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Influence of aggregate chemical and mineralogical composition on stripping in bituminous mixtures

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The influence of aggregate chemical and mineralogical composition on moisture sensitivity was investigated using 11 aggregates from typical tropical and temperate climates and one bitumen. Mix design and compaction were based on Swedish Road 94 hot mix base specifications and moisture damage was determined using resilient modulus and tensile strength ratios. As much as practically possible, air voids, gradation, compaction level, bitumen content and curing were controlled. Mixtures from aggregates containing sodium and potassium exhibited relatively high moisture sensitivity. The converse was apparent for aggregates with calcium, magnesium and iron. No significant correlation was observed between the strength ratios and contents of Al_2O_3 and SiO_2. Stripping was generally high for aggregates with quartz and alkali feldspars, although one aggregate with practically 100% quartz showed low moisture sensitivity. Statistical analysis showed good correlation between resilient modulus and tensile strength ratios.

Keywords: Stripping; Aggregate; Resilient modulus; Tensile strength; Moisture sensitivity

AMS Subject Classification: 65K05; 90C30

1. Introduction

Deterioration of bituminous mixtures due to separation of bitumen films from mineral aggregates in presence of water (commonly known as stripping), has been known for as long as bituminous paving exists. The loss of adhesion between bitumen and aggregate substantially reduces tensile strength and this has an impact on the durability of the pavement, since the bituminous mix ceases to act as a coherent structural unit. Water can also decrease cohesive strength of the mastic (bitumen/filler). Quality of aggregates is amongst the many factors that influence this complex phenomenon of moisture sensitivity. Variability in aggregates from various sources (with diverse composition) and differences in correlations between the composition and moisture damage have been observed as evidenced by considerable research efforts in many publications. Results reported have not been conclusive because field performance has contradicted some of the findings. Thus, although such aspects as bitumen characteristics, design, construction practice, traffic loading and environment influence moisture sensitivity, aggregates with desired composition (suitable minerals and chemical species) can produce more durable pavements.

Stripping occurs at the interface, and aggregates constitute one side of this interface. Aggregates typically provide a heterogeneous surface onto which specific bitumen chemical functionalities preferentially adsorb by chemical interaction with aggregate adsorption sites. Consequently, stripping is influenced by aggregate surface characteristics like chemical stability, pore size distribution, polarity and surface energy, which are determined directly by composition. Besides, it is not regular practice in hot mix technology to consider such fundamental characteristics in specifying aggregates. Accordingly, an understanding of the relation between moisture sensitivity and composition of mineral aggregates is fundamental in controlling material selection that would lead to more durable pavements.

The purpose of the work reported in this paper was to examine how chemical and mineralogical composition of aggregates relates to moisture sensitivity. The approach used in this study involved relating moisture induced loss

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in resilient modulus and tensile strength to composition of aggregates from different sources. Both resilient modulus and tensile strength were used because the former is a measure of cohesion in the mastic (or stiffness) while the latter relates to interfacial adhesion. The study employed eleven aggregates of diverse chemistry and mineralogy and one bitumen.

2. Theoretical background

During service, bituminous mixtures are always exposed to moisture which may cause separation of bitumen films from the aggregate through stripping. In a real pavement, the factors influencing stripping are many and a lot of research has been, and continues to be directed towards this area. Yet the fundamental causes of stripping are still complex and are not fully understood. Aggregates constitute the biggest part of the mixture (over 94% by weight) and provide a surface onto which the bitumen/mastic adheres. The resistance of adhesive bonding to stripping relates to aspects of the aggregate like surface charge, polarity, porosity, type of adsorption sites and surface energy, which are directly determined by the minerals and chemical elements present in the aggregates. Consequently, aggregate composition probably influences resistance to moisture damage.

The sticking of bitumen onto an aggregate and its replacement by moisture depends partly on interaction of the polar groups at the interface and interfacial Van der Waals forces, e.g. Keesom orientation forces, Debye induction forces and London dispersion forces (Curtis *et al.* 1993). Some of these forces depend on the type and magnitudes of aggregate surface charges, which themselves depend on the nature of minerals and metallic ions present. Mertens and Wright (1959) adequately describe the mechanisms leading to the presence of polar components on aggregate surfaces. Aggregate surfaces may also have broken bonds that result from a break in coordination bonds holding together the aggregate atomic crystal lattices. This break in bonds happens during quarrying and crushing. Water or other contaminants in the air can be attracted to the fresh surfaces to satisfy broken bonds. Since water is normally available, the driving force for the adsorption of water on the freshly crushed aggregate faces is that it reduces the free energy of the system. These processes seem to relate to aggregate mineralogy. The common minerals in aggregates include silica, feldspars, carbonates and clays (Roberts *et al.* 1991).

Silica mineral (SiO_2) abundant in quartz constitute the bulk of quartzite and granite. During quarrying, unsatisfied charges form by breaking the silicon–oxygen bonds. Hydration occurs when water vapour releases OH^- and H^+ ions to the unsatisfied charges on silicon and oxygen, respectively. This results in a hydroxylated surface with surface silanol groups. Equilibrium is established between these silanols and water depending on the pH of the contact water (Scott 1978). Water with a high pH (OH^- ions) stimulates the dissociation of H^+ ions from silanol groups causing the surface to become more negatively charged. At low water pH, silica surfaces become positively charged. Water molecules can form strong hydrogen bonds with siliceous surface silanols which may cause replacement of the bitumen polar parts. Vuorinen (1999) shows a similar behaviour in Al_2O_3.

Feldspar minerals have mobile species within their crystal structures (Jones *et al.* 2004). For example, orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) have alkaline earth metals like potassium, sodium and calcium, respectively, as their mobile species. Other minerals with such metallic elements include olivine $(Mg,Fe)_2SiO_4$ and augite $(Ca,Mg,Fe)(Si,Al)_2)_6$. The nature of interaction between these metallic elements and the bitumen components determines the sensitivity of adhesion to moisture.

Limestone mainly comprises $CaCO_3$, which after crushing exposes electropositive surface characteristics. This is because its interior bonds are broken leaving calcium and carbonate ions on the newly formed surfaces. Hydration of these ions by water vapour, results in a characteristic electropositive surface. These surface species are available for competition between water and bitumen polar functionalities.

Clay minerals acquire charges from structural imperfections due to ionic isomorphous substitution. Depending on the valences of the substituting and substituted cations, a net negative or positive charge may result on the clay (Gast 1977). Hydroxyl groups present on the edges of clay structures may lead to a pH dependent charge in the presence of water. Micas like biotite $[K(Mg,Fe^{2+})_3(Al,Fe^{3+})Si_3O_{10}(OH)_2]$ may be poor adherends (Stuart 1990). Micas are also friable and this might lead to premature damage in presence of water.

When moisture enters the interface, its molecules being more polar, can often be more strongly adsorbed on the aggregate surface than the bitumen component, thus displacing it. There can be cases where ionic bonds between bituminous carboxylic acids and metallic ions like calcium in the mineral surface (e.g. limestone) may not be affected by water. Plancher *et al.* (1977) found out that carboxylic acids in the bitumen were strongly adsorbed on siliceous aggregates, but were present in very small amounts. At the same time, carboxylic acids tend to be displaced first from the aggregate in presence of moisture (Petersen *et al.* 1982).

This background on previous fundamental research underlines the dependence of moisture sensitivity on aggregate composition. While the influence of moisture damage on pavement performance and maintenance costs is not clearly defined, the global upsurge in use of anti-stripping additives and the use of many different moisture sensitivity tests shows that moisture damage is still an important issue. During the last few years, efforts to transfer experience and research available on moisture damage have resulted in significant contributions, such as the "National Seminar on Moisture Sensitivity" held in San Diego, in 2003. An additional review of relevant aspects can be found in Bagampadde *et al.* (2004).

3. Experimental

3.1 Materials

Eleven aggregates were used in this study and were designated as A–L. The first seven were obtained from seven active quarries in a tropical setting around Lake Victoria. Several bituminous wearing courses made of aggregates from some of these quarries have shown stripping potential shortly after tropical rainy seasons. The other four aggregates were from a temperate climate area, where stripping signs were observed during spring on roads, constructed with some of these aggregates (Höbeda 1998). Each of these aggregates was sampled in accordance with ASTM D75-87 at the quarry stock piles. One 70/100 pen bitumen (according to EN 12591), produced from Venezuela (Laguna) crude oil, was used. The bitumen was characterized on the basis of several rheological and chemical properties.

3.2 Test methods

3.2.1 Aggregate characterization tests. The aggregates were characterized based on chemical and mineralogical composition. Each of the aggregate tests is described in detail below:

- Chemical composition data were collected by analysing the aggregates for silica, alumina, potassium, sodium, iron, magnesium, calcium and manganese. The amounts (wt%) of the elements were obtained in terms of oxides although oxides may not necessarily naturally occur in aggregates (Rice 1958). Contents of potassium, sodium, iron, magnesium, calcium and manganese were determined by digesting 200 mg of aggregate samples, ground to minus 100 mesh sieve, with 10 ml of hydrofluoric acid (conc. 40%) reagent mixed with 3 ml of perchloric acid (conc. 70%). The mixture of the acids and the sample was heated in a 50 ml beaker for 1 h on a hot plate having a surface temperature of 200°C and then allowed to cool at room temperature for five minutes. The resulting solution was diluted with distilled water, filtered and analysed using an atomic absorption spectrophotometer. Alumina (Al_2O_3) and silica (SiO_2) are insoluble in the acid mixture used above and were determined separately. Alumina was determined by a gravimetric method through precipitation with 8-hydroxyquinoline. Silica was determined by a spectrophotometric method, where the samples were digested by fusion with sodium hydroxide, and the resulting solution complexed with molybdate for analysis. For more details on methods used in the determination of alumina and silica, the reader is referred to Jeffery and Hutchison (1981).
- Aggregate mineralogy was determined by sawing large samples ($50 \times 50\,mm^2$), followed by thin sectioning onto glass slides to a nominal 30 μm thickness for examination. Optical microscopy (400 ×) was used to determine colour, grain size and mineral crystals in the aggregates. Minor phases below a detection limit of 1–2% were not revealed. It was possible to identify the rock names of the aggregates based on the procedure by Strekeisen (1978). The minerals identified included quartz, feldspars, mica and ferromagnesian. Limestone and dolomite were excluded, since they were not found in the source quarries.

3.2.2 Bitumen characterization tests. Bitumen was evaluated for rheology using penetration at 25°C (EN 1426), softening point (EN 1427), ductility at 25°C (ASTM D113), Brookfield viscosity at 135°C (ASTM D4402), dynamic mechanical analysis (DMA), and functional groups using Fourier transform infrared spectroscopy (FTIR). The last two were conducted as follows:

- Viscoelastic data were collected using DMA with sinusoidal strain set at a frequency of 1 rad/s (0.159 Hz) and temperature sweeps (−30 to 80°C) using a dynamic shear rheometer (Rheometrics—RDA II) instrument. Samples were placed between 8 mm diameter plates set at a gap of 1.5 mm.
- Functional group analysis was done using FTIR by employing an infinity 60AR (Mattson, resolution $0.125\,cm^{-1}$) for absorbances of wave numbers ranging from 3400 to $500\,cm^{-1}$. Bitumen solutions (5% by weight) were prepared in carbon disulfide (CS_2). Background and sample scans were performed using attenuated total reflectance (ATR) prisms and sealed cells of zinc selenide (ZnSe) windows.

3.2.3 Mixture design and compaction. Mixtures used in this study were designed to comply with the Swedish standard AG16 hot mix base material having aggregate nominal maximum size of 16 mm (Road 94). For each aggregate, the batches were in fractions of 0/4, 4/8, 8/11 and 11/16 mm, and were blended to fit within gradation limits according to Road 94, as shown in figure 1. Typically, 10 kg of each aggregate required to prepare at least five specimens of diameter 100 mm and approximate height 100 mm was heated in an oven at 140°C for 4 h. Bitumen was heated at 140°C for 1 h before mixing with the aggregate. According to Swedish road standards (Road 94), an AG16 mix may consist of different penetration grade bitumens. However, the binder content depends on the bitumen grade used. In order to make meaningful comparisons of the influence of aggregate composition on stripping, a similar target binder content corresponding to 70/100 pen bitumen was chosen for all mixtures studied

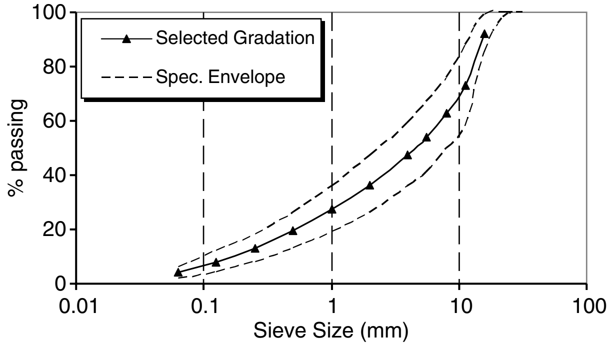

Figure 1. Gradation curve used for all aggregates (Road 94).

(4.9% w/w). Subsequently, 515 g of hot bitumen was added to the 10 kg of hot aggregate and mixing was done at 140°C using an electric mixer. After thorough mixing, the mixture was put on an electrically heated pan, remixed using a metallic scoop to avoid segregation and covered awaiting compaction.

About 2 kg of the loose mix (enough for a specimen 100 mm diameter and about 100 mm height) was placed in a hot compaction mould. Compaction of each specimen was done at 100°C using a gyratory compactor (Model ICT-150R/RB from Finland). The specimen height attained was not exactly 100 mm because during compaction, height was the only variable controlled to attain the targeted air voids content of 7 ± 1% (v/v) for proper vacuum saturation during conditioning. The compacted specimens were taken out of the moulds and allowed to cool at room temperature for 24 h. The air voids were checked by measuring the Rice specific gravity (EN 12697-5:2003) and bulk specific gravity (EN 12697-6:2003) of the specimens. Each of the specimens was sawn into two cylindrical specimens of 100 mm diameter and 40 mm height, making a total of ten specimens for each bitumen/aggregate combination.

3.2.4 Moisture sensitivity testing. The ten specimens of 100 mm diameter and 40 mm height were randomly assigned to two groups of size five. One group was kept as a control at room temperature, and the second group was treated through conditioning. During conditioning, test specimens were subjected to 30 min of vacuum saturation at 67 hPa to achieve between 50 and 80% saturation, followed by 7 days of soaking at 40°C (EN 12697-12:2003). All the ten specimens were then cooled for 2 h to a testing temperature of 10°C. Resilient modulus (ASTM D4123) and split tensile strength (EN 12697-23:2003) were determined using a servo-hydraulic testing system (MTS 810, Teststar II). The experimental runs were completely randomized to minimize bias.

To be sure that failure of the specimens was due to stripping, a close examination of the split failure surfaces (diametral planes) was made on each specimen. Where stripping was present, it was clearly discerned without any fracture or crushed surfaces of aggregates. For the ten specimens of each aggregate, retained strength, defined as the ratio of mean strength of conditioned specimens to the mean strength of dry specimens, was used as a measure of moisture sensitivity. Retained resilient modulus and retained tensile strength ratios (MRR and TSR, respectively) were used with 70% as the boundary between mixtures resistant and sensitive to moisture. This value is the same as what was previously used by Lottman (1978) and Tunnicliff and Root (1982).

3.3 Experimental design

With the intent of this research being to determine how aggregate chemical and mineralogical composition influences stripping in bituminous mixtures, a suitable experimental design was made. A matrix of one bitumen and 11 different aggregates, with ten replicate specimens per bitumen–aggregate combination, was tested. Each of the ten replicates were prepared from one batch and, as much as practically possible, kept identical with respect to aggregate type, air voids content range, aggregate gradation, level of gyratory compaction, bitumen content and 24-h storage. An analysis was done to establish whether any variability in MRR or TSR was due to various levels of aggregate mineral and chemical composition as the main factors.

4. Results

The results of bitumen and aggregate characterization, and moisture damage evaluation of the bituminous mixtures are presented.

4.1 Bitumen characterization

Some bitumen characteristics are shown in table 1. As can be seen, the rheological characteristics of the bitumen were all within specification limits, except the Brookfield viscosity, which was marginally below the lower limit of 350 mPa s at 135°C.

Figure 2 shows visco-elastic response results determined using DMA described in section 3.2. In this study, temperatures of 140 and 100°C, respectively, were used during mixing and compaction. It is indicated (Read and Whiteoak 2003) that values of 155 and 95°C, respectively,

Table 1. Bitumen characteristics.

Characteristic	Value	Swedish specification limits	Methods
Penetration at 25°C (× 0.1 mm)	84	70–100	EN 1426
Softening point (°C)	44.5	43–51	EN 1427
Ductility at 25°C (cm)	136	100 +	ASTM D113
Rotational viscosity at 135°C (mPa.s)	346	350–450	ASTM D4402
Total acid number (mgKOH/g)	3.6		ASTM D664

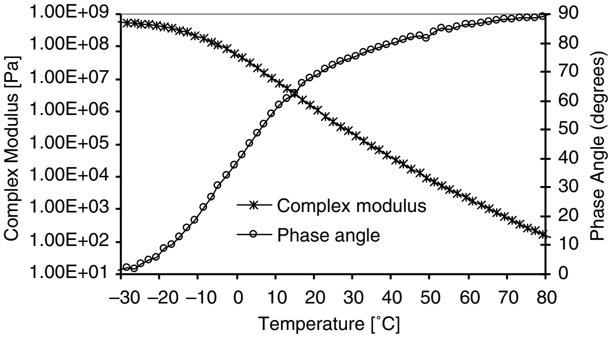

Figure 2. Phase angle and complex modulus versus temperature.

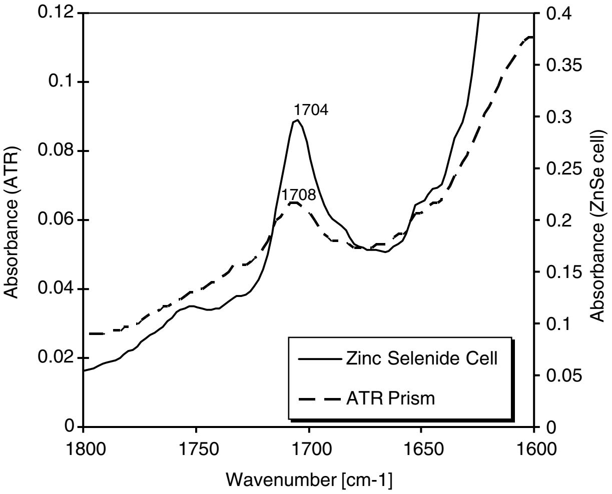

Figure 3. Carbonyl region for FTIR spectra.

are suitable for the two processes in using this grade of bitumen ($T_{\mathrm{R\&B}} = 44.5^{\circ}\mathrm{C}$, cf. table 1). Although the mixing temperature used was lower than 155°C, the bitumen could easily flow and properly coat the aggregate, since it was viscous (Newtonian) with phase angle approximately 90° at this temperature (figure 2).

The chemical nature of the bitumen with respect to functional groups determines bond strength (Petersen and Plancher 1998). Figure 3 shows FTIR absorption spectra around the carbonyl region on expanded abscissa scale from ATR prism and ZnSe cell. The characteristic peak in the carbonyl region near 1700 cm^{-1} results from ketones and/or dimerized or hydrogen bonded carboxylic acids. Ketones are not naturally occurring, but are formed as the bitumen oxidizes. The carboxylic acids occur in nature, usually in relatively small amounts. The small broad band on the right shoulder of the carbonyl peak results from 2-quinolone types (Petersen 1986). To interpret these peaks, bitumen acid number was determined in accordance with ASTM D664-95. The bitumen showed a high mean acid number of 3.6 mg/g (table 1), suggesting that the carbonyl peaks could perhaps be mainly due to acids in the bitumen. Previous research has shown that acids strongly adsorb onto aggregates although they are water susceptible (Petersen and Plancher 1998).

4.2 Aggregate chemical composition

Aggregate chemical composition data for constituent elements are given in table 2, as percent by weight of the corresponding oxides. Figure 4 gives the composition in terms of percentage total contents of Al_2O_3 and SiO_2 that were insoluble in HF/$HCLO_4$ acid mixture (referred to as acid insolubles in this paper) and total contents of the others (referred to as acid solubles). Based on the chemical characterization used in this study, aggregates C and E show a significantly lower content of percent total Al_2O_3 and SiO_2 compared to the other aggregates. Aggregate L contains almost 100% acid insolubles which would possibly attract water molecules through hydrogen bonding or dipole interactions as described in section 2. The rest of the aggregates exhibited intermediate compositions.

4.3 Aggregate mineralogical composition

Mineralogical composition data of the aggregates studied are listed in table 3. Different percentages of quartz, feldspar, mica and ferromagnesian minerals are given for the aggregates. Based on these results, the aggregates were classified according to four groups with each group having

Table 2. Chemical contents of the aggregates studied (% by weight).

	% by Weight							
Aggregate	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	MnO_2
From the tropics								
A	75.50	13.60	1.30	0.50	2.90	4.50	1.70	0.03
B	83.60	0.70	0.01	0.03	0.03	0.20	15.40	0.02
C	30.90	34.10	10.10	7.60	4.20	0.51	12.30	0.24
D	77.30	3.00	14.01	0.02	4.02	0.10	1.50	0.03
E	32.90	22.60	14.60	3.50	11.40	1.92	12.80	0.30
F	79.20	11.50	0.52	0.10	3.30	4.30	1.00	0.10
G	77.50	12.90	1.30	0.50	1.80	4.94	1.00	0.06
From the temperate								
H	71.20	14.30	4.30	0.30	2.82	5.35	1.61	0.06
J	71.90	19.00	1.64	1.14	2.70	1.70	1.80	0.11
K	53.70	22.40	8.10	0.54	2.80	1.64	10.63	0.20
L	89.50	9.30	0.04	0.06	0.06	0.40	0.64	0.04

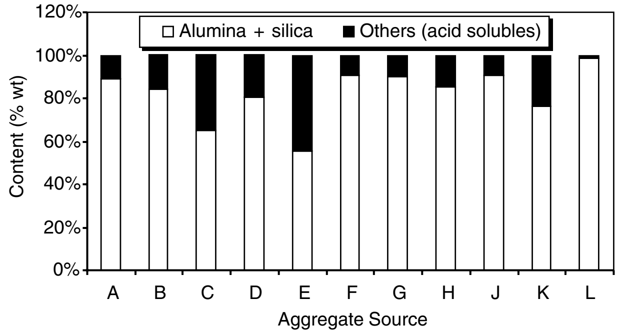

Figure 4. Contents of chemical elements in the aggregates studied.

a more or less uniform mineralogy, which was regarded as a main factor in the analysis. The grouping is summarized in table 4. Group one aggregates contain quartz, alkali feldspars and mica. Group two consists of aggregates predominantly containing quartz, while group three aggregates contain medium quantities of quartz and feldspar (either alkali or lime feldspars). Group four aggregates are predominantly composed of ferromagnesian minerals.

4.4 Loss of mix strength due to water soaking

The average indirect split tensile strength (MPa) and resilient modulus (MPa), for five specimens per sample of the mixtures (both in dry and conditioned states), are shown in figures 5 and 6, respectively. The coefficient of variation (CV) for each set of five specimens at a particular test condition (dry or conditioned) and aggregate type, showed a fair repeatability. 2 of 18 cases (11%) and 3 of 18 cases (17%), respectively, of resilient modulus and tensile strength had a CV less than 15%. The losses in strength were observed for many of the mixtures. Table 5 gives the results of wet-to-dry strength ratios (MRR and TSR) obtained. These results show that mixtures from all aggregates except C, and perhaps L, may be sensitive to moisture (ratios less than 70% as described in the experimental design). A closer analysis of results revealed that aggregates A, E and H exhibited significantly low strength ratios (both TSR and MRR). For the rest of the aggregates, the two ratios seem to show a similar trend. The average air voids contents were practically all within the 7 ± 1% range to ensure proper water infiltration during vacuum saturation (table 5).

5. Analysis and discussion

A statistical analysis of the results was made, at a 0.05 confidence level, with the following three objectives: (1) identify mixtures that are moisture sensitive based on MRR and TSR data; (2) determine whether the MRR and TSR data show the same tendency regarding moisture sensitivity; and (3) establish whether there is a correlation between moisture sensitivity and aggregate composition, assuming that mixture volumetric properties are the same (no differences due to the mixing and compaction procedures).

5.1 Identification of mixtures prone to stripping

A two-tailed *t*-test was done on the MRR and TSR data from all the 11 aggregates studied to check whether moisture reduced the strength. For each of the five sample observations obtained in dry and wet states, respectively, sample means and estimates of standard deviation were

Table 3. Mineralogical composition of the aggregates investigated (%).

Aggregate	Rock type	Quartz	Feldspar	Mica	Ferromagnesian	Remarks
A	Granite Gneiss	20–30	55	15–20	–	Alkali feldspars (Orthoclase—$KAlSi_3O_8$, Albite—$NaAlSi_3O_8$), and Mica (Biotite–Black Mica, Muscovite–White Mica).
B	Quartzite	60–80	–	–	–	Made of purely quartz of fine to medium size and traces of iron oxide in surface fissures.
C	Amphibole	–	15–20	–	70–80	Contains Hornblende–Calcium–iron–magnesium silicate with some sodium and Aluminium. Also has Plagioclase (Anorthite–$CaAl_2Si_2O_8$).
D	Quartzite	75–80	–	–	–	This rock was predominantly a quartzite of granitic origin and traces of anorthite feldspar—$CaAl_2Si_2O_8$.
E	Olivine Melilite	–	–	–	60–70	Igneous rocks poor in silica and alkalis. It is a ferromagnesian silicate with olivine $(Mg,Fe)_2SiO_4$ and melilite $(Ca,Na)_2(Al,Mg,Fe^{++})(Si,Al)_2O_7$.
F	Granite	35–45	40–55	15–25	–	Mostly contains quartz and alkali feldspar (mainly albite); and Mica (Biotite–Black Mica, Muscovite–White Mica).
G	Granite Gneiss	20–25	60–70	5–10	–	Has quartz and mainly alkali feldspars (Orthoclase–$KAlSi_3O_8$, Albite—$NaAlSi_3O_8$), and some Mica (Biotite–Black Mica, Muscovite–White Mica).
H	Granite Gneiss	40–45	50–55	–	–	Mostly contains quartz and plagioclase mainly—$CaAl_2Si_2O_8$
J	Syeno-granite	25–30	55–60	–	–	Has quartz and mainly alkali feldspars (Orthoclase—$KAlSi_3O_8$, and Albite—$NaAlSi_3O_8$).
K	Tonalite	15–20	55–60	–	15–20	Mostly plagioclase—$CaAl_2Si_2O_8$, silica SiO_2 and Clinopyroxene (Augite)
L	Quartzite	99.8	–	–	–	Almost composed of quartz and traces of opaque with coarse texture.

Table 4. Grouping of the aggregates based on minerals present.

Group	Description of mineralogy	Aggregates included
1	Granitic with a little quartz (15–45%), alkali feldspars and mica	A, F and G
2	Quartzites which predominantly quartz (60–100%) and traces of other minerals	B, D and L
3	Granites that contain low to high quartz and are feldsparthic	H, J, and K
4	Essentially contains ferromagnesian mineral	C and E

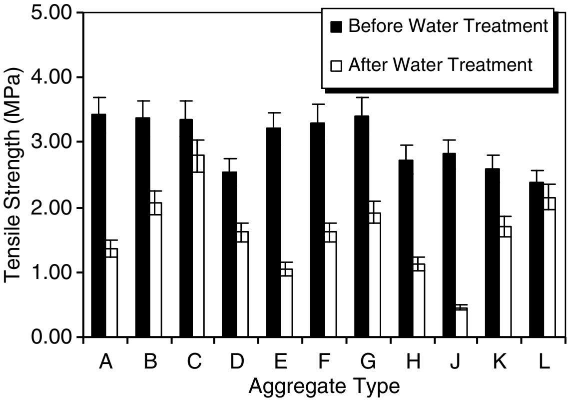

Figure 5. Tensile strengths for dry and conditioned bituminous mixtures (10°C).

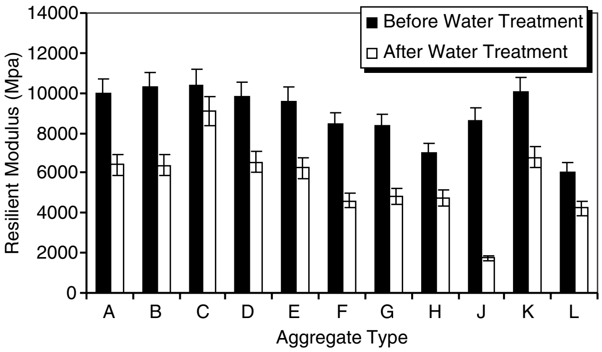

Figure 6. Resilient moduli for dry and conditioned bituminous mixtures (10°C).

used. The decision criteria were formulated as presented in table 6. Three regions of the *t*-distribution were formed and arbitrarily named LOW, MED and HIG, respectively; equivalent to whether MRR or TSR is significantly less than, equal to, and greater than 70%. The results of this analysis are shown in table 7.

The results in table 7 indicate that, in general, prediction of moisture sensitivity based on MRR and TSR could lead to similar judgments. The trends in MRR and TSR seem to be similar in all cases, except for three aggregates, A, E and H. It is also noted that for these three aggregates, MRR is higher than TSR. No apparent similarity in chemical and mineralogical composition of these three aggregates can be recognized (tables 2 and 4).

Mixtures from aggregate A were rather sensitive to moisture, i.e. TSR $<$ 70%, but show average moisture resistance on the basis of MRR results. This aggregate is a granite with quartz (SiO_4), alkali feldspars (55%) and mica minerals (table 3). The results in table 8 show that the aggregate has a content of 89% acid insolubles, of which, 76% is SiO_2. The silica and alkali feldspars could be poor adherends to the bitumen that was used in this study.

Mixtures from aggregate B show both MRR and TSR values within the MED range, in other words, an average resistance to water sensitivity. The aggregate contains mainly silica (84%) but also some iron (15.4%), as seen in table 2. Presence of iron could be an important factor in the observed average resistance to stripping.

Mixtures from C show MRR and TSR values significantly higher than 70%. This aggregate has relatively low percentages of total acid insolubles (approx. 65%, figure 4). Regarding mineralogical composition, aggregate C contains 70–80% ferromagnesian and 15–20% lime feldspar minerals. The aggregate shows a rather high level of about 30% for the contents of CaO, MgO and Fe_2O_3 (table 2). The low water sensitivity could be attributed to ionic bonds of the insoluble salts from Ca, Mg and Fe, which possibly bridge the interface.

Table 5. MRR and TSR mean values of mixtures containing the eleven aggregates.

Aggregate	MRR (%)	TSR (%)	G_{mm} Mean*	G_{mm} St. dev	G_{mb} Mean*	G_{mb} St. dev	Air voids (%)
A	64.3	39.8	2.498	0.181	2.332	0.164	6.65
B	61.9	61.5	2.710	0.145	2.548	0.174	5.98
C	87.0	83.0	2.720	0.105	2.556	0.142	6.03
D	66.5	63.4	2.452	0.385	2.301	0.159	6.16
E	65.1	32.7	2.493	0.204	2.329	0.144	6.58
F	54.6	48.9	2.465	0.204	2.294	0.106	6.94
G	57.8	56.1	2.385	0.220	2.216	0.080	7.09
H	68.4	41.0	2.442	0.135	2.289	0.076	6.27
J	20.1	16.0	2.650	0.318	2.473	0.288	6.68
K	67.5	65.6	2.497	0.266	2.309	0.333	7.53
L	69.8	90.4	2.446	0.091	2.279	0.228	6.83

*Average of five replicate specimens (diameter 100 mm and approximate height 100 mm) for each aggregate.
G_{mm} = the maximum specific gravity of the mixtures (EN 12697-5:2003); G_{mb} = bulk specific gravity of the mixtures (EN 12697-6:2003).
(Actual values of resilient modulus and tensile strength are presented in figures 5 and 6).

Table 6. Decision criteria for the mixtures from the different aggregates.

Region	Condition	Decision	Inference
LOW	$t < -2.306$	Reject H_o	MRR or TSR $<$ 70%: Mixture is sensitive to stripping
MED	$-2.306 < t < 2.306$	Not reject H_o	MRR or TSR = 70%: Mixture has average resistance
HIG	$t > 2.306$	Reject H_o	MRR or TSR $>$ 70%: Mixture is resistant to stripping

H_o: MRR or TSR = 70% is tested against H_1: MRR or TSR $\neq$ 70%;
$t_{cr} = t_{n1+n2-2,\ 0.025} = t_{8,\ 0.025} = 2.306$.

The results indicate that MRR and TSR for mixtures from aggregate D are within the MED range. This aggregate contains about 80% acid insolubles, of which 77% is SiO_2 (table 8). On the other hand, the aggregate contains a non-alkaline feldspar arnothite ($CaAl_2Si_2O_8$), as can be seen in table 3. Data in table 2 show calcium content of 14% for this aggregate. The average MRR and TSR observed could be due to calcium, which probably contributes to moisture resistance, as noted before.

For aggregate E, as is the case with A and H, the MRR data shows intermediate resistance within the MED range, while TSR shows high moisture sensitivity (32.7%). The level of acid insolubles in aggregate A is about 56% (table 8). Data in table 3 shows that the aggregate is a melilite $(Ca,Na)_2(Al,Mg,Fe^{++})(Si,Al)_2O_7$. The contents of calcium and sodium are 15 and 11%, respectively (table 2). The acid insolubles (silanols/aluminols) and the sodium ionic salts could cause the water sensitivity due to possible interaction through hydrogen bonding.

Both mixtures from aggregates F and G show rather low MRR and TSR values (<60%). These aggregates are both granites and contain almost a similar set of minerals, namely quartz, alkali feldspars and mica (table 3). They both show high contents of total acid insolubles (>90%), with SiO_2 contributing significantly as can be seen in tables 2 and 8. All these minerals and oxides (SiO_2 and Al_2O_3) could give surfaces that are more reactive with the more highly polar water than weakly polar bitumen components.

Mixtures from aggregate J showed the lowest MRR and TSR values, practically below 20% (table 5). The aggregate contains mainly quartz and alkali feldspars. The acid insoluble content is very high (90%, as seen in table 8) with larger contribution from SiO_2. All its contents of CaO, MgO and Fe_2O_3 were low (table 2). Presence of SiO_2 and alkali metals (sodium and potassium) probably contributes to the high moisture sensitivity.

Aggregate K gave mixtures with MRR and TSR values both within the MED range. The aggregate contains anorthite, quartz and augite $(Ca,Mg,Fe)(Si,Al)_2)_6$, as shown in table 3. The results in table 2 reveal that this aggregate contains about 8% of CaO and 11% of Fe_2O_3. The presence of calcium and iron could be the reason for the intermediate resistance to moisture damage.

Regarding aggregate L, mixtures showed very high TSR (90%), as can be seen in tables 5 and 7. On the other hand, the MRR data shows intermediate resistance to moisture sensitivity (70%). This aggregate is a quartzite with practically 100% quartz, as shown in table 3. The high TSR and intermediate MRR values for such a siliceous aggregate were unexpected within the framework of the discussion made so far. Several studies found in the literature indicate that this type of aggregate is considered to be rather water sensitive. On the other hand, this aggregate showed the lowest strength and modulus values in dry condition.

5.2 Comparison MRR and TSR results

Analysis was done to determine whether the MRR and TSR data (table 5) show the same tendency regarding

Table 7. Statistical inferences on MRR and TSR for mixtures from the different aggregates.

				Statistical inference on wet-to-dry strength ratios					
		t-value for		MRR (%)			TSR (%)		
Aggregate	$\lvert t_{critical} \rvert$	MRR	TSR	HIG	MED	LOW	HIG	MED	LOW
A	2.306	−1.014	−6.338		§				β
B	2.306	−1.892	−2.180		§			§	
C	2.306	5.326	3.072	x			x		
D	2.306	−0.603	−1.781		§			§	
E	2.306	−1.050	−10.455		§				β
F	2.306	−5.204	−8.922			β			β
G	2.306	−4.461	−5.931			β			β
H	2.306	−0.298	−6.182		§				β
J	2.306	−16.22	−20.689			β			β
K	2.306	−0.513	−0.915		§			§	
L	2.306	−0.036	3.750		§		x		

x = mixture resistant to moisture, § = mixtures with average resistance, and β = mixture sensitive to moisture.

Table 8. Summary of aggregate total acid insoluble content, and MRR and TSR data.

	Aggregate code										
Variable	A	B	C	D	E	F	G	H	J	K	L
SiO_2 (%)	75.5	83.6	30.9	77.3	32.9	79.2	77.5	71.2	71.9	53.7	89.5
Al_2O_3 (%)	13.6	0.7	34.1	3.0	22.6	11.5	12.9	14.3	19.0	22.4	9.3
Total Acid Insolubles (%)	89.1	84.3	65.0	80.3	55.5	90.7	90.4	85.5	90.9	76.1	98.8
MRR (%)	64.3	61.9	87.0	66.5	65.1	54.6	57.8	68.4	20.1	67.5	69.8
TSR (%)	39.8	61.5	83.0	63.4	32.7	48.9	56.1	41.0	16.0	65.6	90.4

moisture sensitivity. Resilient modulus represents stiffness of a bituminous mixture, while indirect tensile strength represents the maximum load that a specimen resists before fracture under a diametral compressive load. It is believed that stiffness, as well as indirect tensile strength, reduce when stripping occurs in a mixture (Roberts *et al.*, 1991). Accordingly, the resilient modulus and tensile strength ratios (MRR and TSR) are used in many tests (e.g. ASTM D4867 and AASHTO T283), to determine moisture sensitivity.

A paired comparison of the strength ratios was made using the data in table 5. This was done using a *matched pairs t-test* at a 0.05 level of significance. The *t*-statistic ($t = 1.699$) was less than the critical value ($t_{0.025,10} = 2.228$). In other words, the hypothesis that the mean difference between MRR and TSR is significant was rejected. This analysis indicates a good correlation between the ratios from resilient modulus and indirect tensile strength.

5.3 The effect of aggregate composition on moisture sensitivity

Statistical analysis was done to establish whether there is a relationship between moisture sensitivity and aggregate composition, assuming that mixture volumetric properties are the same. Table 8 shows the results of aggregate chemical constituents in terms of contents (%wt) of silica (SiO_2), alumina (Al_2O_3) and their total as acid insolubles, along with average values of MRR and TSR. All aggregates contain high totals of acid insolubles, except C and E with values of about 65 and 56%, respectively. It is worth noting that, except for these two aggregates (C and E), the higher percentage of acid insolubles is due to the SiO_2 content. Scatter diagrams were prepared to establish a possible dependence of MRR and TSR on percent contents of SiO_2, Al_2O_3 and total acid insolubles, respectively, as shown in figure 7. The results indicate a large amount of random scatter without any clear relationship between MRR or TSR (%) and the independent variables. These results seem to suggest that moisture damage has no significant relationship with the contents of SiO_2, Al_2O_3 and acid insolubles. This observation is similar to work described by Blazek *et al.* (2000), who indicated no relationship between bitumen wet adhesion, and SiO_2 and Al_2O_3 contents.

Dependence of stripping on mineralogical composition was analysed based on the four mineralogical groups in table 4, by arranging the MRR and TSR data as shown in table 9. The effect of this independent random mineralogical grouping on variability in the MRR and TSR data was tested at a 0.05 level of significance. Analysis of variance (ANOVA) for one-way classification of the data showed that the group means for both MRR and TSR were not significantly different ($p > 0.05$). In other words, on the basis of the analysis done, mineralogical

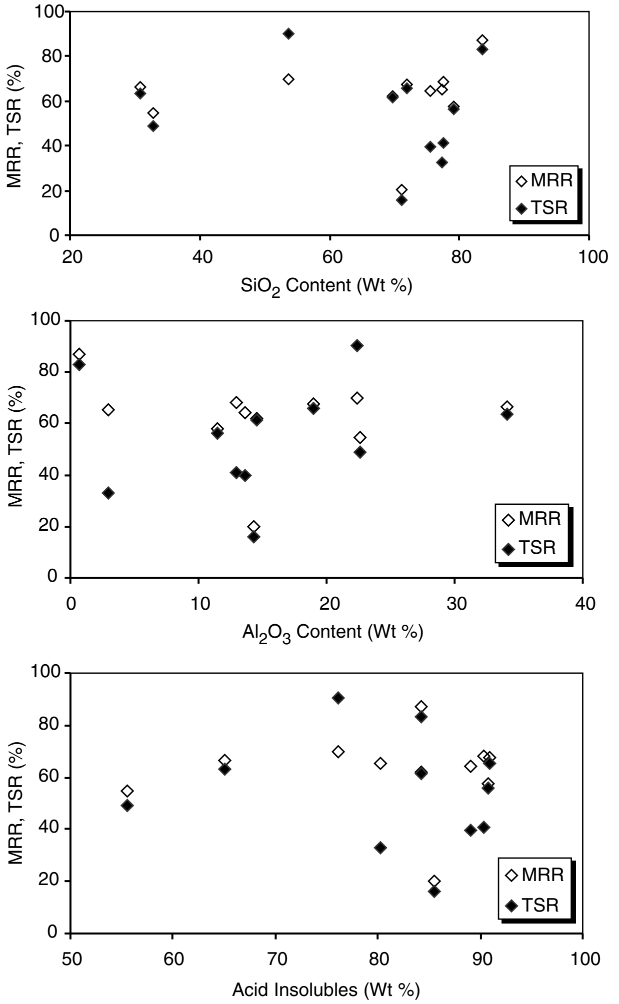

Figure 7. Mean MRR and TSR versus SiO_2, Al_2O_3 and total acid insolubles.

Table 9. MRR and TSR data for the different mineralogical groups formulated.

Mineralogical group	Aggregate	MRR (%)			TSR (%)		
1	A, F and G	64.3	54.6	57.8	39.8	48.9	56.1
2	B, D and L	61.9	66.5	69.8	61.5	63.4	90.4
3	H, J and K	68.4	20.1	67.5	41.0	16.0	65.6
4	C and E	87.0	65.1		83.0	32.7	

grouping of aggregates investigated did not affect moisture sensitivity of the mixtures prepared with the bitumen studied. The MRR and TSR ratios for the aggregates are presented in their respective mineralogical groups as shown in figure 8. The group means are included in the figure. Although the foregoing analysis shows that the mineralogical groups do not significantly affect variability in MRR and TSR, there are some differences within some groups. Within group 3, for example, MRR and TSR values (20 and 16%, respectively) for mixtures from aggregate J were very low compared to those from aggregates H and K. The data in table 2 shows that the sums ($SiO_2 + Al_2O_3$) for H, J and K are approximately 86, 91 and 76%, respectively. Correspondingly, the sums ($CaO + MgO + Fe_2O_3$) and ($Na_2O + K_2O$), respectively, are 6, 6 and 19% and 8, 4 and 4%, for the three aggregates. These chemical composition data do not provide a reasonable explanation for the differences in moisture sensitivity of the aggregates in group 3.

Some observations are worth noting from the data presented in figure 8 and tables 3 and 7. The data in table 3 reveals that aggregates B, D and L contain high quartz contents of 60–80, 75–80 and 99.8%, respectively. Mixtures from these aggregates gave MRR and TSR values, which in general expose average resistance to moisture damage, except the high TSR value for L (table 7). On the other hand, aggregates A, F, G and J contain medium contents of quartz given as 20–30, 35–45, 20–25 and 25–30%, respectively (table 3). The same table shows that these aggregates contain alkali feldspar contents of 55, 40–55, 60–70 and 55–60%, respectively. Mixtures from these aggregates gave MRR and TSR values that, on the whole, indicate high moisture sensitivity (table 7). Consequently, these results suggest that possibly moisture sensitivity of mixtures from aggregates predominantly composed of quartz (like B, D and L) is not necessarily high.

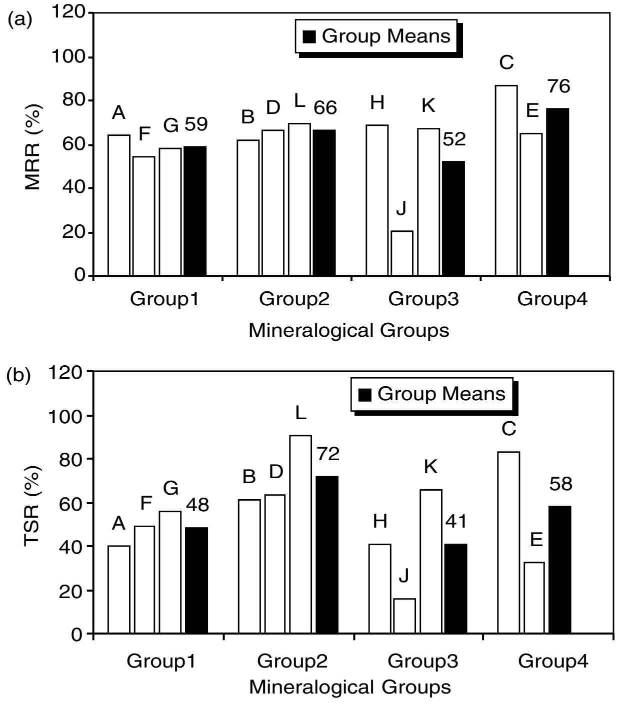

Figure 8. MRR (diagram a) and TSR (diagram b) for different groups based on mineralogical composition.

6. Conclusions

On the basis of the results from this study, the following conclusions can be drawn:

1. Mixtures from aggregates containing alkali metallic elements like sodium and potassium exhibited relatively high moisture sensitivity for the bitumen used in this study. On the other hand, there were no indications of moisture sensitivity for aggregates containing calcium, magnesium and iron.
2. No significant correlation was observed between the retained strength ratios (moisture sensitivity) and the contents of alumina (Al_2O_3) and silica (SiO_2) in the aggregates investigated.
3. Moisture sensitivity was observed to be high in mixtures having aggregates with high contents of both quartz and alkali feldspars. However, one aggregate with practically 100% quartz showed high resistance to moisture damage.
4. Further verification studies are needed to understand the underlying mechanisms of the stripping phenomenon. For example, this study needs to be broadened to include different sources of bitumen with a wide compositional difference, particularly with respect to nitrogen content and carboxylic acid content, and extended to other stripping evaluation methods.

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