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1 Improving moisture sensitivity and mechanical properties of Sulfur

2 Extended Asphalt mixture by Nano- Antistripping Agent

3
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14 Abstract

15 Moisture damage and fatigue cracking are the most common defects of Sulfur Extended Asphalts
16 (SEAs). Moisture damage in asphaltic mixtures occurs due to the weak cohesion and adhesion that
17 cause the creation of different forms of pavement defects. Various methods have been implemented in
18 order to enhance the asphalt mixture's resistance to the moisture damage. One of the main methods is
19 the addition of anti- striping agents (ASAs) which reinforce the bonding between asphalt binder and
20 aggregates. In this study, a series of laboratory testing has been performed to appraise the mechanical
21 properties and moisture sensitivity of the SEA mixtures modified with ASA. In addition, Googas as a
22 new generation of modified-sulfur-mix additive and ASA (nanotechnology Zycotherm) were
23 employed to make warm-mix asphalt (WMA) specimens, through modification of neat asphalt (PG
24 64-22). Furthermore, four types of mixtures with different additives, containing ASA and sulfur, were
25 prepared, and the moisture susceptibility, resilient modulus, rutting resistance, and fatigue behavior
26 were measured. Obtained results, demonstrated the improvement of mechanical characteristics due to
27 the sulfur modification, exclusively for rutting phenomenon. Moreover, nanotechnology Zycotherm
28 (NZ) as an ASA enhanced the adhesion between aggregates and sulfur-extended asphalt; thus, the
29 resistance of SEAs against moisture damage and fatigue cracking improved.

30 **Keywords: WMA; Sulfur; Antistripping agent; Moisture susceptibility; Mechanical properties**

32 1. Introduction

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33 Asphalt is a visco-elastic binder that experiences elastic behavior during rapid loading or at
34 low environmental temperatures and viscous behavior during slow loading or at high
35 temperatures. This temperature- dependent behavior causes a desire to improve the properties
36 of asphalt to resist more against the rutting phenomenon, which usually appears at high
37 temperatures, and against cracking phenomenon, which mostly happens at low temperatures
38 [1]. On the other hand, temperature variations between warm and cold months, as well as,
39 increased traffic volume of trucks, create critical pressures in the structure of pavements.
40 Such conditions have caused an increased desire to improve asphalt properties. There are
41 various methods to modify the asphalt properties [2]. One of the most popular and common
42 procedure is using of modifier additives such as sulfur.

43 Since four decades ago, many studies have demonstrated that sulfur can modify and improve
44 the properties of asphaltic pavements [3]. Application of sulfur as an asphalt binder
45 performance extender is an economical solution to decrease virgin binder usage as well as
46 toxic gas emission. In spite of implementation problems, it was observed that Sulfur
47 Extended Asphalts (SEAs) could improve pavement's mechanical properties such as stiffness
48 compared to conventional asphalt mixtures [4]. The use of sulfur to improve the quality of
49 asphalt began in 1970 and was commercially used during the 1970s and 1980s. Without
50 appropriate technology at the time, handling and safety issues also were of concern, as molten
51 sulfur was difficult to apply and occasionally generated H_2S which had prevented its
52 application during those years. Therefore, there was an interruption period by using sulfur as
53 an asphalt modifier in the 1980s [5], but eventually, the concept of sulfur extended asphalt
54 (SEA) reappeared with the emersion of a new version of solid dust-free sulfur pellets. Solid
55 dust-free sulfur facilitates the displacing of sulfur in a solid pellet shape. This new product
56 was improved by using polymeric compounds in the sulfur pellets. By this change, it became
57 possible to add new product to the asphaltic mixtures while emission of hazardous gasses like

58 H₂S and annoying odors reduced considerably compared to the conventional-liquid sulfur
59 extended asphaltic mixture [6]. This new product reduced mixing temperature to about 135°C
60 while compaction temperature is reduced to about 90°C. Many of the mentioned safety
61 problems seemed to be disappeared, if the asphalt concrete was constructed at a mixing
62 temperature of 135 ± 5°C. Moreover, the new sulfur pellets could be poured directly into the
63 asphalt-aggregates mixture during the mixing operation [6]. As a result, there was no concern
64 about difficulties of blending it with asphalt before adding the binder to the aggregates. Since
65 mixing operation should be done in the temperature range lower than conventional HMA, it
66 should be considered as a Warm Mix Asphalt. Mixing temperature of WMA is approximately
67 16-55°C lower than conventional HMA, therefore, using the new sulfur extended asphalt as
68 WMA can reduce required energy to produce and compact asphalt mixture [7].

69 The bonding between asphalt and aggregates is considerably important as it affects the
70 integrity of asphaltic pavement. Such bonding forms at the beginning of the mixing process
71 when asphalt coats aggregates and this bonding should resist against stresses during its
72 lifetime in the asphaltic pavement, while, insufficient adhesion leads to a low performance of
73 the pavement. Divito et al. [8] showed that pavement strength depends on: (1) the asphalt's
74 cohesive resistance, (2) the resistance of adhesive bond between the asphalt and the surface
75 of aggregate, and (3) the interlock between the aggregates particles. ASAs are substances
76 designed to improve chemically the adhesion between the asphaltic binder and the
77 aggregates. They are available in both liquid and solid forms. One of the most common ASAs
78 which has been extensively used to improve the HMA's resistance against moisture damages
79 is hydrated lime. Other common conventional ASAs are fly-ash and Portland cement. In
80 addition, Liquid ASAs in the form of cationic surface-active agents (principally amines) have
81 become popular in recent years [9]. In this study, a liquid ASA commercially named

82 Zycotherm was used to make the aggregates hydrophobic while providing improved bonding
83 with the sulfur- extended asphalt binder.

84 **1.1. Literature review**

85 Bencovitz and Boe [10] demonstrated that sulfur could be mixed with asphalt as an extender
86 and make asphalt cement which can modify the asphalt rheological characteristics. For the
87 first time, Sulfur-Extended Asphalt was constructed by Kennepohl et al. [11] and practically
88 applied in asphaltic pavements in the early 1980s as a asphalt extender to decrease asphalt
89 consumption. Some case studies by Beatty et al. [12] showed that SEA has better function in
90 comparison with conventional HMA.

91 In recent studies performed on SEAs by Strickland et al. [13] and Timm et al. [14], sulfur was
92 applied in the form of a solid pellet which could be melted at a temperature round 120°C and
93 added as asphalt extender with the ratio between 30% and 40%. These pellets were pretreated
94 to decrease toxic gas emissions like hydrogen sulfide and also to lower the temperature of
95 mixing and compaction operations. At mixing operation, some of the sulfur homogenizes
96 with the asphalt at 120°C and decreases its viscosity. The remnant crystallized and covered
97 aggregates as the temperature is reduced. They showed that dissolved, and crystallized sulfur
98 makes the mixture stiffer and leads to a more resistant asphalt mixture at high temperatures,
99 and consequently less vulnerable to permanent deformation phenomenon. SEA also
100 advantaged the sulfur as asphalt extender and decreased asphalt consumption about 20-25%
101 of the binder weight [15]. Strickland et al. [16] suggested keeping the volume ratio of the
102 total binder phase (asphalt and sulfur) constant at asphaltic mixture before sulfur extending
103 and after that. This was recommended since the density of sulfur pellets is different from the
104 base asphalt. They established a relationship between asphalt and sulfur content in the SEA
105 based on the following Equation:

106

$$\text{Sulfur + asphalt\%} = \frac{100AR}{100R - P_s(R - G_{bitumen})} \quad (1)$$

107 In which:

108 Sulfur + asphalt % = sulfur- extended binder content by the weight of WMA sample; A =
 109 asphalt content by the weight of conventional HMA sample (%); R = specific weight ratio
 110 (sulfur to asphalt); P_s = sulfur content in extended binder; and $G_{bitumen}$ = specific weight of
 111 the asphalt.

112 Strickland et al. [16] did an experimental investigation on the functional properties of SEA in
 113 the laboratory. Results indicated deteriorated tensile-strength ratio (TSR) but improved
 114 dynamic modulus in various ranges of temperature and frequency. According to the results
 115 obtained by life cycle costs analysis of SEA pavement structures conducted by Cooper et al.
 116 [17] Using SEA amplified the predicted rutting and fatigue resistance and the overall
 117 pavement service lives compare to unmodified HMA at various traffic intensities. It was also
 118 shown that SEA has the potential to reduce construction and maintenance costs in
 119 comparison with a conventional HMA produced with the same binder grade. In a study
 120 conducted by Timm et al. [14], dynamic moduli and moisture susceptibility of SEA were
 121 evaluated. Results indicated that SEA was more vulnerable against moist condition as had
 122 lower TSR in comparison with conventional asphalt mixture: however, the SEA dynamic
 123 modulus increased.

124 **1.2. Research Objective**

125 Mechanical properties and moisture sensitivity of anti-stripping agent-modified SEA were
 126 evaluated in this paper by the experimental method. Nano-based anti-stripping agent named
 127 commercially zycotherm and petroleum base sulfur named commercially Googas were used
 128 respectively to replace a portion of asphalt and strengthen the bond between the binder (sulfur
 129 and asphalt) and aggregate's surface. In this study, moisture sensitivity test, rutting
 130 performance, resilient modulus and fatigue behavior were evaluated for the proposed

131 samples. Asphalt mixture tests were carried out on four different mixtures including one
 132 conventional HMA and three modified WMA (in different combinations of Sulfur and ASA
 133 additives).

134

135 **2. Test materials and mixing**

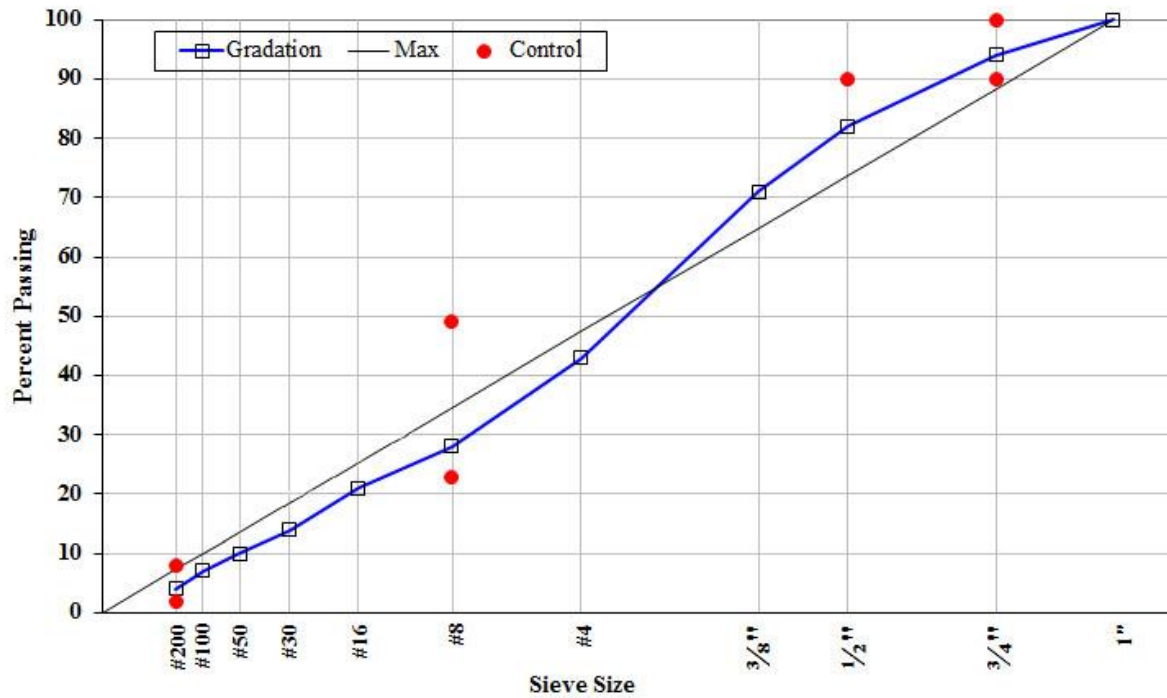
136 **2.1. Materials**

137 **2.1.1. Asphalt binder and aggregates**

138 Materials used in this experimental investigation included a PG 64-22 virgin asphalt binder,
 139 with the physical properties that are shown in Table 1. Used aggregates have desired
 140 mechanical properties such as enough strength, toughness and hardness. Also, crushed
 141 aggregates were used to make higher stability. The Superpave mix design [18] was used to
 142 prepare the asphalt mixtures and filler material (grinded limestone) were used to meet the
 143 aggregate gradation criteria shown in Fig. 1.

144 **Table 1**
 145 Physical properties of used asphalt binder

Properties	PG grade	Purity grade	Flash point	Softening point	Penetration Grade at 25°C	Ductility at 25°C	Viscosity at 135°C	Density
Unit	-	(%)	(°C)	(°C)	(mm/10)	(cm)	(mPa.s)	-
Value	64-22	99	262	54	67	104	349	1.03



146

147

Fig.1. Aggregate Gradation

148

149 **2.1.2. Sulfur**

150 Googas is produced by compounding neat sulfur, plasticizer and some other additives, which
 151 is higher than the range of evaporation, melting and freezing points of sulfur. This polymeric
 152 sulfur material has been produced in the ZENIT Company (R&D unit) in granular shape
 153 (solid pellet). Produced sulfur pellets can be substituted directly for about half of asphalt in
 154 the asphalt concrete and modify the asphalt which was used initially. Using Googas decreases
 155 energy consumption via decreasing the temperature needed for mixing and compacting
 156 operations. As the asphalt is more expensive than this material, it can decrease the costs of
 157 asphalt production and energy consumption [19]. Physical properties of Googas material are
 158 shown in Table 2.

159

160

161

162 **Table 2**
 163 Physical properties of Googas.

Test title	Result
Physical shape	Granule
Color	Gray
Water solubility	Non-soluble
Relative specific weight to water	1.89 gr/cm ³
Average size of pellets	2 mm
Melting point	Minimum 90°C

164

165 **2.1.3. Nanotechnology zycotherm (NZ)**

166 Nanotechnology Zycotherm (NZ) is a WMA additive produced by Zydex Company, Gujarat,
 167 India. This additive provides two significant benefits for WMA mixtures. It lowers
 168 production and compaction temperatures, while simultaneously reducing the moisture
 169 susceptibility of asphaltic pavements as an anti-strip agent. The first effect is the result of a
 170 reduction in viscosity of asphalt and the second is due to reinforced bond between binder and
 171 aggregates. NZ is an organosilane compound and can form silanols (Si-OH) groups. As
 172 silanols are so reactive, siloxane bonds (Si-O-Si) can be formed between NZ and inorganic
 173 surface-like sand and gravel surfaces which constitute from silanol groups. This additive
 174 could be used in different asphaltic mixtures consisting of modified or unmodified asphalt
 175 binders. This is very compatible with crumb rubber or polymer modified asphalt binder [20].
 176 Since Googas is a polymeric sulfur product, it could be a suitable additive to modify the
 177 studied SEA. Using NZ does not affect binder grading or change any other binder properties.
 178 Physical properties of zycotherm additive are shown in Table 3.

179

180

181

182 **Table 3**
 183 Physical properties of zycotherm.

Properties	Result
Form	Liquid
Color	Pale yellow
Flash point	> 80°C
Explosion hazard	Not known
Density	1.01 g/ml
Freezing point	5°C
Solubility	Miscible with water
PH value	10 % solution in water neutral or slightly acidic
Viscosity	300 cP (25°C)

184

185

186 **2.2. Mixing and HMA sample preparation**

187 **2.2.1. Mixing NZ in asphalt**

188 The optimum amount of NZ additive was determined 0.15% by weight of asphalt.
 189 Viscoelastic characteristics of modified asphalt and ITS parameter of NZ-modified asphalt
 190 mixtures were analyzed to achieve this optimum amount, according to the values in Table 4
 191 and Fig. 5, respectively.

192 The technique which was used to mix NZ in the asphalt binder includes three following steps.

193

- 194 1. The stirrer speed was set high enough (300 rpm) to create a 2-3 cm deep vortex
 195 before mixing zycotherm in molten asphalt at 150°C.
- 196 2. Zycotherm was added to the center of the vortex at ten drops per minute while
 197 maintaining the stirrer speed (According to the dosage of 0.15% by weight of
 198 asphalt, adding 1ml or 1g of zycotherm should take approximately 2 minutes for
 199 660g of binder).

200 3. The mixing operation performed for 10 minutes to make a completely
201 homogeneous blend.

202 Within the mixing process, the temperature was set at 150°C and kept constant by
203 applying an oil bath heated by a hot plate.

204

205 **2.2.2. SEA mixtures preparation**

206 The optimum binder content (OBC) was determined following Superpave mix design. The
207 OBC for SEA samples was modified by the equation (1). The OBCs were found to be 5.5%
208 and 4.3% for conventional and SEA mixtures, respectively. The research team used 35%
209 Googas by weight of asphalt for constructing sulfur contained samples, which was the
210 optimum amount obtained by doing Indirect Tensile Fatigue (ITF) and Loaded- Wheel
211 Tracking (LWT) tests. Following steps were taken for making SEA mixtures:

- 212 1. Used sulfur (Googas) pellets were heated to 60°C before adding to the aggregate-
213 asphalt mixture.
- 214 2. The ASA-modified asphalt was mixed with the hot aggregates at 120°C.
- 215 3. Preheated sulfur pellets were poured into the mixture.
- 216 4. The obtained blend was mixed completely at 120°C to make all pellets melted and
217 diffused all over the mixture.

218 Following types of asphaltic samples were constructed and tested:

- 219 • Conventional HMA mixtures (CHMA) – mixture made with the neat AC asphalt.
- 220 • ASA-modified WMA mixtures (AWMA) – mixture made with ASA-modified
221 asphalt.
- 222 • Sulfur- extended WMA mixture (SWMA) – mixture made with sulfur extended
223 asphalt binder.

- 224 • ASA- modified and sulfur extended WMA mixture (ASWMA) – mixture made
225 with ASA- modified binder extended by sulfur.

226 Triplicate specimens were constructed for every type of asphaltic sample.

227

228 **3. Testing program**

229 **3.1. Scanning electron microscopy (SEM)**

230 Taking a photo in nano and micro scales is one of the most precise methods to evaluate the
231 efficiency of used mixing procedure. In this study, the SEM method was applied to observe
232 the morphology of sulfur-modified binder as well as investigate the effectiveness of used
233 mixing method to obtain a homogeneous blend.

234

235 **3.2. Asphalt binder tests**

236 To obtain the optimum percentage of NZ as an antistripping agent additive and evaluate the
237 properties of used binders, empirical rheological tests were performed on neat and NZ-
238 modified asphalt binders in different NZ percentages. The research team applied the asphalt
239 tests in accordance with the relevant standards. The penetration degree test is a classic test
240 which determines the hardness of asphalt binder according to the ASTM-D5 standard [21]
241 [22]. Also for determination of softening point degree, the ASTM-D36 was applied [23].
242 Ductility test was performed to evaluate the cohesion of used asphalt; in this test specimens
243 were stretched at 25°C with a constant speed of 5 cm/min in accordance with the ASTM-
244 D113 [24]. A Brookfield rotational viscometer apparatus was applied to measure the
245 Viscosity of different asphalt binders. During this test, the temperature was set at 135°C
246 according to the ASTM-D4402 standard [25]. A number 21 spindle and a specimen size of
247 8.5 grams were used for this study.

248

249 **3.3. Asphalt tests**

250 Different asphaltic samples including CHMA, AWMA, SWMA and ASWMA were
251 constructed according to the aforementioned procedures, afterward; Resilient Modulus (RM),
252 ITF, LWT and Indirect Tensile Strength (ITS) tests were conducted on them as follow:

253

254 **3.3.1. Resilient modulus test**

255 In this study, the resilient modulus of asphaltic mixtures was evaluated by the indirect tensile
256 method according to ASTM standard [26] [27]. This test can be used to achieve a good
257 understanding of the elastic properties of studied asphaltic mixture. A Nottingham Asphalt
258 Testing apparatus was applied to determine the resilient modulus of different samples.
259 Dimensions of used cylindrical specimens were 101.6 mm and 65mm in diameter and
260 thickness respectively. The time of an entire loading cycle is 1.0 s long, which consists of 0.1
261 s loading and unloading time and 0.9 s resting time. When the indirect tensile method is
262 applied for evaluation of elastic properties, the following equation could be utilized to
263 calculate the resilient modulus parameter:

$$RM = \frac{P(v+0.27)}{t \cdot \Delta H} \quad (2)$$

264 Where RM = resilient modulus (MPa); t= sample height (mm); v = Poisson ratio; P =
265 maximum dynamic load; and ΔH = recoverable horizontal deformation (mm).

266

267 **3.3.2. Modified Lottman test**

268 Moisture susceptibility of the specimens was determined by modified lottman test according
269 to AASHTO T283 [28]. Specimens used for Modified Lottman test should be compacted to
270 reach the air voids of 7% ± 1.0. Dimensions of prepared specimens for this test are 150 mm
271 and 95 mm respectively for height and diameter. Six specimens were prepared for every
272 sample including three for unconditioned and three for conditioned mode. Unconditioned

273 specimens were not under moisture conditioning before the test, but conditioned specimens
274 were treated by the following stages:

275

276 • Immersing in water (up to 55–80% saturation level).

277 • Freezing at -18°C for 16 h.

278 • Placing in a 60°C water bath for 24h.

279

280 When this process completed, the ITS for both conditioned and unconditioned specimens was
281 measured at 25°C. The average ITS was considered as the final values for both conditioned
282 and unconditioned specimens. The TSR parameter is defined as the fraction of conditioned on
283 unconditioned ITS.

284

285 **3.3.3. Indirect tensile fatigue (ITF) test**

286 Research team utilized a Nottingham Asphaltic Mixture Tester to perform the fatigue test.

287 Nottingham tester measures the fatigue life and strains by applying repetitive Indirect Tensile

288 stress to the prepared samples in accordance with relevant ASTM standard for indirect tensile

289 method [26]. The tested specimens were in cylindrical shape and standard dimensions (40

290 mm height and 100 mm diameter). Asphalt mixtures were mixed and compacted in

291 accordance with the superpave mix design standard for construction of specimens [18]. The

292 frequency of loading was 1 Hz and it continued until the specimen experienced the failure

293 point. The failure point was also defined as 12.7 mm final vertical deformation or occurring

294 rupture in the loaded specimen. Controlled stress mode was chosen as the condition of

295 loading for the fatigue test in this study. In the controlled stress mode, the applied stress

296 should be kept constant to increase the strain of loaded specimen.

297 In this study 5, 15 and 25°C were chosen as the temperature of test to simulate the fatigue
298 phenomenon at the low-temperature condition. Two stresses of 100 kPa and 300 kPa were
299 selected as the constant values of applied load. A common equation (Wohler’s fatigue
300 equation) is usually used to show the relationship between the number of cycles to failure and
301 tensile strain. Such an equation could be obtained if the linear diagram of the relationship
302 between the “loading number to the failure point” (fatigue life) and the “applied strain” be
303 drawn on a logarithmic scale using a regression analysis [29]. Developed fatigue equations
304 would be in the form of Wohler’s fatigue equation (Eq. (3)):

$$N = a \left[\frac{1}{\varepsilon_t} \right]^b \quad (3)$$

305 Where “N” = loading number to the failure point; ε_t = measured strain; “a” and “b” =
306 coefficients effected by asphalt mixture properties.

307

308 **3.3.4. Loaded- Wheel tracking (LWT) test**

309 The LWT test has been applied for asphaltic mixtures accelerated performance testing in
310 terms of its rutting resistance according to AASHTO T324 [30]. A Hamburg wheel rut tester
311 was used to measure rut depth of different sample influenced by repetitive loading condition
312 in which specimens with a 30 - 30 - 6 cm dimensions were used to simulate rutting
313 phenomenon of real loaded pavement. In this study, the wheel track testing was carried out
314 by applying 703-N steel wheel on the submerged specimen at temperature 50 °C. The wheel-
315 tracker apparatus was programmed to finish rolling after 20,000 cycles or when the maximum
316 displacement recorded by LVDT was 20 mm. The maximum allowable permanent
317 deformation was determined to be 6 mm after 20,000 passes at 50°C. This value is required
318 to consider a sample resistant against rutting phenomenon.

319

320

321 **4. Results and discussions**

322 **4.1. SEM analysis results**

323 One of the most reliable methods to evaluate mixing operation-effectiveness is to take photos
324 in micro and nano scales by SEM microscopes [31]. Morphology of neat asphalt and Googas-
325 modified asphalt is illustrated in Fig. 2. Photos were taken at a voltage of 5 KV with 300-
326 60000 magnification scale. As illustrated in Table 2, the average size of unmixed Googas
327 pellets was about 2mm. To use the full potential of Googas as asphalt extender, it is necessary
328 to dissolve it in asphalt and make a homogeneous blend as much as possible. As shown in
329 Fig. 2-D, a major part of Googas pellets almost dissolved into the asphalt bulk and made it
330 more viscous, but other part was not fully dissolved at high mixing temperature and,
331 therefore, became crystallized at lower temperatures which can be seen in Fig. 2-C. In these
332 two figures white parts are sulfur and black parts are asphalt. In Fig. 2-D dissolved sulfur can
333 be distinguished because of high focus of picture as could be understood from the scales. In
334 SEA mixtures, sulfur gets cooled and crystallized around the coarse aggregates and makes the
335 mixture stiffer than before. Extra stiffness caused by dissolved and crystallized sulfur
336 improves rutting performance of SEA [7].
337 Increased viscosity normally raises the necessary temperature for mixing and compaction
338 operations, while Googas which is a polymeric sulfur product, reduces these temperatures
339 beside increment of viscosity that could be so favorable. This mechanism occurs due to the
340 improved properties of Googas product compared to the neat sulfur as a result of applied
341 treatments.

342

343

344

345

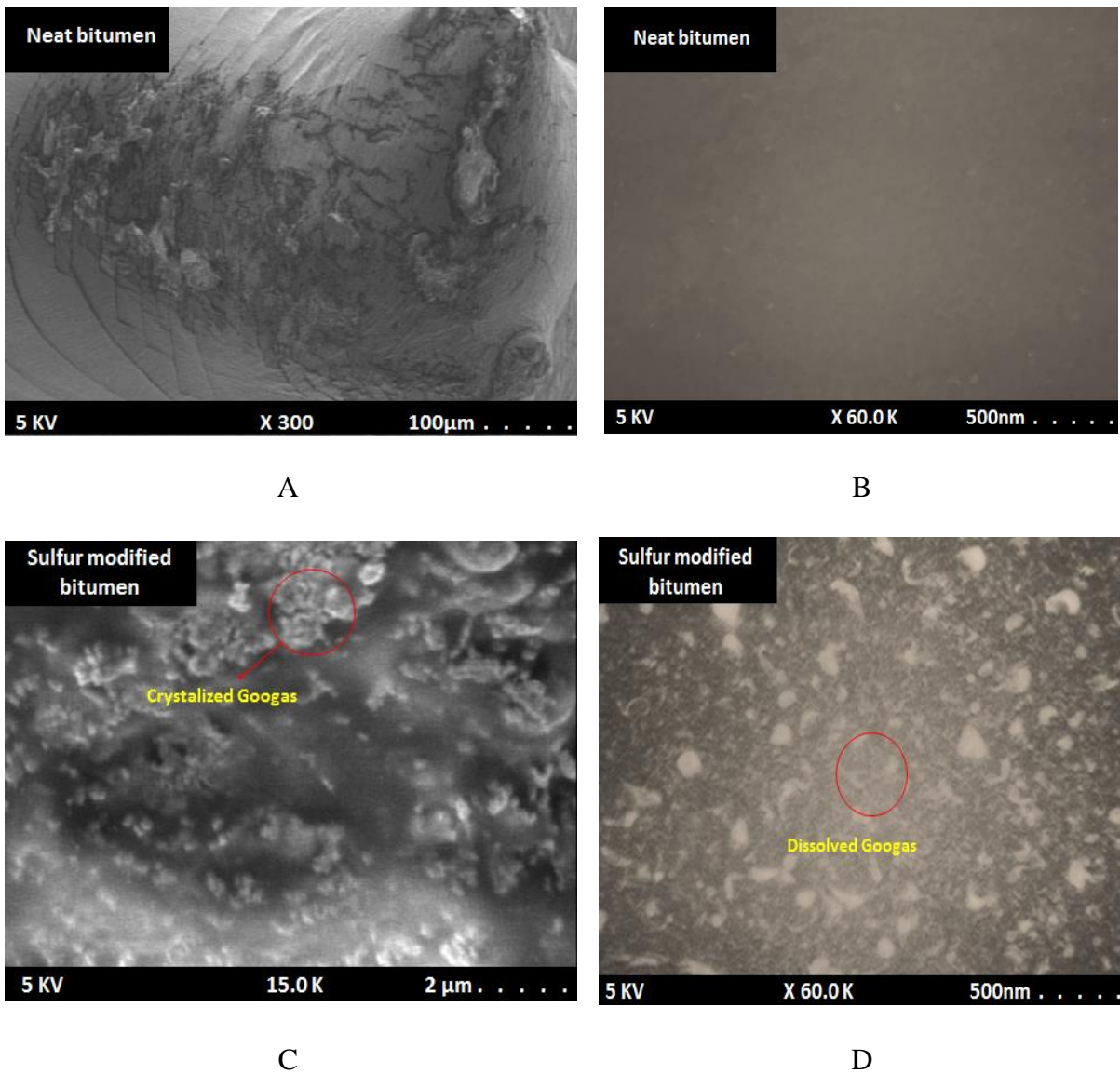


Fig. 2. SEM images of sulfur - modified/unmodified asphalt, (A) Neat asphalt - 100µm; (B) Neat asphalt – 500nm; (C) sulfur-modified asphalt binder - 2µm; (D) sulfur-modified asphalt binder – 500nm.

346 **4.2. Asphalt binder test results**

347 To obtain the optimum percentage of NZ as an antistripping agent additive and evaluate the
 348 properties of the used binders, empirical and rheological tests were performed on the neat
 349 asphalt, the NZ modified asphalt in different NZ percentages as well as sulfur and/or NZ
 350 modified asphalts in optimum percentages. As shown in Table 4, the more the NZ content,
 351 the more penetration degree, and consequently, the less softening point observed. These

352 changes were due to the lower viscosity of NZ- modified asphalt compared to the neat
 353 asphalt. As shown in Table 4, NZ- modified asphalt has better ductility than the neat one.
 354 This improvement could be attributed to the formation of bonds between chemical
 355 compositions of AC with NZ particles. The viscosity data of different samples including neat
 356 and modified asphalt at a temperature of 135 °C was collected by standard Rotational
 357 Viscosity (RV) test. As it is shown in Table 4, all samples had a viscosity value less than the
 358 SHRP limit of 3000MPa.s at 135 °C. Addition of NZ to asphalt should not affect the binder
 359 grading negatively, so 0.15% NZ was chosen as the optimum percentage of ASA additive.
 360 According to the rheological and empirical tests' results, adding sulfur made asphalt more
 361 brittle by increasing RV and softening point as well as decreasing ductility and penetration
 362 degree, while using ASA restores these properties to the neat asphalt condition to a high
 363 extent.

364

365 **Table 4**
 366 Basic properties of NZ and/or Sulfur modified asphalt.

property	PG	Rotational viscosity at 135°C (mPa.s)	Ductility at 25°C at	Penetration at 25°C	Softening Point (°C)
Standard Unit	ASTM D 6373 -	ASTM-D4402 (mpa)	ASTM D113 (cm)	ASTM-D5 (mm*0.1)	ASTM-D36 (°C)
Neat asphalt	64-22	349	104	67	54
Modified asphalt with 0.1% NZ	64-22	336	110	69	51
Modified asphalt with 0.15% NZ	64-28	329	114	70	49
Modified asphalt with 0.20% NZ	58-28	325	120	71.3	48
ASA- modified asphalt (15%NZ)	64-28	329	114	70	49
Sulfur- modified asphalt (35% Googas)	70-10	412	92	58	52
ASA and sulfur- modified asphalt (15%NZ and 35% Googas)	70-22	371	101	60	46

367

368

369 4.3. Asphalt test results

370 4.3.1. Resilient Modulus Test

371 In general, a pavement which has high resilient modulus is expected to resist appropriately
372 against permanent deformation [32]. Results of resilient modulus test at different
373 temperatures for CHMA, AWMA, SWMA and ASWMA mixtures have been illustrated in
374 Fig. 3. As seen, the stiffness of studied mixes reduced by increasing the temperature.
375 According to the Fig 3, the resilient modulus of asphaltic samples amplified by about 30%
376 and 100 % respectively for SEAs (SWMA and ASWMA) and sulfur- unmodified samples
377 (CHMA and AWMA) by lowering the temperature from 25 °C to 5°C. At any constant
378 temperature, the highest stiffness quantity was achieved for SWMA follow by ASWMA,
379 CHMA, and AWMA mixtures. As depicted in Fig 3, in comparison of CHMA with AWMA,
380 the rate of resilient modulus reduction due to the addition of ASA is more considerable at
381 lower temperatures. On the other hand, in comparison of CHMA with SWMA, the rate of
382 resilient modulus improvement due to the addition of Googas was more considerable at
383 higher temperatures. The reduction of the binder viscosity around the aggregate particles at
384 high temperatures was the main reason for this difference. Dissolved sulfur in the asphalt
385 made it stiffer, and more viscose in different temperatures; also, crystallized sulfur around the
386 aggregates made a more powerful bond between sulfur- modified binder and aggregates.
387 Therefore, the binder film around the aggregates was more stable for SEAs samples
388 compared to the other samples especially at higher temperatures [33]. According to the
389 viscosity test data, increasing NZ content had decreased binder viscosity that led reduction of
390 binder film around aggregates; therefore, as illustrated in Fig.3, AWMA has lower stiffness
391 modulus in comparison with CHMA at different temperatures. As obviously portrayed in Fig.
392 3, the highest resilient modulus improvement rate of SWMA and ASWMA occurred at higher
393 temperatures. Using ASA reduced SEA mixture's resilient modulus slightly, but this
394 deterioration was negligible especially at higher temperatures.

395

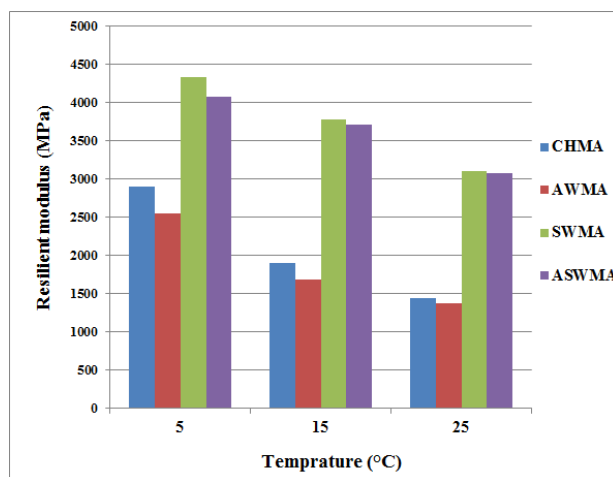


Fig. 3. Comparison of resilient modulus values at 5, 15 and 25°C.

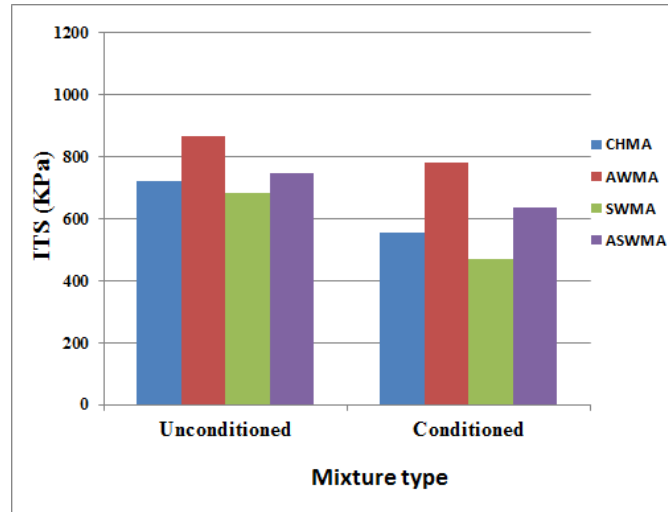
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399 4.3.2. Moisture resistance performance

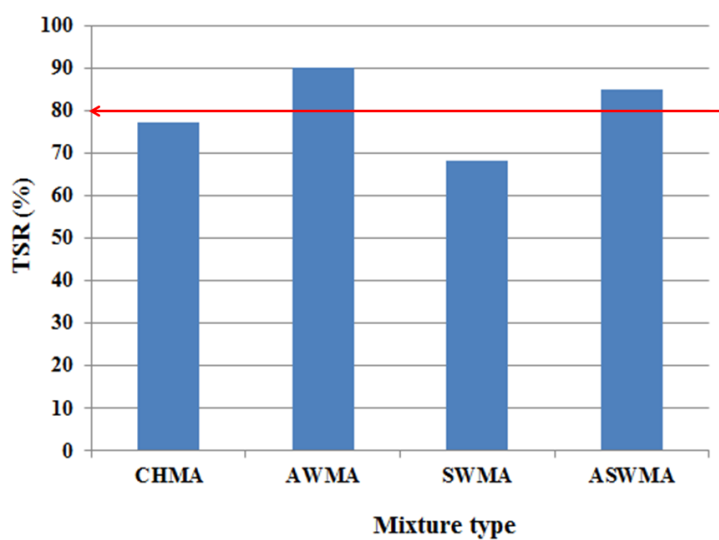
400 The results of the ITS test are summarized graphically in Fig.4 and Fig. 5. Diagrams in Fig. 4
 401 show a reduction (approximately 19%) in the splitting tensile strength of the ASWMA versus
 402 the AWMA in a conditioned situation as a consequence of adding Googas. The same
 403 parameter increased 41% for AWMA in comparison with CHMA due to applying ASA-
 404 modified asphalt. By considering 80% as the minimum acceptable TSR value, CHMA and
 405 SWMA samples showed inadequate moisture resistance (respectively 77% and 68%). Fig. 5
 406 shows that both AWMA and ASWMA had an acceptable resistance to moisture damage, with
 407 TSR value above 0.8 for each mixture (0.90 for AWMA and 0.85 for ASWMA). Therefore,
 408 AWMA and ASWMA samples which were modified by NZ as an anti- stripping agent
 409 showed improved moisture susceptibility compared to CHMA and SWMA samples.
 410 Comprehensively, these comparisons demonstrated that Googas lowers indirect tensile
 411 strength (ITS) and tensile strength ratio (TSR), but ASA improves them significantly.



412

413

Fig. 4. The indirect tensile strength of unconditioned and conditioned specimens.



414

415

Fig. 5. TSR values vs. mixture type.

416

417 4.3.3. Fatigue performance

418

As results of performed fatigue tests, the correlations between the number of cycles and the

419

strain level applied to the specimens at 5, 25 and 40 °C under 100 and 300 KPa stresses are

420

illustrated in Fig. 6. Results indicated the beneficial effects of NZ and deteriorative effect of

421

Googas on the fatigue life of studied mixtures. Also, reduction in the mixtures' temperature

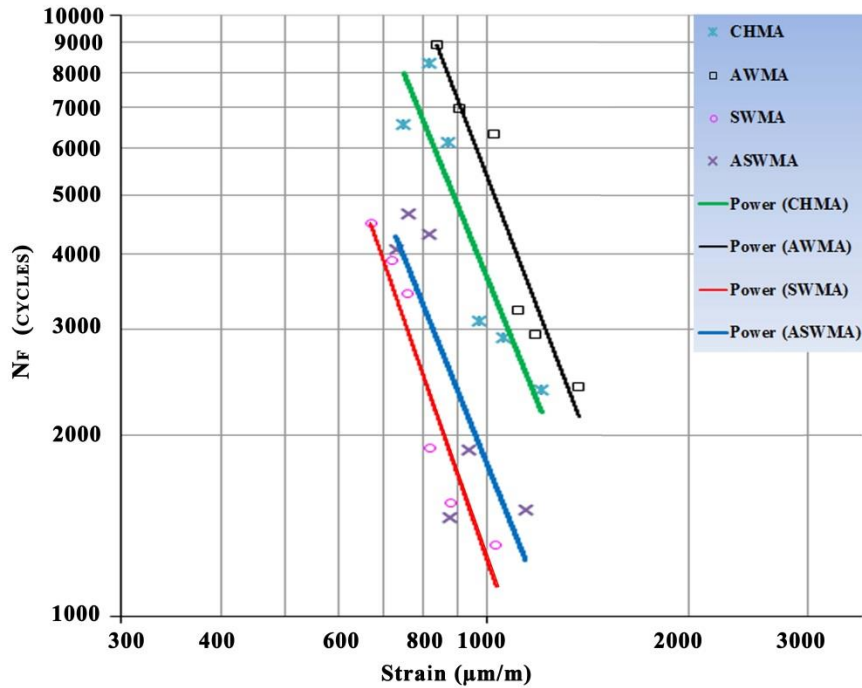
422

led to the increment of the fatigue life at aforementioned stress levels. Fig. 6 compares the

423

fatigue curves of four specimens including CHMA, AWMA, SWMA and ASWMA. Between

424 these specimens, AWMA showed the finest performance following CHMA, ASWMA and
425 SWMA. As mentioned earlier, the crystallized part of sulfur particles and dissolved part in
426 the asphalt during the mixing process, decreases the binder's ductility and flexibility; thus, a
427 lower fatigue resistance and flexibility were observed in the SEA mixtures. However,
428 considering stiffness properties exhibited in the previous section, the improved resilient
429 modulus of SEA mixtures will decrease strain magnitude applied to the pavement structure.
430 This phenomenon could have a beneficial effect on the SEAs fatigue behavior in real
431 condition, in which the pavement structure bears stress-controlled vehicular loading instead
432 of strain-controlled loading, as was chosen as loading condition in the laboratory [7].
433 AWMA had the longest fatigue life which could be justified by the lower stiffness and
434 viscosity of this sample as well as a developed bond between asphalt and aggregates as a
435 result of ASA- modification. On the other hand, as demonstrated by ITS test in the previous
436 section, using NZ can lead to high tensile strength in NZ- modified asphalt mixtures.
437 Improved tensile strength leads to the postponing of micro-cracks generation and propagation
438 which subsequently postpones fatigue failure. As illustrated in Fig.6, the ASWMA had
439 slightly flatter slope compared to the SWMA, which demonstrates that NZ-modified SEA
440 possesses higher fatigue life at a greater strain. Coefficients of fatigue equations are shown in
441 the table. 5.



442

443

Fig. 6.ITF test results.

444

Table 5

446 Coefficients of the fatigue equations.

Asphalt mixture	Coefficient of the fatigue equations		R^2
	a	b	
CHMA	6E+11	-2.74	0.841
AWMA	3E+12	-2.91	0.918
SWMA	6E+12	-3.22	0.903
ASWMA	4E+11	-2.78	0.764

447

448 4.3.4. Rutting performance

449 The rutting resistance of the four evaluated samples is illustrated in Fig. 7. As it was

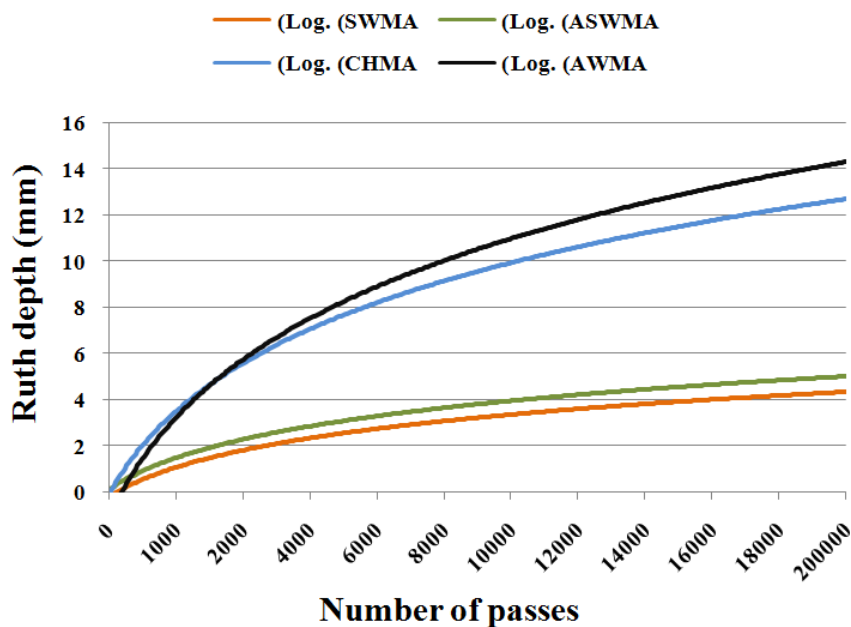
450 mentioned previously, maximum permissible rut depth of 6 mm after 20,000 cycles at 50°C

451 is acceptable. As seen in Fig. 7, the results of the Hamburg testing showed that both the

452 ASWMA and SWMA had met the desirable deformation resistance considering the stated

453 criterion. These two samples almost showed a similar rate of increase and ultimate resistance

454 which demonstrate that adding NZ as the anti-stripping agent does not have a considerable
 455 effect on the rutting resistance of asphaltic mixtures. On the other hand, sample AWMA
 456 showed the weakest resistance against rutting at 20,000 cycles, followed by CHMA, as
 457 shown in Fig. 7. Both of these samples were not modified with sulfur, therefore had less
 458 stiffness than SEA samples and consequently were weaker against rutting phenomenon.
 459 As shown in Fig. 7, specimens ASWMA and SWMA showed a rutting value at 20,000 cycles
 460 that were less than 6.0 mm; therefore, SEA samples had sufficient rutting resistance, unlike
 461 two other samples.



462
 463 **Fig. 7.** Wheel track test results at 50 °C.

464
 465 **5. Conclusion**

466 This study evaluated the effectiveness of using a new generation of modified- sulfur and ASA
 467 additives in the production of warm-mix asphalt. In this study, the moisture susceptibility and
 468 some of the mechanical properties of conventional HMA and ASA and/or sulfur- modified
 469 mixtures were evaluated and compared. The modification of asphalt mixture with Googas
 470 (treated sulfur) and the use of nanotechnology Zycotherm as the anti-stripping agent resulted

471 in an efficient additives combination which leads benefiting improved properties of SEAs
472 while omitting or attenuating its defects. In addition:

473

474 • As it was shown in SEM pictures, mixing procedure was a successful technique to
475 mix Googas in asphalt mixtures and make an almost homogeneous Googas-asphalt
476 matrix. Some parts were dissolved to an acceptable degree and some crystallized at
477 micro and nano scales.

478 • Extending a portion of asphalt by Googas led to a mixture with a higher resilient
479 modulus which was more resistant to permanent deformation. This increase was about
480 50 % and 100 % at low and high temperatures respectively. Using ASA reduced SEA
481 mixture's resilient modulus slightly, but this deterioration was negligible especially at
482 higher temperatures (lower than 4%).

483 • Obtained results by Lottman test demonstrated that Googas reduced indirect tensile
484 strength (ITS) about 8 % and tensile strength ratio (TSR) about 12 %, but on the other
485 hand, ASA improved them significantly by about 42 % and 28 % respectively.
486 Therefore, moisture susceptibility of ASA-modified SEA (ASWMA) was
487 significantly improved compared with unmodified SEA. As a result, modification of
488 SEA by the use of ASA (Zycotherm) was a successful method to reduce moisture
489 susceptibility of SEA mixture.

490 • SEA mixtures showed the least fatigue life. However, the greater modulus of SEA
491 mixtures reduced the magnitude of strain induced in the sample (about 20 %).
492 Furthermore, antistripping agent increased fatigue life (about 25 %) by developing
493 adhesion between asphalt and aggregates.

494 • As a result of higher stiffness, the rut depth of SEA mixtures decreased by about
495 300% at the last cycle of the loading process in comparison with conventional asphalt

496 mixture. Using ASA attenuated this improvement slightly, but the reduction was
497 negligible (about 25%).

498 Overall, conclusions of this research indicate that mechanical characteristics of asphaltic
499 mixture improve by sulfur modification, essentially about rutting phenomenon. On the other
500 hand, nanotechnology Zycotherm as an anti-stripping agent could improve adhesion between
501 aggregates and sulfur- extended asphalt, therefore, improve the deteriorated parameters
502 caused by sulfur modification, such as moisture susceptibility and fatigue resistance.

503

504

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