In fact, most of the bitumen-aggregates bonds are formed by the polar bonds, which are easily broken in the presence of another polar material (such as water), and stripping occurs. However, the bond formed between the bitumen

and basic aggregates such as limestone is a type of covalent (non-polar) bond which is not easily broken in the presence of water. This is one of the main reasons for the higher resistance of limestone aggregates to moisture-induced sensitivity because when water enters the bitumen-aggregate system, these bonds do not easily break, and they prevent the asphalt mixture from experiencing a significant decrease in resistance under moist conditions compared to dry conditions.

Furthermore, the total SFE of quartzite aggregates is much higher than that of limestone and granite aggregates. In fact, more energy is required to create a crack in the space of granite aggregates than limestone aggregates. Nevertheless, this is not important in the assessment of moisture sensitivity, because the two main mechanisms of moisture sensitivity include rupture in the bitumen membrane (cohesive failure) and rupture at the bitumen-aggregate contact surface (adhesive failure), and moisture sensitivity is not the cause of fracture in the interior space of aggregates.

Table 12 displays the outcomes of measuring the SFE elements for both the virgin bitumen and modified bitumens containing varying percentages of MCCP. As expected, since the bitumen possesses acidic properties, its acidic SFE element slightly surpasses its basic counterpart.

This observation suggests a lack of sufficient adhesion between the bitumen and acidic aggregates like granite and quartzite. Consequently, this deficiency in adhesion serves as one of the primary causes for moisture-induced sensitivity in asphalt pavements constructed using such acidic aggregates.

Calcium carbonate, being a natural substance with basic properties, plays a significant role in modifying the behavior of bitumen. As shown in Table 12, the incorporation of MCCP in bitumen leads to a reduction in its acidic properties and an increase in its basic properties. This alteration in the chemical composition of bitumen enhances its ability to form a coating on the surface of aggregates. Particularly, it improves the adhesion of bitumen to acidic aggregates such as granites, which are more prone to moisture susceptibility. While coating and adhesion are distinct concepts, a good coating is considered a favorable condition for achieving strong adhesion. Consequently, the presence of MCCP reduces the likelihood of stripping and the separation of bitumen from acidic aggregates, thereby decreasing the occurrence and probability of moisture susceptibility in HMA. This enhancement in adhesion helps maintain the integrity and durability of the asphalt mixture, as more primary energy is required to initiate the stripping phenomenon. Ultimately, the addition of MCCP contributes to the overall resistance of the asphalt mixture against moisture-related issues.

Table 8 The results of *t*-test on the TSR parameter of modified HMA in 1 freeze-thaw cycle

Aggregate	CaCO$_3$	Levene's Test for Equality of Variances		*t*-test for Equality of Means							
		F	Sig.	*t*	*df*	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
									Lower	Upper
Limestone	2%	1.241	0.328	−2.919	4	0.043	−4.66667	1.59861	−9.10512	−0.22821
				−2.919	3.469	0.052	−4.66667	1.59861	−9.38643	0.05310
	4%	0.000	1.000	−3.550	4	0.024	−7.00000	1.97203	−12.47522	−1.52478
				−3.550	3.971	0.024	−7.00000	1.97203	−12.49112	−1.50888
Granite	2%	6.400	0.065	−3.479	4	0.025	−3.66667	1.05409	−6.59330	−0.74004
				−3.479	2.439	0.055	−3.66667	1.05409	−7.50294	0.16961
	4%	7.000	0.057	−5.543	4	0.005	−8.66667	1.56347	−13.00756	−4.32577
				−5.543	2.190	0.025	−8.66667	1.56347	−14.86417	−2.46917
Quartzite	2%	1.241	0.328	−2.919	4	0.043	−4.66667	1.59861	−9.10512	−0.22821
				−2.919	3.469	0.052	−4.66667	1.59861	−9.38643	0.05310
	4%	0.679	0.456	−5.689	4	0.005	−13.00000	2.28522	−19.34478	−6.65522
				−5.689	3.630	0.006	−13.00000	2.28522	−19.60796	−6.39204

Table 9 The results of t-test on the TSR parameter of modified HMA in 3 freeze-thaw cycles

Aggregate	CaCO$_3$	Levene's Test for Equality of Variances		*t*-test for Equality of Means							
		F	Sig.	*t*	*df*	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
									Lower	Upper
Limestone	2%	0.000	1.000	−4.543	4	0.010	−5.66667	1.24722	−9.12950	−2.20383
				−4.543	4.000	0.010	−5.66667	1.24722	−9.12950	−2.20383
	4%	0.235	0.653	−10.854	4	0.000	−12.00000	1.10554	−15.06948	−8.93052
				−10.854	3.723	0.001	−12.00000	1.10554	−15.16165	−8.83835
Granite	2%	0.400	0.561	−5.000	4	0.007	−3.33333	0.66667	−5.18430	−1.48237
				−5.000	3.200	0.013	−3.33333	0.66667	−5.38189	−1.28478
	4%	3.213	0.148	−6.645	4	0.003	−12.33333	1.85592	−17.48620	−7.18047
				−6.645	2.424	0.013	−12.33333	1.85592	−19.11944	−5.54723
Quartzite	2%	0.114	0.752	−3.157	4	0.034	−5.66667	1.79505	−10.65054	−0.68280
				−3.157	3.958	0.035	−5.66667	1.79505	−10.67164	−0.66169
	4%	0.818	0.417	−7.300	4	0.002	−15.00000	2.05480	−20.70505	−9.29495
				−7.300	3.637	0.003	−15.00000	2.05480	−20.93658	−9.06342

In addition to improving adhesion to acidic aggregates, the incorporation of MCCP in bitumen also enhances its adhesion to highly polar aggregates. This is due to the increase in the polar characteristics of bitumen caused by MCCP modification. Simultaneously, there is a slight increase in the non-polar SFE element of bitumen when modified with MCCP. This change is the most significant result of using MCCP in bitumen.

The increase in the non-polar element of SFE has two major effects. Firstly, the total SFE of bitumen is heavily influenced by its non-polar element. When the non-polar element increases from 14.01 (ergs/cm^2) in the base bitumen to 20.54 (ergs/cm^2) in samples with 2% MCCP, the total SFE also increases by the same amount. This decrease in cohesion failure probability is directly related to the total SFE. The higher the total SFE, the less likely cohesion failure will occur.

The second effect of the increment in the non-polar element of SFE is on cohesion failure. The increase in this element results in the non-polar bonds playing a more significant role in bitumen-aggregate adhesion. It is important to note that non-polar bonds are more resistant to

Table 10 The results of *t*-test on the TSR parameter of modified HMA in 5 freeze-thaw cycles

Aggregate	CaCO$_3$	Levene's Test for Equality of Variances		*t*-test for Equality of Means							
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
									Lower	Upper
Limestone	2%	0.400	0.561	−6.500	4	0.003	−4.33333	0.66667	−6.18430	−2.48237
				−6.500	3.200	0.006	−4.33333	0.66667	−6.38189	−2.28478
	4%	2.118	0.219	−5.461	4	0.005	−13.00000	2.38048	−19.60926	−6.39074
				−5.461	2.249	0.025	−13.00000	2.38048	−22.22876	−3.77124
Granite	2%	0.082	0.789	−3.900	4	0.018	−5.66667	1.45297	−9.70075	−1.63259
				−3.900	3.741	0.020	−5.66667	1.45297	−9.81335	−1.51998
	4%	0.082	0.789	−8.488	4	0.001	−12.33333	1.45297	−16.36741	−8.29925
				−8.488	3.741	0.001	−12.33333	1.45297	−16.48002	−8.18665
Quartzite	2%	0.800	0.422	−3.098	4	0.036	−4.00000	1.29099	−7.58438	−0.41562
				−3.098	2.941	0.055	−4.00000	1.29099	−8.15540	0.15540
	4%	2.286	0.205	−11.750	4	0.000	−15.66667	1.33333	−19.36859	−11.96474
				−11.750	2.876	0.002	−15.66667	1.33333	−20.01496	−11.31837

Table 11 SFE elements of aggregates (ergs/cm^2)

Aggregate type	Γ^+	Γ^-	Γ^{AB}	Γ^{LW}	Γ^{Total}
Limestone	21.3	508.9	208.2	67.2	275.4
Granite	34.1	531.2	269.2	68.1	337.3
Quartzite	41.3	552.1	302.0	57.1	359.1

Table 12 SFE elements of bitumens (ergs/cm^2)

Bitumen type	Γ^+	Γ^-	Γ^{AB}	Γ^{LW}	Γ^{Total}
PG 64–16	1.89	0.68	2.27	14.01	16.28
PG 64–16 + 2% MCCP	1.67	0.93	2.49	20.54	23.03
PG 64–16 + 4% MCCP	1.59	1.14	2.69	24.36	27.05

breaking in wet environments compared to polar bonds. This observation highlights the weak polar characteristics of bitumen, where the non-polar element of SFE is much larger than its polar element. This phenomenon indicates the presence of non-polar covalent bonds in bitumen.

The combination of enhanced adhesion to both polar and non-polar aggregates, along with the decreased probability of cohesion failure, contributes to the improved performance and resistance of the asphalt mixture against moisture susceptibility. The modification of bitumen with MCCP effectively alters its surface properties, providing a more durable and resilient asphalt mixture.

There is no direct relationship between the parameters of SFE of bitumen and the sensitivity of asphalt mixtures to moisture. In order to determine the impact of SFE parameters on moisture sensitivity mechanisms, the values of CFE, AFE, ER$_1$, and ER$_2$ should be calculated based on the provided equations. Based on the values of

these two parameters, the effect of additives on the performance of asphalt mixtures against cohesion and adhesion failures under water presence can be investigated.

Table 6 consists of three columns. The first column represents the values of the free energy of cohesion under dry conditions (W_{BB}). The higher the value of this parameter, the more energy is required to create debonding in the bitumen, indicating a lower probability of cohesion debonding. The second column represents the values of the free energy of adhesion between bitumen and aggregate (W_{AB}). Higher values in this column indicate a higher energy requirement for debonding at the asphalt-aggregate interface. The third column represents the overall tendency of the asphalt mixture towards debonding in the presence of water ($W_{AB}W_{wet}$). The closer the value of this parameter is to zero, the more thermodynamically stable the asphalt mixture is, indicating a lower probability of stripping.

The AFE is always positive, showing the need for energy to separate the two materials, and larger positive values indicate better adhesion to the bitumen. Table 6 gives the results of SFE for various combination of aggregates, virgin bitumen, and MCCP-modified bitumens

The results of the cohesive energy parameter (WBB) in Table 6 show that the value of this parameter, which was equal to 57.2 (ergs/cm^2) in the base bitumen, rises to 65.1 and 69.6 (ergs/cm^2) by adding 2 and 4% MCCP, respectively. These changes indicate that the use of MCCP increases the energy required for the mastic failure, which is directly related to the cohesion failure.

Based on the data presented in Table 6, it can be observed that the AFE between the two materials is consistently positive across all samples, indicating that energy is needed to separate the elements from each other. The findings related to bitumen-aggregate AFE suggest that there is stronger adhesion between the virgin bitumen and granite aggregates compared to the other two types of aggregates. Therefore, the separation of the virgin bitumen from the unit surface of granite aggregates is more difficult and requires more energy under dry conditions (without water). In addition, by increasing the SFE in all samples, the application of MCCP increases the energy needed to rupture the bitumen-aggregate contact surface under dry conditions.

The results given of Table 6 demonstrate a change in the bitumen-aggregate AFE from a positive value in dry conditions to negative in the presence of water in all samples. Since water has larger SFE elements compared to bitumen, this trend was expected. As a result, when the bitumen, water, and aggregates come into contact, the presence of water causes a change in the free energy of the system towards the state with the lowest energy level. This phenomenon ultimately leads to what is known as "stripping," where there is a reduced adhesion between the bitumen and aggregates due to water interfering with their bonding mechanism. If the AFE in the presence of water is low, the state with the least energy will occur more quickly.

The results of bitumen-aggregate AFE in the presence of water, also referred to as "debonding energy", show that samples manufactured with quartzite aggregates have a higher negative AFE in comparison with those made with the other two aggregates. This indicates that more energy is released as a result of the bitumen's detachment from the unit area of aggregates due to water penetration. Therefore, the tendency to stripping is more in quartzite aggregates than granite and limestone. Moreover, the use of MCCP reduces the debonding free energy, which means a reduction in the desire of the system to achieve a stable state with the least energy, and improves its resistance to moisture sensitivity.

The results of the ER_1 and ER_2 bond energy parameters are presented in Fig. 10 Comparison of these results, obtained from the combination of SFE elements of bitumen and aggregates, reveals that the use of MCCP enhances the resistance of samples to moisture sensitivity by increasing the values of these parameters. In fact, the increase in these values indicates that, by adding MCCP

to the bitumen, its coating ability on the surface of aggregates is improved, irrespective of the type of aggregate, thereby reducing the thermodynamic potential which leads to moisture sensitivity in HMA.

In order to achieve durability and minimize the impact of moisture, it is important for the AFE between the asphalt binder and aggregate to be maximized. Additionally, the energy of debonding when water displaces the binder from the binder-aggregate interface should be minimized, as it is a driving force for moisture damage. By measuring the SFE elements of different asphalt binders and aggregates, the energy parameter (ER_1) was calculated. Combinations of binders and aggregates with higher values of ER_1 are expected to exhibit lower sensitivity to moisture damage.

From a thermodynamic perspective, the wetting and spreading behavior is determined by the balance between adhesive and cohesive forces, which can be quantified by a spreading coefficient (S). A higher value of S indicates a greater work of adhesion relative to the cohesive energy of the adhesive. Conversely, when the absolute value of the surface energy of adhesion between asphalt and aggregate under wet conditions is lower, the likelihood of aggregate stripping in the presence of water is reduced. Therefore, a higher value of ER_2 indicates a reduced sensitivity of the mixture to moisture damage.

Finally, the *t*-test was performed to determine the difference in the results of ER_1 and ER_2 parameters. In this test, the values of the bond energy parameters of the modified samples and the control sample were compared. According to the Levene's test results, the significance level is > 0.05, and the variances of the samples are equal. Therefore, the first row of each structure for the *t*-test in Table 13, which has a prerequisite for equality of variances, is investigated. According to the data presented in the table, based on the amount of the sig. value which is < 0.05
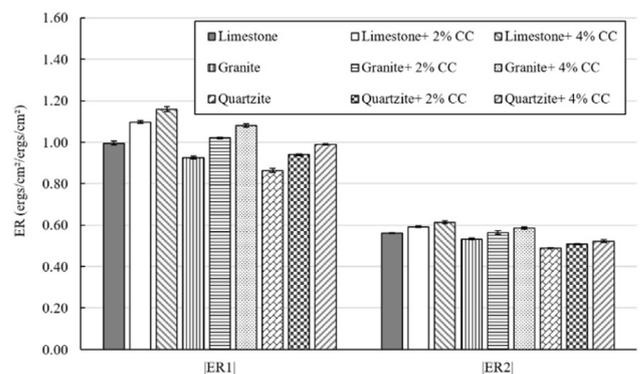

Fig. 10 ER_1 and ER_2 bond energy parameters of different HMA

for all samples, the assumption of the inequality of variances is confirmed at the 99% confidence level. This suggests a significant difference between the results of modified and control samples. In other words, the MCCP in HMA had an appropriate performance and reduced their moisture sensitivity potential.

The reduction in moisture susceptibility potential of asphalt pavement has several real-world benefits. Firstly, it improves the overall durability and longevity of the pavement. This leads to a longer service life for the pavement, reducing the need for frequent repairs or premature replacement. Secondly, it enhances the structural integrity of the pavement. Moisture-induced sensitivity can weaken the bond between the asphalt binder and the aggregate particles, resulting in decreased load-bearing capacity and structural stability. By reducing moisture susceptibility, the pavement can better withstand heavy traffic loads and resist deformation, ensuring a safer and more reliable road surface. Furthermore, improved moisture resistance helps in maintaining the smoothness and ride quality of the pavement. Moisture-related distresses, such as potholes and surface roughness, can create discomfort for drivers and increase vehicle maintenance costs.

4.4 Cost analysis

The cost of this agent is about $30 per tonne. If 5.5% bitumen and 4% MCCP are considered as the optimum bitumen content and optimum agent content respectively, the cost of using MCCP as an anti-stripping agent would be less than 10 cents per ton of HMA. Therefore, it is quite economical due to the improvement it makes in the performance of the HMA.

$$1t \times 0.055 \times 0.04 \times 30\$ = 0.066\$ = 6.6 \text{ cents}$$

5 Conclusions

Heavy costs are incurred annually by the maintenance and repair of moisture-induced sensitivity in the pavements. There are different ways to reduce this kind of sensitivity, with the main two methods being the use of liquid anti-stripping agents in the bitumen to improve CFE and AFE properties, and the application of suitable materials to coat the surface of aggregates in order to decrease their hydrophilic tendency. In this research, it was attempted to optimally protect HMA against moisture sensitivity using suitable anti-stripping materials and changes in HMA' characteristics. For this purpose, the MCCP was selected

because of its close alkali properties to those of hydrated lime and its easier operation. The results of this study can be summarized as follows:

- The use of MCCP in bitumen increases the ITS of modified bitumen samples compared to control ones due to improvement in adhesion properties.
- Addition of MCCP to bitumen significantly improves the TSR parameter index of the HMA regardless of the type of aggregates. The degree of this improvement was raised with an increase in the percentage of MCCP. Due to the low cost of this agent, the use of 4% MCCP is technically and economically feasible.
- The application of MCCP in bitumen decreases the acidity of the virgin bitumen and increases its basicity. This enhances the adhesion of modified bitumen to acidic aggregates such as granites which are susceptible to moisture sensitivity.
- Addition of MCCP to bitumen improves its adhesion to the high-polar aggregates by increasing the acid-basic (polar) properties of the bitumen.
- The use of MCCP decreases the desire of the system to achieve a stable state with the least energy and improves the resistance of the HMA to moisture by reducing the debonding free energy.
- The increase in the bond energy parameters of HMA containing MCCP indicates that adding this agent to the bitumen leads to an increase in the ability of the bitumen to coat the surface of aggregates, irrespective of the type of aggregates, thus decreasing the possibility of occurrence of moisture sensitivity in HMA.
- Based on the results obtained in this research, the following recommendations are made:

1. It is recommended to investigate the field performance of using MCCP in small-scale construction projects. This can help evaluate the effectiveness and real-world performance of this material under practical operational conditions.
2. Additionally, the use of MCCP should be examined for its impact on other important functional properties of asphalt mixtures, such as rutting, fatigue cracking, and low-temperature cracking. These investigations can provide a better understanding and comprehensive evaluation of the overall performance of asphalt mixtures when using MCCP.

Table 13 The results of *t*-test on the bond energy parameters of modified HMA

Bond Energy	Aggregate	CaCO$_3$	Levene's Test for Equality of Variances		*t*-test for Equality of Means							
			F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
										Lower	Upper	
ER1	Limestone	2%	0.235	0.653	−9.045	4	0.001	−0.10000	0.01106	−0.13069	−0.06931
					−9.045	3.723	0.001	−0.10000	0.01106	−0.13162	−0.06838
		4%	0.500	0.519	−10.733	4	0.000	−0.16000	0.01491	−0.20139	−0.11861
					−10.733	3.670	0.001	−0.16000	0.01491	−0.20290	−0.11710
	Granite	2%	3.200	0.148	−12.969	4	0.000	−0.09667	0.00745	−0.11736	−0.07597
					−12.969	2.941	0.001	−0.09667	0.00745	−0.12066	−.07268
		4%	0.235	0.653	−14.171	4	0.000	−0.15667	0.01106	−0.18736	−0.12597
					−14.171	3.723	0.000	−0.15667	0.01106	−0.18828	−0.12505
	Quartzite	2%	6.400	0.065	−8.854	4	0.001	−0.09333	0.01054	−0.12260	−0.06407
					−8.854	2.439	0.007	−0.09333	0.01054	−0.13170	−0.05497
		4%	6.400	0.065	−13.598	4	0.000	−0.14333	0.01054	−0.17260	−0.11407
					−13.598	2.439	0.002	−0.14333	0.01054	−0.18170	−0.10497
ER2	Limestone	2%	0.000	1.000	−7.778	4	0.001	−0.03667	0.00471	−0.04975	−0.02358
					−7.778	4.000	0.001	−0.03667	0.00471	−0.04975	−0.02358
		4%	3.200	0.148	−7.603	4	0.002	−0.05667	0.00745	−0.07736	−0.03597
					−7.603	2.941	0.005	−0.05667	0.00745	−0.08066	−0.03268
	Granite	2%	2.571	0.184	−3.889	4	0.018	−0.03667	0.00943	−0.06284	−0.01049
					−3.889	2.560	0.040	−0.03667	0.00943	−0.06981	−0.00352
		4%	0.400	0.561	−9.500	4	0.001	−0.06333	0.00667	−0.08184	−0.04482
					−9.500	3.200	0.002	−0.06333	0.00667	−0.08382	−0.04285
	Quartzite	2%	0.000	1.000	−5.657	4	0.005	−0.02667	0.00471	−0.03975	−0.01358
					−5.657	4.000	0.005	−0.02667	0.00471	−0.03975	−0.01358
		4%	3.200	0.148	−4.919	4	0.008	−0.03667	0.00745	−0.05736	−0.01597
					−4.919	2.941	0.017	−0.03667	0.00745	−0.06066	−0.01268

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