Changes in Chemmical Composition of Asphalt Binder in Hot Arid Climates

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Abstract:

One of the main distresses affecting asphalt pavement is the premature surface cracking. This problem has been observed in hot arid climates such as North Africa and the Middle East. In these climates, a complex change in the composition of the asphalt binder occurs. These changes affect the binder properties by increasing the binder viscosity, stiffness and softening point and reducing penetration and ductility. However the loss of flexibility in the binder will make the asphaltic mix susceptible to shrinkage cracking in the large temperature ranges that occur in these climates.

An experimental program has been carried out to evaluate the process of hardening by monitoring the changes in asphalt composition. Two sets of samples were collected: the first set (fresh asphalt) was collected from Zawia refinery; the second set was collected from selected sites in the southern part of Libya, to find out the effect of hardening due to ageing and exposure to solar radiation at different depths from the surface. Field samples ranged in age from 0 to 23 years, each sample was sawn into slices of 20 mm thick through its depth to represent the change of exposure to environmental effects. A chromatographic column was used for determining the asphaltene content and chemical composition of asphalt. The results showed that asphalt binders in hot arid climates subjected to a rapid process of hardening reflected in high changes in chemical composition.

Introduction:

Hot arid regions are characterized by their very high pavement temperature and substantial daily temperature fluctuations, which sometimes fluctuating between an average maximum of 75°C to an average minimum of 5°C of pavement surface temperature (Imbarek and Ali, April, 2002 and; Imbarek and Ali, October, 2002)

Ageing and hardening of bituminous materials are considered to be the main contributing factors to the performance and durability of bituminous pavements in the long term. Durability of a paving mixture is usually defined as its resistance to weathering, ageing, and traffic loading or as the ability to resist change due to these destructive or deteriorative factors.

Bituminous pavements may fail due to cracking, disintegration, and instability, any of which may result from improper selection and use of types and amounts of asphalt. From the practical point of view, the desired durability properties of any bituminous paving binder imply that the material should resist deterioration resulting from chemical and physical changes during production, in addition to weathering and traffic during service, especially changes in hardness or consistency. The increase in hardness may result in loss of ability to deform without fracture and in loss of adhesion and fatigue resistance.

This study was undertaken to investigate recovered bitumen from existing pavements to study the influence of thermal oxidation and volatilization factors on the hardening of bitumen.

Being more specific, the objective of this investigation is monitoring the changes of chemical composition and loss of volatile compound.

Chemical Composition of Bitumen:

According to the Shell Bitumen Handbook (2003) the methods available for separating bitumen into fractions can be classified as follows:

1. Solvent extraction;
2. Adsorption by finely divided solids and removal of unabsorbed solution by filtration;
3. Chromatography;
4. Molecular distillation used in conjunction with one of the above techniques.

Substitution:

By means of absorption chromatography, bitumen can be separated into four functional groups with related properties with regard to chemical reactivity and rheological properties. These four groups are:

1. Asphaltenes:

These are n-heptane insoluble black or brown amorphous solids containing, in addition to carbon and hydrogen, some nitrogen, sulphur and oxygen. Asphaltenes are generally considered to be highly polar. The molecular weights of asphaltenes range from 1000 to 100000. Asphaltenes constitute 5 to 25% of the bitumen.

2. Resins:

Resins are soluble in n-heptane. Like asphaltenes, they are largely composed of hydrogen and carbon and contain small amounts of oxygen, sulphur and nitrogen. They are dark brown in colour, solid or semi-solid and, being polar in nature, they are strongly adhesive. Resins separated from bitumens are found to have molecular weights ranging from 500 to 50000.

3. Aromatics:

Aromatics comprise the lowest molecular weight naphtene aromatic compounds in the bitumen and represent the major proportion of the dispersion medium for the peptised asphaltenes. They constitute 40 to 65% of the total bitumen and are dark brown viscous liquids. The average molecular weight range is in the region of 300 to 2000. They consist of

non-polar carbon chains in which the unsaturated ring systems (aromatics) dominate and they have a high dissolving ability for other high molecular weight hydrocarbons.

4. Saturates:

Saturates consist of straight and branch chain aliphatic hydrocarbons together with alkyl-naphtene and some alkyl-aromatics. They are non-polar viscous oils which are straw or white in colour. The average molecular weight range is similar to that of aromatic and the components include both waxy and non-waxy saturates. This fraction forms 5 to 20% of the bitumen.

Colloidal Stability of Asphalts:

Two key parameters that control the stability of asphaltene micelles are the ratio of aromatics to saturate and that of resins to asphaltenes. These two ratios are explored in the evaluation of relationship between the group chemical composition and the physical properties of asphalts. They are expressed in terms of two indices: asphaltene index and Gaestel index.

Asphaltene Index, I_A:

This is the changing rate of asphaltene content and it is can be found suitable:

$$I_A = \frac{\text{Asphaltenes+Resines}}{\text{Saturates+Aromatics}}$$

Gaestel Index, I_C:

The resins play an important role in the stability of asphaltenes. They are believed to disperse the asphaltenes, preventing them from separation

as a separate phase. The solubilizing power of the resins is affected by the degree of aromatic in the molecules. This is also evaluated using n-heptane asphaltenes.

$$I_C = \frac{\text{Asphaltenes+Saturates}}{\text{Resins+Aromatics}}$$

When the value of $\mathbf{I}_C$ increases, colloidal stability decreases. Thus, the colloidal stability index should be found primarily helpful when comparing the stabilities of different asphalt samples

Field Investigation:

Four asphalt roads constructed by specialized companies were selected for this study. Three roads in **Sabha** and one in **Zawia**; **Sabha** roads were taken as a case study of hardening and ageing of asphalt roads located in the Sahara desert (southern part of Libya), that has hot arid climate, while **Zawia** road was taken as a case study of hardening and ageing of asphalt during construction.

A number of site visits have been made and asphalt samples were taken for laboratory analysis from different locations of the four roads as shown in Table (1).

Table (1) Roads Selected for the Study

Age (year)	Location	Description
0	Zawia	Two-lane main rural highway
8	Brak-Adri	Two-lane main rural highway
13	Brak-Sabha	Two-lane main rural highway
23	Brak-Ashkdha	Two-lane main rural highway

Experimental Programs:

An experimental program has been carried out to evaluate the process of hardening by monitoring the change in chemical composition of the asphalt. Field samples ranged in age from newly constructed (0 year) to twenty three years were collected from actual pavements in the area selected for the case study. Four roads were selected as shown in Table (1). From each road three core samples 110 mm diameter and the full thickness were taken from selected sites, to find out the effect of hardening due to aging and exposure to solar radiation at different depths from the surface. The experimental program was divided to the following three stages:

First Stage: - Used Material

In this stage, field samples of different ages were collected from selected sites. Each sample was sawn into slices of 20 mm thick through its depth to represent the change of exposure to environmental effects. Also grade 60/70 penetration fresh asphalt samples were supplied from Zawia refinery, tests on its physical properties and separating into fractions were carried out.

Second Stage: - Extraction and Recovery

The asphalt binder sample to be tested was obtained by the extraction and recovery of the binder from asphalt concrete mix. In this test, a sample of the asphalt is soaked in dichloromethane (methylene chloride) to remove the bitumen from the aggregate into solution. The solvent removed was carried out by a rotary evaporator, which has the advantage that it removes the solvent very rapidly from the solution.

Third Stage:

One further analysis test for monitoring the hardening of the bitumen binder was carried out. The chemical analysis to measure the changes of chemical composition fractions of the binder using Glass Chromatographic Column.

Fresh Asphalt Fractionation :

The asphalt containing the four defined fractions is first separated into n-heptane insoluble asphaltenes and the n-heptane soluble petrolenes. The petrolenes are then adsorbed on calcined F-20 alumina and further fractionated into the saturate, naphtene aromatic and polar aromatic fractions by downward solvent elution in a glass chromatographic column. Eluted fractions are recovered by solvent removal under vacuum prior to final weighing. The three eluted fractions plus the n-heptane precipitated (n-c_7) asphaltenes comprise the four fraction were defined above ..

1. Asphaltenes (heptane insoluble) in fresh asphalt :

This method describes a procedure for the determination of heptane insoluble asphaltene content of asphalt. The test was performed in the laboratory according to (BS 143/90).

2. Separation of petrolenes into three fractions :

A liquid chromatographic method was used for fractionation of petrolenes according to ASTM D4124 method. These test methods cover the separation of four fractions from petroleum asphalts.

Testing of recovered asphalts :

1. Samples :

Field samples of different ages (0 to 23 years) were collected from actual pavements in the area selected for the case study. Four roads are selected as shown in table (1). Each sample was sawn into slices of 20 mm thick through its depth.

2. Extraction of Asphalt from Field Sample ASPHALT Mixture:

The asphalt sample to be tested was obtained by the extraction and recovery of the binder from asphalted concrete mix. In this test, a sample of the asphalt is soaked in dichloromethane (methylene chloride) to remove the bitumen from the aggregate into solution. The asphalt solvent solution is separated from the fine mineral matter by filtration and centrifuging using the apparatus as described in (ASTM D2172 method A).

3. Recovery of Asphalt from Solution:

The asphalt solvent solution from the previous extraction by method A of Test Methods ASTM D2172 was centrifuged for a 40 min at 1000 rpm in centrifuge tube to remove dust and other suspended matter. The solvent is removed using a rotary evaporator as described in BS EN 12697-3, which has the advantage that it removes the solvent very rapidly from the solution.

4. Recovered Asphalt Fractionation :

I. Samples :

Field samples of different ages (0 to 23years) were collected from the roads selected for the case study as shown in table (1). The asphalt

binder used in the analyses was extracted from the top 20 mm of the road surface.

II. Separation of Asphaltenes and Petrolenes :

The sample was ground into small pieces. Then an accurately weighed amount of bitumen sample (approx. 50 gr.), placed in an extraction thimble, and extracted using 250 ml n- heptane solvent in Soxhlet extractor for a 6 hour period. The extract was filtered (either slow or medium grad filter paper) in a 500 ml beaker, where the extract left in the venting hood about 8 hours to let to the solvent to be evaporate. Then the dry residue beaker putted in the oven at 80^0C for 30 min, and then left to be cooled in desiccators for 30 to 60 min, then the extract is weighted. The extract obtained is petrolenes. Then the remaining asphalt material extracted, using 250 ml dichloromethane solvent in Soxhlet extractor for 6 hours period. Transfers the extracts obtained with dichloromethane solvent to evaporating dish and left in the venting hood until the solvent evaporating, and then dry in a (104^0C) oven until a constant mass is achieved. Record the net mass, the extract obtained is asphaltene.

III. Separation Of Petrolenes Into Three Fraction:

The petrolenes extracted from field sample asphalt mix were separated into three fractions by using the same method as explained above.

Experimental Results and Discussion:

Chemical composition of both, fresh and recovered asphalts are presented and discussed. A brief summary of the range of experimental conditions for each of the two asphalts will also be given.

1. ASPHALTIC CONTENT

The formation of asphaltenes that results from weathering (oxidation and/or volatilization), has long been observed. The increase in viscosity (hardening of asphalt) and the change in colloidal structure (from sol or sol-gel to gel-type materials) or the increase in complex flow that accompanies the increase in asphaltene content have been postulated by many researchers as the cause for asphalt failure by cracking. Thus the change in asphaltene content was used in this study as an important parameter in asphalt durability evaluation.

The percentages of asphaltenes as given by the precipitation method for all recovered asphalts studied with time of ageing and changes of chemical fraction with time are given in Figure. (1).

Hardening of the asphalt binder in this kind of environment (hot arid climate) takes places mainly by two process; volatilization and oxidation. The speed of hardening processes are illustrated in figure (1), in which chemical composition fractions of the asphalt binder recovered from 20 mm from surface and the pavement service time are plotted. At the beginning of service time (age = 0 year). The asphaltene fraction is 19.54 whereas the fresh asphalt has asphaltene content of 12.27. Similarly, there is gradual decrease in resin fraction. The fresh asphalt has resin content of 39.9 whereas the resin content of 0 year asphalt has decreased to 34.61. On the other hand, the saturate and aromatic fractions have little change. These illustrate the significance of the oxidative ageing that takes place during mixing, transport and construction. After 8 years, the asphaltenes content is 35.8 whereas the fresh asphalt binder has asphaltenes content of 19.54. The asphaltenes content increased by 2.9 times in eight years, 3.4 times in thirteen years and 3.7 times in twenty three years. Similarly, there is a

gradually decrease in resins fraction. The resins fraction has dropped (22%), (34%) and (42%) after 8, 13 and 23 years respectively. Also, the percentage of aromatic fraction decreased sharply from 0 to 8 years and then slowly from 8 to23 years. These rates of decline indicate that, the high speed of hardening process. The hardening will continue in the following years but at slower rate. In addition, the percentage of saturates fraction increase whereas the rate of change is minimal.

These results indicate the loss of volatile compounds and loss of the branch chains of resinous to form asphaltenes by the process of evaporation and oxidation

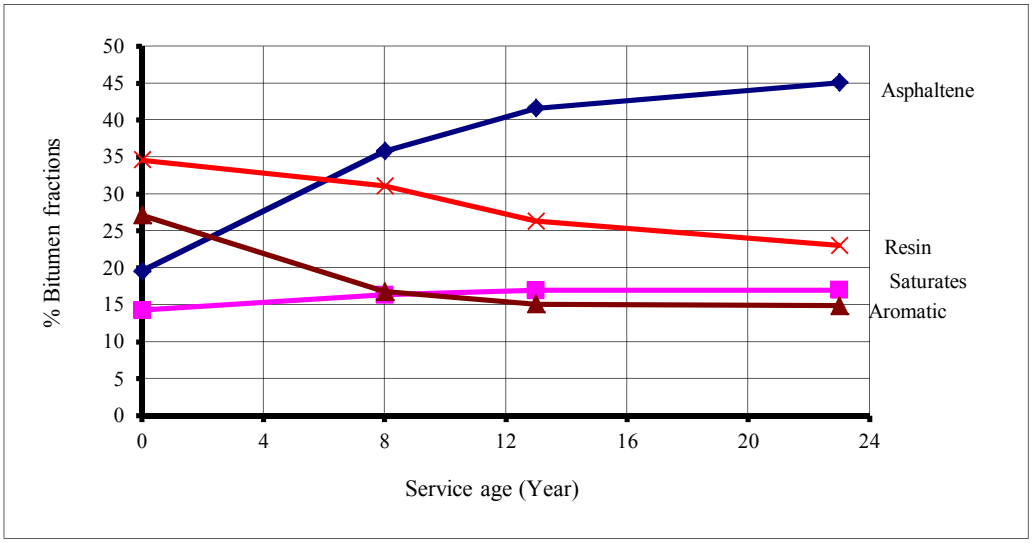

Figure (1) Changes in the Asphalt Chemical Fractions during Service Time

2. The Colloidal Instability of the Asphalt:

Asphaltenes and Gaestel Indices which bear direct relationship to the content of asphaltenes can be conveniently used to estimate the extent of colloidal stability. These indices have been plotted against asphaltenes

content in Figure (2). It is clearly seen in the Figure that both I_A and I_C increase correspondingly with increasing asphaltene content for ageing asphalts. The increasing values of these two indices reflect the instability of the aging asphalts.

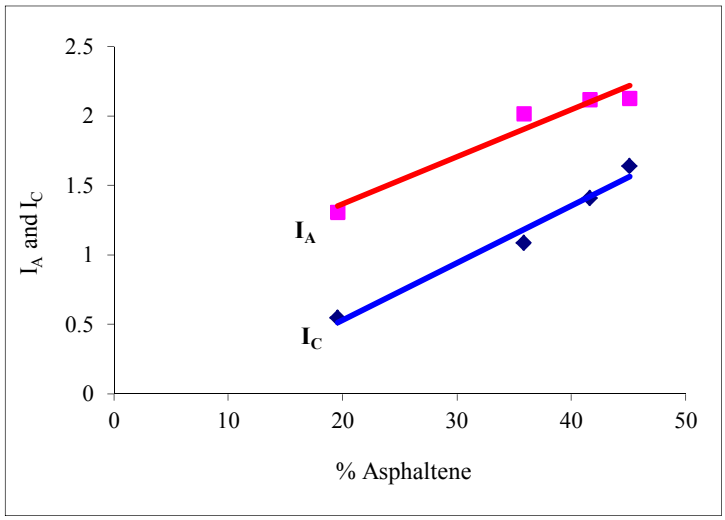

Figure (2) Relationship between Colloidal Stability Indices and percent of asphaltene

Conclusions:

The compositional analysis of the asphalts were investigations in this study. The obtained results from these investigations showed that asphalt binders in hot arid climates subjected to a rapid process of hardening reflected in the high changes in chemical composition. This early hardening and ageing of the binder increase the mix stiffness, making the pavement surface vulnerable to thermal cracking. The main results of these analyses may be summarized in the following conclusions:

1. The chromatographic analysis of the recovered asphalt binder from top 20mm of the pavement surface showed that:

a. Asphaltenes content of the binder in hot arid climates were found to increase by 2.9 times in 8 years, 3.4 times in 13 years, and 3.7 times in 23 years.

b. The resins content has decreased about 22 percent in 8 years, 34 percent in 13 years and 42 percent in 23 years.

c. The aromatics content decreased about 53 percent in 8year, 58 percent in 13 years and 58.4 percent in 23 years.

2. The fractions content of fresh asphalt are 12.1, 12.27, 35.7 and 39.9 for saturates, asphaltenes, aromatics and resins respectively.
3. Both indices I_A and I_C are a direct function of the asphaltenes content; the asphalt of higher asphaltenes content , the greater is the colloidal instability.

Refernces:

[1] M.O.Imbarek, and M .K .ALI, "Hardening and Aging of Bituminous Materials in Hot and Arid Regions", Proceedings of the European Symposium on Performance of Bituminous and Hydraulic Materials in Pavements, Nottingham, United Kingdom, 11-12 April 2002.

[2] M.K.ALI, and M.O.Imbarek, "Premature Surface Cracking of Bituminous mixes in Sahra", 1st National Conference on the Building Materials and Structures, Sabha, Libya, 14 -16 October, 2002.

[3] Omer M S, Gnabah T Hand El-mudi M 0, "Mechanism of distress of asphalt Pavements in arid desert areas", 2nd Maghrib Road Conference, Biskara, Algeria, 8-9 November 1994.

[4] VAN DER VEN, M. 1998, "Advanced Course in Bitumen Technology" Pretoria, South Africa.

[5] DIMPFL, L.H. 1985. The fundamentals of asphalt manufacture and supply. Chevron Research Company, Richmond, California, United States of America.

[6] The Shell Bitumen Handbook 2003. Shell Bitumen U.K., Surrey, United Kingdom.

[7] S.A.Jawashi (1993). "The Preparation and Differential Scanning Calorimetric Analysis of Pure Sara Fractions from Athabasca Tar Sand" Unpublished master's Thesis, University of Sal ford, Department of Chemistry and Applied Chemistry.

[8] L.O.Oyekunle, "Certain Relationships between Chemical Composition and Properties of Petroleum Asphalts from Different Origin", Oil & Gas Science and Technology- Rev.IFP, Vol.61 (2006), No.3, pp.433-441.

[9] Baginska .K, and Gawel. I. (1997) the Chemical Structure and Properties of Bitumens of Different Origin, Petroleum Science and Technology, 22, 5&6, 647-664.

[10] MCGENNIS, R.B., SHULER, S. AND BAHIA, H.U. 1994. Publication No FHWA-SA-94-069: Background of SUPERPAVE Asphalt Binder Test Methods, U.S. Department of Transportation, Federal Highway Administration, United States of America.

[11] JONES, D.R, and YOUTCHEFF, J.S, (1991) Towards an Understanding of the Relationships between Bitumen Chemistry and Pavement Performance: the SHRP Bitumen Research Program. SHRP National Research Council, Washington D.C United States of America.

[12] R.F.A.BERKERS, "INFLUENCE OF CHEMICAL COMPOSITION ON THE PERFORMANCE OF BITUMEN", M.Sc.Thesis, Department of Civil Engineering, Tswane University of Technology, Pretoria, Gauteng Province, South Africa, April 2005.

[13] MALAN, G.W. et al "A Field Study of Premature Cracking in Asphalt" pVII-43 – VII-49, Proceedings of 5th Conference on Asphalt Pavements for South Africa, South Africa1998.

[14] RICHARD.F.COONS and PAUL.H.WRICHT "An Investigation of the Hardening of Asphalt Recovered from Pavements of Various Ages", AAPT 1968.

[15] Anil Srivastaval and Ronald Van Rooijen "Bitumen Performance in Hot and Arid Climates", 24-26 October 2000 Amman, Jordan.