The Effect Of Sulfur Waste And ABS On Asphalt Cement Properties

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ABSTRACT

Nineveh is one of the Iraqi provinces 400 km north Baghdad capital and having an industrial company for sulfur production. This company produces nearly 20-25% of the total production as waste materials. This research investigates the ways of recycling the sulfur waste (SW) in solving the higher cost problem coming from import of waterproofing materials and presents information on the program and laboratory test data. Materials used in test program included 40/50 asphalt cement, Alkyl benzene sulfonate (ABS) and sulfur waste (SW). Five SW contents 0, 1, 3, 5 and 7%, and 1% of ABS in terms of asphalt cement by weight were used. Tests including physical properties, compatibility, storage stability, aging properties, temperature susceptibility and water permeability were carried out in accordance with the ASTM procedure. The test results revealed that SW is a reliable material for paving asphalt cement and being readily available can be widely used in water proofing construction materials, and this offers profound engineering and economic advantages.

Keywords: Sulfur waste, Alkylbenzene sulfonate, Asphalt, Modifier, Water proofing material.

تأثير فضلات الكبريت والالكيل بنزين سلفونيت على خصائص الاسفلت

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الخلاصة

تمتلك محافظة نينوى شركة لصناعة الكبريت. تنتج هذه الشركة ما يقارب 20 إلى 25% من الناتج الكلي كمخلفات. تتحرى هذه الدراسة عن إمكانية إيجاد وسائل لاستخدام مثل هذه الفضلات في إنتاج مواد مانعة الرطوبة وبأقل كلفة ممكنة بدلا من استيرادها من الخارج، كما تضمنت الدراسة عرض معلومات وافية عن برنامج الفحوصات المختبرية التي تم اجراؤها على المزيج المنتج والمواد الداخلة في تركيبته والمتضمنة الاسفلت ذو النفاذية 40-50, الالكيل بنزين سلفونيت والفضلات الكبريتية. استخدمت الفضلات الكبريتية بعدة نسب (5,3,1 و7% من وزن الاسفلت) مع 1% من الالكيل بنزين سلفونيت في انتاج عدة انواع من الاسفلت المستخدم كمانع رطوبة. اجريت الفحوصات الفيزياوية, التجانس, ثباتية الخزن, التقادم, تأثير الحرارة و نفاذية الماء على المزيج المنتج بموجب المواصفات الأمريكية. أوضحت الدراسة إمكانية استخدام الفضلات الكبريتية مع الالكيل بنزين سلفونيت في انتاج اسفلت رخيص الثمن يصلح لأعمال التسطيح وقطع النضوح بدلا من استيراده وبالعملة الصعبة خاصة وان هذه الفضلات متوفرة محليا.

الكلمات الدالة: فضلات الكبريت: الكيل بمزين سلفونيت: اسفلت: محسنات: مواد مانعة رطوبة.

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Introduction:

Roofing materials (asphalt and joint sealant) are regarded as one of the important primary materials used in the field of civil engineering work. Their selection must always be a matter of compromise between price and performance. It is speculated that the current annual worldwide consumption of waterproofing materials is over 120 million tons [1]. Asphalt and joint sealant are used in civil engineering work or in road paving construction because it is a strong cement, readily adhesive, highly waterproof, and durable. It is because of these superior qualities that asphalt and joint sealant are so widely used in the field of civil engineering work.

The behavior of asphalt cement in service is governed by their initial engineering properties as well as by the mechanical and environmental conditions to which they are subjected [2]. Available asphalt from refinery is too soft for roofing in high temperature areas in summer, and too brittle for a subzero temperature in winter in various parts of the country. The durability of asphalts is largely influenced by its chemical composition. It has been observed that Iraqi asphalts obtained from imported as well as indigenous crude contain 9 to 29% asphaltenes, 20 to 41% polar aromatics, 21 to 41% nephthene aromatics and 8 to 16% saturates [3]. The control of chemical composition of asphalt cement is a difficult task for refineries.

The available asphalts are not ideal for dam proofing and waterproofing applications. The waxy asphalt cement from indigenous crudes contains 8 to 16% wax, which causes softening of binder at high temperature and reduction in adhesion. Under these situations, it is essential to modify the asphalt cement using modifiers to improve its engineering properties. Among various types of modifiers, polymers are probably the most promising. Despite the large number of polymeric products, relatively few are suitable for modification of asphalt cement and are compatible with asphalt cement [4].

Polymer-modified asphalt binders are known to have better engineering properties. Improved properties have been reported in major areas of pavement deteriorations; high temperature rutting resistance, low temperature thermal and fatigue crack reduction etc. [1, 3, 5-17].

Because the polymer modifiers that have been employed beneficially as asphalt modifiers are rather expensive, a need exists for alternative, lower-cost modifiers that nonetheless impart improved properties comparable to those achieved by using the more expensive polymers.

Nineveh is one of the Iraqi provinces (400 km north Baghdad capital) having an industrial company for sulfur production. This company produces nearly 20-25% of the total production as waste materials. Sulfur waste (SW) is a fine gray to green powder mainly composed of sulfur, carbon and ash. It consists of 88 to 90 percent sulfur, 10 to 12 percent carbon, and small amount of ash (0.1 percent) [18].

The melting point of SW varies depending on the sulfur concentration and ranges between 140 to 145oC. In general, the sulfur waste specific gravity ranges between 2.03 to 2.215. Most used SW cannot be directly recycled and must be discarded. Although it is possible to incinerate waste sulfur to recover significant heat energy, most waste sulfur is disposed of by burial in landfills. Like most materials that are disposed of in landfills, waste sulfur does not degrade. Although estimates vary, the amount of waste sulfur produced and landfilled annually is roughly 7,000 to 20,000 tons. At a landfill disposal cost of at least $95/ton, this quantity of discarded waste sulfur costs the sulfur industry between $665,000 and $2000, 000 per year. This makes it especially desirable to develop alternative, more cost-effective methods for disposing of this material, and particularly methods for recycling it.

The present study concentrated on investigating the use of SW with asphalt cement to manufacture an economically water proofing and damp proofing asphalt cement. Their selection must always be a matter of compromise between price and performance. Among the reasons for the popularity of manufacture of SW asphalt cement as waterproofing materials are the wide range of the useful physical properties, the low cost and the ease of processing.

From a technological stand point, the typical specifications for water proofing and damp proofing asphalt cement include: The ability to prevent the surface of various shapes and types from water leakage; economical aspects, and ease of use.

The aims of this paper are: (1) to use SW as a modifier with 40/50 paving asphalt in the manufacture of waterproofing asphalt cement; (2) Raising waterproofing asphalt cement performance to sustain Iraqi continental climate; and (3) Diminishing costs by applying cheap raw materials. Besides investigating the development of water proofing asphalt cement, the experimental work aimed at achieving one or both of the following objectives: (1) to determine the physical properties of SW-modified asphalt binder (SWMAB) with and without Alkyl benzene sulfonate (ABS) as a catalyst and compare the results with 40/50 penetration grade asphalt cement; (2) to evaluate temperature susceptibility of SWMAB with and without ABS and compare the results with asphalt cement; and (3) to optimize the short-term aging performance of SWMAB with and without ABS by proper selection of SW concentration.

Experiment

40-50 penetration grade asphalt was selected for this study. Some properties of this asphalt are listed in Table 1.

Asphalt has high asphaltene content (32.65%). This asphalt is a less compatible (gel type), and is usually considered the type, which have been used widely in the highway construction projects in Nineveh Government (400km North Baghdad Capital). Note that compatibility is a compositional property that correlates with various physical properties [3].

Asphalt has long been classified as gel or sol type. Gel-type asphalts usually exhibit pronounced non-Newtonian behavior, whereas sol-type asphalts are more Newtonian. Gel-type asphalts generally contain large amounts of asphaltenes, and sol-type asphalts are characterized by low asphaltene content. Using the classical asphalt science terminology, sol-type asphalts are more compatible, while gel-type asphalts are less compatible [3]. Less compatible (gel-type) asphalt is known to be highly susceptible to oxidative age hardening. While highly compatible (sol-type) asphalt is not susceptible to oxidative age hardening. It is anticipated that the SW will dissolve when interacting with asphalt.

Table 1 Physiochemical properties of asphalt cement

Property	Result	ASTM limits
Penetration(25°C, 100g, dmm)	42	40-50
Softening point, °C	54	50-58
Ductility (25°C, cm)	150^+	100 min
Specific gravity	1.053	1.01-1.06
Flash point, °C	263	240 min
Loss of heat and air, %	0.25	0.2 max
Ashaltene, %	32.65	---
Solubility, %	99.21	99 min
Residue ductility (25°C, cm)	142	---
Residue penetration, % of original	88	---
Increase of softening point after TFOT, °C	2	---

The SW is a residual material of sulfur production unit. It was obtained from Al-Meshrak state company (30 km north of Mosul). The physiochemical properties of these materials are shown in Table 2.

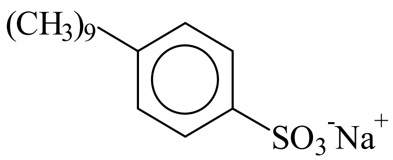
Table 2 Physiochemical properties of sulfur waste

Element	% wt.
Sulfur	88-90
Carbon	10-12
Ash	0.1
sp. gr.	2.03

The ABS was brought from al-Kornesh market in Mosul city. The price of this material was 0.133 $/kg. The physiochemical properties of ABS are shown in Table 3.

Two groups of SWMAB were prepared. The first group was labelled as $SWMAB_0$. The second group was then treated with 1% ABS (by wt. of asphalt) as catalyst and labelled as $SWMAB_1$. Eight different concentrations of SW-modified asphalt (SWMA) were thus prepared by first heating the asphalt to 140°C. Upon reaching 140°C, a weighed amount of SW with and without ABS (1, 3, 5 and 7% by weight of asphalt) was slowly added while mixing at 140°C using a slow-speed stirrer, and blending was done for a period of 8-12 minutes to obtain a homogeneity binder. Hence, it should be mentioned that the ABS percentage was chosen based on the previous study adapted by the author [19]. After completion, the SWMAB was removed from the can, divided into small pans, cooled to room temperature, sealed with aluminum foil, and stored for the following tests:

Table 3 Physiochemical properties of ABS

Property	Test result and unit
Color	White
Chemical unit	
Price	0.133$/kg

- Physical tests such as penetration, ductility, softening point . . . etc.
- Temperature susceptibility.
- Short term aging using thin film over test (TFOT) , which simulates the aging effect of the asphalt mixture production and construction
- Compatibility test
- Permeability test

  All tests followed the ASTM [20] standards.

RESULTS AND DISCISSION
Physical tests

Due to the difference in the solubility parameter and density between SW and asphalt, phase separation would take place in SW-modified asphalts during storage at elevated temperatures or at high mixing temperatures. Droplets of the SW melt dispersed in asphalt are usually accumulated at a high temperature and static state due to the recrystalization of sulfur. If a mixture of SW and asphalt is kept at high temperature, the SW will separate out from the asphalt, which will result in the difference in properties. The physical properties of SW-asphalt binders with and without ABS were evaluated and the results are presented in Table 4.

Table 4 The main properties of SWMABs

%SW	Penetration		Ductility		Flash point °C	Softening point °C	
	$SWMAB_0$	$SWMAB_1$	$SWMAB_0$	$SWMAB_1$	$SWMAB_1$	$SWMAB_0$	$SWMAB_1$
0	42	42	150^+	150^+	263	54	54
1	36.8	39	111	127	259	52	58
3	27	31.8	86	102	241	49	64
5	22.2	24.6	78	87	219	61	69.2
7	16.9	19	62	69	202	66	78
ASTM D312	25-50		10 min		232 min	63-77	
ASTM limits	40-50		100^+		>240	50-58	
SCRB[20]	40-50		100^+		-	51.62	

From this Table, it can be seen that the modified asphalts with varying SW content show good properties after reaction with ABS. The ductility values of $SWMAB_0$ and $SWMAB_1$ at 3% SW are 86 and 102, respectively. For these two modified asphalts the penetration values are 27 and 32, respectively. The results also revealed that the softening point of virgin asphalt modified by 3% SW with the addition of 1% ABS raised by 19%, whereas, it decreased by 9% with the absence of ABS. These results confirm that the physical properties, elasticity, compatibility and storage stability of SW-modified asphalt had been improved effectively with the addition of 1% ABS (by wt. of asphalt) due to the formation of a chemically crosslinked network in the modified binders, and the photomicrographs in Figure 7 insure these results.

Temperature susceptibility

The temperature susceptibility of asphalt binders is quantified by penetration index (PI) using the following equation mentioned by Yang [21]:

$$pentrationindex(P.I) = \frac{20-500A}{1+50A}$$

$$A = \frac{\log(Pen.@T) - \log 800}{T - T_{R\&B}}$$

Where

T= Testing temperature &

$T_{R\&B}$=Ring and Ball softening point.

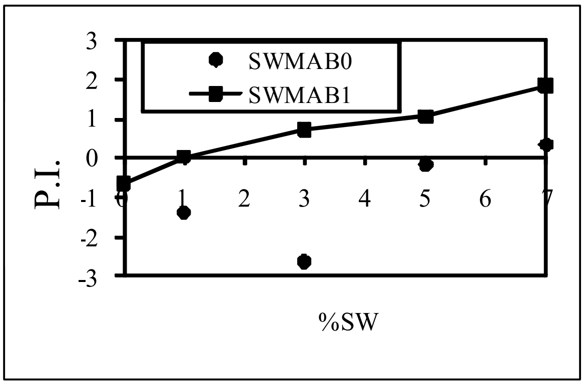


Fig. 1 P.I. of SWMABs

Calculated values of PI for SW-modified asphalt and asphalt cement are given in Figure 1. A higher value of PI indicates the lower temperature susceptibility of binder. From this Figure, it can be observed that the values of P.I. for virgin, 3% $SWMAB_0$ and 3% $SWMAB_1$ samples are -0.644, -2.621 and +0.7307, respectively. This significant fact demonstrates that SW will lead to make this binder less susceptible to temperature and more favorable for hot climates with the addition of ABS.

Aging susceptibility of SW binders

Fig. 2 and 3 show the ductility and softening point properties of aged SWMAB1. From these Figures, it can be seen that ductility decreases, while softening point increases. Moreover the values of ductility remain (100^+) up to 1% SW content.

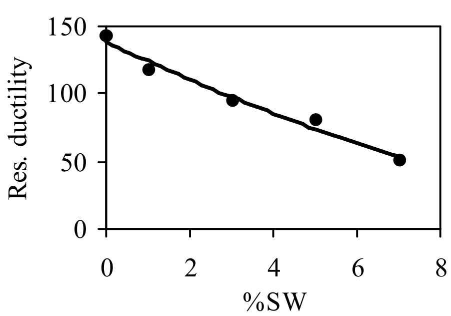


Fig. 2 Ductility of $SWMAB_1$

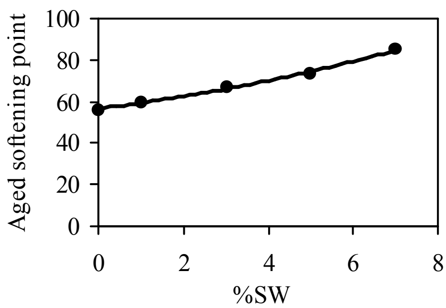


Fig. 3 Softening point of $SWMAB_1$

Fig. 4 shows that the percent loss of SW binders increases as the SW content increases. This is related to that SW occupied much of the volume of the total mixture, which leads to increase in loss by dehydrogenation and oxidation of asphalt in the mixture. The results also indicate that the percentages loss of $SWMAB_1$ less than those obtained with $SWMAB_0$.

The hardening of $SWMAB_1$ binders was determined by the penetration of residue after exposure to heat and air as shown in Fig. 5. Aging was measured by aging index using the following equation:

Aging index = Residue penetration after aging at 25°C/ original penetration at 25°C

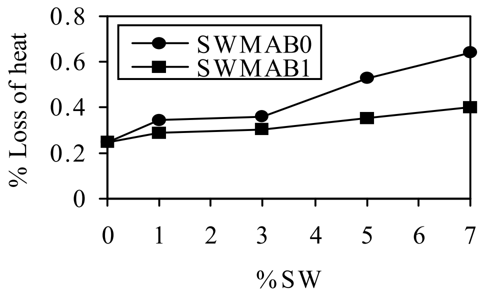


Fig. 4 Percent loss of heat and air of SWMABs

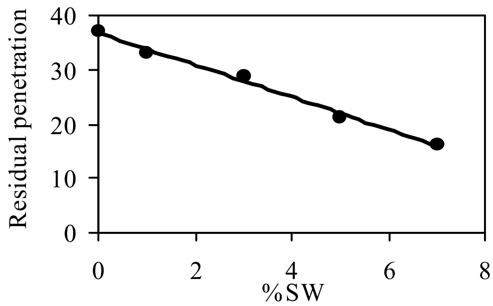


Fig. 5 Residual penetration of $SWMAB_1$

It can be seen from Fig. 6 that aging index increases slightly at 3% SW content due to the increase in bonds between SW and asphalt resulting in the prevention of the brittleness of the resultant binder.

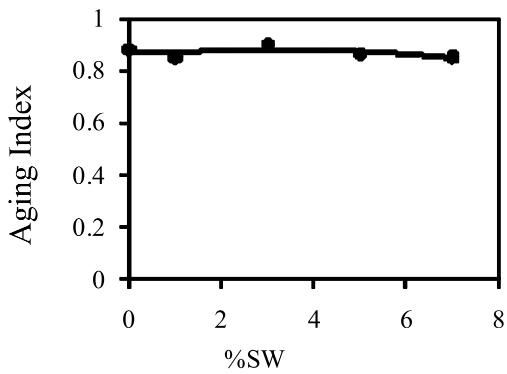


Fig. 6 Aging index of SWAB

Sulfur waste-Asphalt compatibility

After curing the SWMAB0 and $SWMAB_1$ binders into a glass tube in an oven at 140°C for 48 hours, then taken out, and cooled to room temperature. 5-10 mg modified asphalt was then heated and slowly pressed between two glass slides. The sample morphology (compatibility) was observed using an optical microscope with a hot plate. Morphology was monitored at a magnification of 400X at 140°C and as shown in Fig. 7. The photomicrographs demonstrate that 3% SW is well dissolved in $SWMAB_1$ than $SWMAB_0$ at temperature of 140°C and the ductility values in Table 4 insure these results.

Permeability test

Permeability test was conducted on 30 x 30 cm concrete slabs. The slabs were covered with a 3mm of asphalt modified with different sulfur waste contents, then these slabs were placed in a controlled water bath at 70°C for 12 hours. These conditions were designed to simulate typical summer temperatures in Iraq and then the slabs were removed from water bath for density measurements.

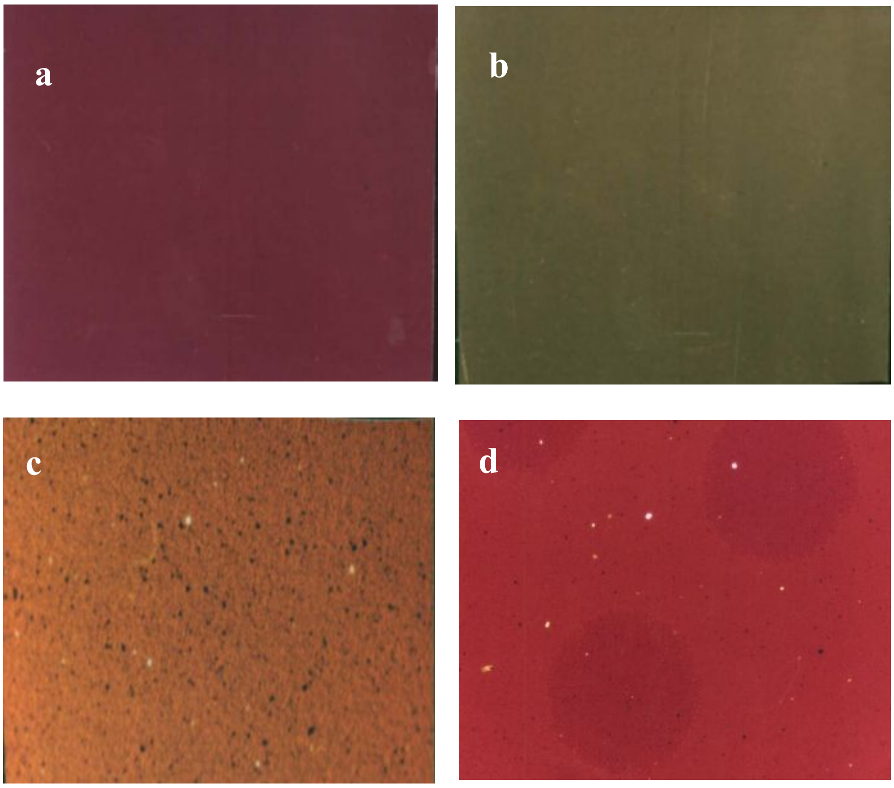


Fig. 7 Photomicrographs of SWMABs
(a = 0.0%, b= 3% $SWMAB_1$, c=5% $SWMAB_1$ & d=3% $SWMAB_0$)

Fig. 8 illustrates the difference in density measurements for $SWMAB_1$. From this Figure it can be seen that no leakage was pronounced up to 3% SW contents, which indicates that SW was completely dissolved in asphalt. Recrystalization of SW was pronounced after this certain content and as a result water leakage occurred.

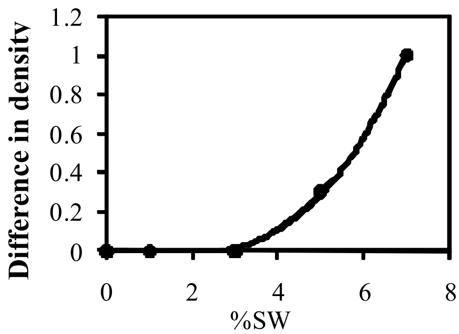


Fig. 8 Difference in density measurements

Economical Consideration

Table 5 demonstrates economical consideration through calculating the cost of the produced waterproofing asphalt (asphalt mastic).

Table 5 Cost of materials used in the production of asphalt mastic

Introduced materials	Cost in $ per ton
Asphalt 40/50	50
Sulfur Waste	15
Alkyl Benzene Sulfonate	133.4
Mixing and packing	-
Total (without Mixing and packing)	64.792

Conclusions:

Based on the testing and analysis presented, the results of the study warrant the following conclusions:

1. The physical properties of modified asphalt with 3% $SWMAB_1$ including softening point, penetration, flash point and ductility are complies with the ASTM D312 specifications for asphalt used in dampproofing and waterproofing type II, and paving construction.
2. The morphology observation confirms that the compatibility, elasticity and storage stability of SW-modified asphalt can be improved in the presence of ABS.
3. Penetration at 25 °C will generally decrease as SW content increases, which indicates an improved shear resistance in medium to high temperatures.
4. The softening point of virgin asphalt modified by 3% SW with the addition of 1%ABS raised by 19%, whereas, it decreased by 9% with the absence of ABS, which indicates improvement in resistance to deformation.
5. A 3% $SWMAB_1$ binder has a very fine network structure at a magnification of 400, as shown in Fig 7b.This fact demonstrates that $SWMAB_1$ binders are more compatible and can be stored for future use.
6. It was found that the penetration index values for $SWMAB_1$ binder are less than those for virgin and $SWMA_0$ binders, which indicated that this binder less susceptible to temperature and more favorable for hot climates; and
7. SW-modified asphalt without ABS was unstable and had phase separation at high temperature, as shown in Fig. 7d.
8. The result indicated that modified asphalt with SW can be used as a water proofing and damp proofing material and it is much cheaper (see Table 5).

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