Studying The Application of Thiopave and Thiocrete Technology in Egypt

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DEDICATION

To

My Parents

And

My Beautiful lolo

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LIST OF ABBREVIATIONS

Sulfur asphalt mixture	SA
Sulfur asphalt module	SAM
Mixture of 0% sulfur and 100% asphalt binder	0/100 SA
Mixture of 20% sulfur and 80% asphalt binder	20/80 SA
Mixture of 30% sulfur and 70% asphalt binder	30/70 SA
Mixture of 40% sulfur and 60% asphalt binder	40/60 SA
American society for testing and materials	ASTM
American association of state highway and transportation officials	AASHTO
Scanning electron microscope	SEM
Dynamic mechanical analysis	DMA
X-ray diffraction	XRD
Differential scanning calorimetry	DSC
Sulfur concrete	SC
Sulfur polymer concrete	SPC
Portland cement	PC
Portland cement concrete	PCC

ABSTRACT

With development of gas processing refineries in Egypt, the current and anticipated future production of sulfur would increase sufficiently to provide substantial quantities of modified sulfur in asphalt paving mixtures and to permit full dependence on sulfur in concrete industry especially in aggressive media. The aim of this work is to avoid all problems associated with the handling, and durability of sulfur, as well as the toxic emissions produced from elemental sulfur during its conversion to more stable modified one by mixing the elemental sulfur with the combination of byproducts of olefinic hydrocarbons and cyclic hydrocarbon bituminous residue at 150^{o}C .

The changes in the structural characteristics and morphology of the prepared modified sulfur were studied using XRD and SEM respectively. Moreover, DSC curves are developed to elucidate the changes in sulfur phases from α-orthorombic to β-mono clinic structure. The technique of nanoindentation is utilized to compare the mechanical properties of modified and pure sulfur including modulus of elasticity and hardness.

Asphalt binder in pavement is substituted by the modified sulfur (Thiopave) by 20wt%, 30wt%, and 40wt% to give three mixtures 20/80 S/A, 30/70 S/A, and 40/60 S/A respectively. Beside the conventional tests, SUPERPAVE binder specifications are conducted on sulfur/asphalt binders. Furthermore the hot mixtures asphalt designs are prepared according to Marshall method. The mechanical properties of the designs are measured including Marshall Stability, Flow, Air voids, and Marshall Stiffness.

Results obtained from this study indicated that THIOPAVE increases the overall mixture strength, and achieve an improved load bearing capacity of the finished road. In addition, Thiopave enables the asphalt to achieve compaction at a considerably lower temperature when compared to base asphalt binder. Thiopave also enables lower temperature production, delivering meaningful reductions in greenhouse gas emissions. This allows the compound to cool and harden quicker and helps reduce the chance of thermal cracking even in adverse weather conditions.

Similarly, the modified sulfur is applied in concrete industry as a cementing material instead of Portland cement (THIOCRETE). The mechanical properties, durability, and corrosion resistance of sulfur polymer concrete (SPC) mortars are studied. Results reveal that (SPC) show higher strength, better durability towards acid media and sea water environment, and higher corrosion resistance than Portland cement concrete mortars (PPC).

Summary

The present thesis is summarized into three main chapters.

Chapter one includes a brief introduction on elemental sulfur forms, and their occurrence, processes, and allotropic transformations are given. Also, a brief description is given on the physical and chemical properties of elemental sulfur including sulfur polymerization and modifications. Moreover, this chapter covers the review of literature and studies conducted on the application of sulfur in pavement (Thiopave) including sulfur/asphalt history, interactions, processing technology, and construction procedures, as well as studies conducted on the application of sulfur in concrete industry (Thiocrete) which includes sulfur concrete compositions, requirements, manufacturing equipments, and its development since 1934 till now.

Chapter two illustrates the chemicals used under this study and the experiments conducted. It is divided into three main parts described as follows:

-In part **(A)**, a modified sulfur is uniquely prepared from 10 wt% mix of (7% residual olefinic hydrocarbons obtained from petroleum distillate fractions C5 + 3% bituminous residue), and 90 wt% of molten sulfur are mechanically mixed at a controlled temperature of 145°C for a period of about 3 h. The changes in the structural characteristics and morphology of the prepared modified sulfur are measured by using XRD and SEM respectively. Also DSC curves are used to elucidate the changes in sulfur phases from α-orthorombic to β-mono clinic structure. The technique of nanoindentation is used to study and compare the mechanical properties of modified and pure sulfur by measuring modulus of elasticity and hardness.

-In part **(B)**, the modified sulfur is applied in pavement (Thiopave) where the asphalt binder is partially substituted with different percentages of modified sulfur: 20 wt%, 30 wt%, and 40 wt%. They are mechanically mixed with high shear rate for at least 30 minutes to attain the required compatibility at a temperature above the melting point of the modified sulfur (120°C), but that does not exceed 150°C. The conventional tests on the prepared sulfur asphalt binder are studied including penetration test, ring and ball softening point, kinematic viscosity, flash point, and ductility test. Also, the superpave binder tests are studied including Brookfield rotational viscometer test, and dynamic mechanical analysis (DMA).

Finally, the hot mixture asphalt designs are prepared according to Marshall method in which the asphalt binder content is partially substituted with 20%, 30%, 40%and 50% of modified sulfur. The mechanical properties are measured including: Marshall stability, flow, air voids, and Marshall stiffness.

- In part **(C),** the modified sulfur is used as a binding agent instead of Portland cement in concrete industry (Thiocrete). Sulfur polymer concrete mortars are prepared by optimizing the modified sulfur percentage with selected fine aggregates (sand and fillers) percentages. Preheated sand and fillers(not up to 145 ^{o}C) are stirred for about 15 minutes in a mixer, and then the melted modified sulfur is mixed into homogenized dry mixture at sulfur melting temperature; 132–145 ^{o}C.

The mechanical properties of sulfur polymer concrete mortars are studied including: Three Point Bending, Compressive Strength, and Shear Strength, and compared with conventional concrete. Moreover, the durability of modified sulfur concrete mortars towards acidic media (10% HCl and 10% H_2SO_4) and sea water is studied and compared with conventional concrete.

Finally, an accelerated corrosion cell is used to compare the rate of corrosion of both of the conventional concrete and sulfur polymer concrete (SPC).

Chapter three is divided as well into three main parts described as follows:

-Part (A) begins with the confirmation study of the prepared modified sulfur. The modification of sulfur is strongly supported by FTIR spectra at which the bond of C=C at 1650 cm^{-1}, associated with olefinic additives, has disappeared, and a bond at 694 cm^{-1}, which is consistent with C-S stretching that is associated with the formation of polysulfide, has appeared. Furthermore, the lower shift in 2θ of the modified sulfur in XRD spectra confirms the structural change of modified sulfur. In addition, the differences observed in the scanning electron microscope configurations of pure and modified sulfur are a quite evidence of sulfur modification since the pores observed in the scan of pure sulfur due to β to α transitions have disappeared in modified sulfur. Results of DSC reveal that the use of olefinic hydrocarbons can effectively prevent the $\alpha \rightarrow \beta$ transformation in sulfur. Based on the data of nanoindentation in pure and modified sulfur, the results confirm that modified sulfur has higher mechanical strength than pure sulfur.

Part (B) discusses the results of physical tests performed to sulfur asphalt mixtures including conventional properties, and SUPERPAVE binder specifications. According to the results of conventional tests, increasing sulfur content from 20% to 40% causes an increase in softening point, and decrease in penetration at 25°C due to the reaction of sulfur with naphthenes-aromatics moiety in asphalt that are partially transformed into